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DE MISE EN PÂTE CHIMICO-THERMOMÉCANIQUE (PCTM)**

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## RÉSUMÉ

L'augmentation incessante des législations environnementales et leur impact économique peuvent trouver une réponse intéressante dans l'utilisation d'un système de traitement biologique combiné, de type anaérobie-aérobie en deux stades pour le traitement d'un effluent de pâte chimico-thermomécanique (PCTM). Ce type de traitement permet des enlèvements efficaces de la  $\text{DBO}_5$  et des acides résineux et gras (ARG), contribuant aussi à l'obtention d'un effluent non toxique et conforme aux règlements. Ce travail de recherche vise à évaluer les cinétiques et les paramètres de conception pour le traitement d'un effluent de PCTM, pour chacun des stades du procédé, à simuler théoriquement les effets des conditions d'opération sur son comportement et, en même temps, à optimiser le procédé global en deux stades. D'autre part, la détermination des mécanismes d'enlèvement des ARG de l'effluent de la PCTM par traitement biologique aérobie fut également évaluée. Les effets des conditions d'opération sur la performance du traitement aérobie de cet effluent ont aussi été étudiés.

Les travaux de recherche furent réalisés dans les locaux du Centre de Recherche en Pâtes et Papiers de l'UQTR. Les réacteurs utilisés étaient de modèle pilote, à volumétrie de 15 litres chacun, et thermiquement contrôlés. Ces réacteurs biologiques étaient également munis de tous les équipements de contrôle nécessaires pour le pH, les débits et l'oxygène dissous. Toutes les mesures analytiques furent également réalisées à l'UQTR en utilisant les méthodes standards et reconnues pour les divers paramètres évalués. Les effluents de PCTM utilisés ont été fournis par deux usines localisées près de Trois-Rivières

Cette recherche a révélé que le taux de l'enlèvement de la  $\text{DBO}_5$  de l'effluent de la PCTM étudié, dans les deux étapes du procédé anaérobie-aérobie en deux stades

, suit très bien un modèle cinétique de réaction du premier ordre et aussi le modèle de Monod. La constante du taux d'enlèvement de la  $\text{DBO}_5$  ( $k = 0,0113 \text{ (mg MSLM/L)}^{-1} \text{ jour}^{-1}$ ) au cours de l'étape (traitement) aérobie est presque dix fois supérieure à celle en traitement anaérobie ( $k = 0,0013$ ). Le taux d'enlèvement des ARG en traitement aérobie peut être bien représenté par la cinétique de réaction du premier ordre, alors que celui en traitement anaérobie s'approche du modèle de Monod. La constante du taux ( $k = 0,049 \text{ (mg MSLM/L)}^{-1} \text{ jour}^{-1}$ ) d'enlèvement des ARG par traitement aérobie est presque 50 fois celle (0,0009) obtenue par traitement anaérobie.

Ce travail a permis d'établir une méthode utile pour l'étude du comportement du procédé de traitement combiné anaérobie-aérobie en deux stades d'un effluent de PCTM en couplant les deux modèles cinétiques observés au cours de chacun des stades. En utilisant les équations fondamentales établies, les effets des conditions d'opération pour chaque stade sur le comportement du procédé en deux stades pour le traitement de l'effluent de la PCTM étudié ont été simulés. Les résultats de simulation ont montré que le stade du traitement anaérobie, avec un temps normal de rétention hydraulique de l'ordre d'un ou deux jours, ne produit pas un enlèvement élevé des ARG. En général, l'opération instable du stade anaérobie pourrait être attribuable à l'opération dans un régime sensible du temps de rétention hydraulique (TRH), au cours duquel l'opération est très sensible à la variation au TRH dû au changement du débit d'affluent.

Il est possible d'optimiser (minimiser ou maximiser) soit le temps total de rétention hydraulique ou l'enlèvement global de la  $\text{DBO}_5$ , pour ce traitement en deux stades de cet effluent de la PCTM par rapport à un enlèvement déterminé de la  $\text{DBO}_5$  dans le stade anaérobie. Le rapport optimal du volume des réacteurs peut alors être déterminé.

Une méthode générale (modèles mathématiques) a été développée pour optimiser la conception d'un tel procédé en deux stades, qui a été appliqué au traitement

des effluents d'usines de pâtes et papiers. En utilisant cette méthode d'optimisation pour le traitement en deux stades de l'effluent de la PCTM, le TRH total nécessaire pour l'obtention d'un enlèvement global de la  $\text{DBO}_5$  peut être minimisé par rapport à l'efficacité d'enlèvement du premier stade. Le rapport de volume des réacteurs  $V_1/V_2$  correspondant au TRH total minimum peut être aussi déterminé. Les résultats expérimentaux du traitement d'un deuxième effluent de PCTM ont permis de prouver que la méthode d'optimisation développée pour la conception de système du procédé anaérobie-aérobie en deux stades est valable. Cette recherche fournit donc les outils théoriques aux usines pour la conception et l'opération d'un procédé anaérobie-aérobie en deux stades.

Cette recherche a aussi démontré que les ARG dans l'effluent de la PCTM, au cours du traitement biologique aérobie, sont éliminés selon trois mécanismes lesquels sont : 1) la bio-oxydation par les microorganismes, 2) l'adsorption sur les boues et 3) l'oxydation par l'air. La bio-oxydation des ARG est le mécanisme majeur d'enlèvement; l'adsorption des ARG sur les boues est un mécanisme important, particulièrement lorsque le TRH est court. L'oxydation par l'air joue un rôle marginal. La révélation de ces mécanismes pourra amener, d'autre part, à mieux comprendre la détoxification d'un effluent par traitement biologique aérobie et pourra aussi être utile pour l'optimisation des procédés aérobies pour la détoxification d'effluents.

Les travaux de recherche furent réalisés en plusieurs étapes soit la caractérisation des sources de polluants à l'intérieur d'une usine, suivie de la traitabilité de la source la plus concentrée d'effluent de PCTM en utilisant successivement les procédés aérobie et anaérobie. Les cinétiques de biodégradation furent mesurées et finalement combinées pour en dériver un modèle mathématique permettant d'optimiser cette combinaison.

Les conclusions spécifiques suivantes peuvent être obtenues de cette recherche.

### **Caractérisation des sources de polluants pour la première usine étudiée**

- 1) Pour la première usine étudiée, quatre effluents possédaient des concentrations et des charges très élevées en  $\text{DBO}_5$ , DCO et ARG; Soit : les effluents du lavage de la PCTM, de l'eau blanche pauvre et de l'eau blanche riche en provenance d'un filtre à disques, ainsi que de l'eau de dilution. L'effluent du lavage de la PCTM, sélectionné pour le traitement biologique dans cette recherche, était la source principale des ARG. À cet endroit, la concentration et la charge étaient respectivement de 45 mg/L et de 3,3 tm/j.
- 2) L'usine rejetait environ 38 tm/j (63,3 kg/TMSA) de  $\text{DBO}_5$ , 0,26 tm/j (0,43 kg/TMSA) d'ARG, 54 tm/j (90 kg/TMSA) de DCO et 7,5 tm/j (12,5 kg/TMSA) de MES de son clarificateur primaire à la rivière.
- 3) Le rapport de  $\text{DBO}_5$ /DCO dans les effluents de cette usine était d'environ 0,5. Les effluents étaient faciles à dégrader biologiquement. Une augmentation du Ph de 5 à 7 augmente généralement les enlèvements de la DCO, des lignosulfonates, et de la couleur de l'effluent.
- 4) Les quantités relatives des ARG individuels dans les dix-sept sources internes d'effluents de cette usine étaient vraiment à peu près constantes et variaient très peu. Parmi les acides résineux, l'acide déhydroabiétique était dominant et représentait environ 37% de la quantité totale.

### **Traitements aérobie et anaérobie**

#### **Traitement aérobie**

- 1) Un temps de rétention hydraulique supérieur à deux jours n'augmente pas les enlèvements de la  $\text{DBO}_5$ , des ARG et de la DCO, mais non des ARG. Une

diminution du temps de rétention hydraulique dans l'intervalle de 2 à 0,5 jours conduit à une chute significative des enlèvements de la  $\text{DBO}_5$  et de la DCO, mais non des ARG. Environ 88% de la  $\text{DBO}_5$  et 95% des ARG dans l'effluent de la PCTM peuvent être enlevés par le traitement aérobie avec un temps de rétention hydraulique de 0,5 jour.

Un pH, dans l'intervalle de 5 à 8, n'a pas d'effet significatif sur les enlèvements de la  $\text{DBO}_5$  et des ARG. Cependant, une augmentation du pH de 5 à 7 augmente généralement les enlèvements de DCO, de lignosulfonates et de la couleur de l'effluent.

Dans l'intervalle de 10 à 50 °C, la température n'a pas d'effet sur l'enlèvement des ARG; cependant, cette condition exerce des influences significatives sur les enlèvements d'autres substrats. De 40 à 50 °C, les enlèvements des substrats, sauf les ARG, diminuent drastiquement, comme on pouvait s'y attendre alors que les bactéries filamenteuses prolifèrent. Ainsi, une température de traitement au-dessus de 40 °C n'est pas appropriée au traitement aérobie d'effluent de la PCTM.

Le niveau d'oxygène dissout n'a pas d'effet sur les enlèvements de la  $\text{DBO}_5$  et des ARG. Toutefois, au point de vue économique, pour des enlèvements de la  $\text{DBO}_5$  et des ARG, le traitement aérobie de l'effluent de la PCTM peut être opéré à un niveau d'oxygène dissout ne dépassant pas 2,5 mg/L. Cependant, une augmentation du niveau d'oxygène dissout contribue aux enlèvements plus élevés de la DCO, des lignosulfonates et de la couleur de l'effluent.

- 2) Une bonne décantation des boues a prévalu pour toutes les conditions étudiées. Les indices du volume des boues obtenus ont été faibles et ont varié entre 30 et 140 mL/g. La biomasse identifiée en situation d'aérobiose, excepté pour une température de 50 °C, consistait principalement de bactéries, ainsi que

protozoaires et métazoaires.

- 3) Un pH de 7 et une température entre 20 et 30 °C sont les meilleures conditions pour le traitement aérobie d'effluent de la PCTM. Un niveau d'oxygène dissout de l'ordre de 2,5 mg/L est nécessaire pour le traitement. Sous ces conditions très favorables, près de 98% de la DBO<sub>5</sub> et des ARG furent enlevés, de même qu'environ 80% de la DCO.

### **Traitement anaérobie**

- 1) Environ 70 à 83% de la DBO<sub>5</sub> et de 55 à 65% de la DCO dans l'effluent de la PCTM peuvent être enlevées par le traitement anaérobie avec un temps normal de rétention hydraulique de 0,5 à 1 jour sous les conditions étudiées. Ces niveaux d'enlèvements sont comparables avec ceux rapportés pour les traitements anaérobies à grande échelle d'effluents des usines de pâtes et papiers.
- 2) Le traitement anaérobie est inefficace pour l'enlèvement des ARG de l'effluent de la PCTM. Avec un TRH de l'ordre de 0,5 à 2 jours, le traitement n'a enlevé que de 20 à 50% des ARG.
- 3) Le taux de la production de biogaz du traitement anaérobie a varié de 0,23 à 0,33 m<sup>3</sup>/kg DCO enlevée, avec une moyenne de 0,26. Le biogaz produit contient de 70 à 80% de méthane.

### **Cinétiques et les paramètres de conception**

#### **Cinétiques et les paramètres de conception pour le traitement aérobie**

- 1) Les taux d'enlèvement de la DBO<sub>5</sub> et des ARG dans le traitement aérobie



(stade) sont mieux représentés par un modèle de réaction du premier ordre que par le modèle de Monod.

- 2) En ce qui a trait à la  $DOB_5$ , les valeurs des deux paramètres de conception  $Y$  et  $K_d$ , relatifs au rendement de la production de boues du traitement aérobique d'effluent de la PCTM et sous les conditions étudiées, étaient de 0,54 MSLM/ $DBO_5$  enlevée et de  $0,01 \text{ jour}^{-1}$  respectivement.
- 3) Les valeurs des deux autres paramètres de conception,  $a$  et  $b$ , pour l'évaluation de la quantité d'oxygène requis furent de  $0,36 \text{ g O}_2/\text{g } DBO_5$  enlevée et de  $0,28 \text{ g O}_2/\text{g MSLM oxydée/jour}$ , respectivement.
- 4) Le coefficient  $\Theta$  obtenu pour l'effet de la température pour le traitement de l'effluent de la PCTM fut de 1,028, d'après l'expression :  $(K_L a)_T = (K_L a)_{20^\circ\text{C}} \times \Theta^{T-20}$ ; cette valeur est à peu près identique à celle de 1,024 utilisée de façon courante pour la conception de traitements biologiques aérobies à pleine échelle.

#### **Cinétiques et les paramètres de conception pour le traitement anaérobie**

- 1) L'enlèvement de la  $DBO_5$  dans l'effluent de la PCTM par le traitement anaérobie peut également être représenté par un modèle de réaction du premier ordre, alors que le taux d'enlèvement des ARG suit approximativement le modèle de Monod.
- 2) Le taux de la production de boues du traitement anaérobie d'un effluent de la PCTM est d'environ  $0.08 \text{ g MSLM/g } DBO_5$  enlevée, ce qui se compare bien avec les valeurs de traitements anaérobies pour d'autres effluents de pâtes et papiers

## **Le comportement et l'optimisation du procédé en deux stades pour le traitement de l'effluent de la PCTM**

Cette recherche a démontré une méthode d'étudier le comportement d'un système de traitement biologique en deux stades, anaérobie-aérobie, en jumelant les modèles cinétiques obtenus pour chacun des stades et, en particulier, la façon d'optimiser la conception de ce système en deux stades en utilisant la méthode mise au point et basée sur les cinétiques des deux stades. En utilisant le deuxième effluent de la PCTM, les résultats expérimentaux montrent une très bonne corrélation avec les performances prédites par les équations fondamentales établies pour ce système à deux stades. La méthode d'optimisation présentée dans cette recherche a été validée expérimentalement pour maximiser l'enlèvement de la  $\text{DBO}_5$  pour un temps fixé de rétention hydraulique.

Les conclusions plus spécifiques obtenues sont les suivantes :

- 1) Les taux d'enlèvement de la  $\text{DBO}_5$  et des ARG obtenus pour les stades individuels aérobie et anaérobie furent différents pour chacun des effluents de PCTM étudiés. Ces résultats démontrent que différents effluents de PCTM possèdent leurs propres caractéristiques et aussi leurs propres taux d'enlèvement des substrats. Par conséquent, les valeurs cinétiques obtenues pour un effluent donné de PCTM ne devaient pas être utilisées pour la conception d'un autre système d'effluent de PCTM.
- 2) Les résultats des effets des conditions d'opération sur le comportement du procédé en deux stades ont indiqué que le stade anaérobie ne pourra pas produire un enlèvement élevé des ARG de l'effluent de la PCTM avec un temps normal de rétention hydraulique de l'ordre d'un ou deux jours.
- 3) En général, l'opération instable du stade anaérobie pourrait être attribuable à l'opération dans un régime sensible au temps de rétention hydraulique (TRH),

pour laquelle l'opération est très sensible à la variation du temps causé par le changement du débit d'affluent.

- 4) L'enlèvement de la  $\text{DBO}_5$  ( $E_1$ ) par le stade anaérobie est le seul paramètre important impliqué pour l'optimisation du système de traitement pour des conditions d'opération déterminées.
- 5) Bien que les méthodes pour l'étude du comportement et pour l'optimisation du procédé en deux stades ont été établies pour le procédé utilisé dans cette recherche, ces méthodes peuvent être applicables à d'autres systèmes anaérobie-aérobie en deux stades, en autant que les taux d'enlèvement des substrats dans chaque stade suivent les mêmes modèles de cinétique, soit celui du premier ordre ou celui de Monod.
- 6) Si les mêmes modèles de cinétique sont applicables, les méthodes établies pour l'effluent de la PCTM peuvent aussi être appliquées à d'autres types d'effluents de pâtes et papiers. A toute fin pratique, le choix d'utiliser un effluent de PCTM dans cette recherche ne limite pas l'application des résultats. Il en fut de même pour le système de traitement en deux stades.

En résumé, la contribution la plus importante de cette recherche est la détermination des méthodes pour les études du comportement (i.e., en couplant les modèles cinétiques observés pour les deux stades) et de l'optimisation de la conception et d'opération d'un procédé anaérobie-aérobie en deux stades (i.e., en utilisant les modèles mathématiques dérivés) pour le traitement d'un effluent de la PCTM. La révélation de divers mécanismes d'enlèvement des ARG au cours du traitement aérobie est une autre contribution importante de cette recherche. Les cinétiques et les valeurs des paramètres de conception trouvées pour le traitement de l'effluent étudié pourra être aussi des informations utiles pour les études de traitabilité d'autres effluents de PCTM.

## SUMMARY

To meet the increasing and tightening stringent environmental effluent legislations and at the same time considering the economic aspect, two-stage anaerobic-aerobic biological treatment offers interesting possibilities, in terms of BOD<sub>5</sub> and resin and fatty acids (RFA) removals, for CTMP effluent treatment which would results in high BOD<sub>5</sub> removal and a non toxic effluent. This research work addresses the questions of evaluating the kinetics and design parameters for the treatment in each stage and of simulating the effects of operating conditions on the behaviour as well as optimizing the design and operation of such a two-stage treatment system. It also contributes to the elucidation of the real mechanisms of detoxification, in terms of RFA removal, during aerobic treatment. The effects of operating variables on the single stage aerobic treatment of the CTMP effluent were also studied.

This research revealed that the removal rate of BOD<sub>5</sub> in the CTMP effluent, in both the anaerobic and aerobic stages (treatments) of the two-stage process, follows very well the kinetics of a first order reaction. The BOD<sub>5</sub> removal rate constant ( $k = 0.0113 \text{ (mg MLSS/L)}^{-1} \text{ day}^{-1}$ ) found for the aerobic treatment is almost 10 times of that ( $k = 0.0013$ ) for the anaerobic treatment. RFA removal rate in aerobic treatment (stage) can be also described by the kinetics of a first order reaction, whereas that in anaerobic treatment follows only approximately the model of Monod. The removal rate constant ( $k = 0.049$ ) of RFA found for the aerobic treatment is almost 50 times of that ( $k = 0.0009$ ) for anaerobic treatment.

The research work has established an useful and valuable method for studying the behaviour of a two-stage anaerobic-aerobic treatment system, through coupling

the kinetic models observed for both stages. Using the basic equations established, the effects of operating conditions in each stage on the behaviour of the two-stage system for the treatment of the CTMP effluent were simulated. Simulation results show that it would not be expected to achieve a high RFA removal from the CTMP effluent with a normal hydraulic retention time of one or two days in the anaerobic stage (treatment). In general, operating the anaerobic treatment in a sensitive hydraulic retention time (HRT) range, in which the operation is very sensitive to the variation in HRT caused by the change in feed flowrate, could be one of the reasons for unstable operation encountered sometimes during the treatment.

A general method (mathematical model) has been established for optimizing the design of such two-stage anaerobic-aerobic system which has been applied to the pulp and paper mill effluent treatment. Using the optimization method developed for the two-stage treatment of the CTMP effluent, the total HRT required to achieve a fixed overall  $BOD_5$  removal can be minimize with respect to the removal efficiency of the anaerobic stage; the corresponding optimal reactor volume ratio can be also determined. Experimental results obtained from the treatment of a CTMP effluent have proven that the optimization method is valid for the design of the two-stage treatment system. This research thus provides mills with valuable theoretical tools for the design and operation of a two-stage anaerobic-aerobic treatment system.

This study also contributes to the understanding of the three mechanisms involved in the removal of RFA during aerobic treatment : biodegradation by micro-organisms, adsorption onto biosolids and air oxidation. Bio-oxidation is the major removal mechanism; adsorption of RFA onto the sludge is also important for RFA removal particularly when the HRT is very short, and finally air oxidation plays a marginal role in the RFA removal. The finding of these removal mechanisms, in turn, would lead to a better understanding of effluent detoxification by aerobic treatment

and would be useful for the optimization of aerobic treatment processes for effluent detoxification.

In addition, the results of the research also showed that pH in the range of 5 and 8 and dissolved oxygen level above 2.5 mg/L have no significant effects on both BOD<sub>5</sub> and RFA removals from a CTMP effluent by aerobic treatment. Aerobic treatment was shown to be very effective for removing both BOD<sub>5</sub> and RFA from a CTMP effluent; whereas anaerobic treatment was found to be very ineffective for RFA removal from this effluent which could be the reason for insufficient anaerobic detoxification of CTMP effluents and other pulp and paper wastewaters. About 88% of the BOD<sub>5</sub> and almost 96% of the RFA in the CTMP effluent studied can be removed by aerobic treatment with an HRT of 0.5 day. Anaerobic treatment removes about 70 to 85% of the BOD<sub>5</sub> from the CTMP effluent with a normal HRT of 0.5 to about 2 day; however, it produces a very poor RFA removal of less than 50%. The combined two-stage treatment with a total HRT of about 1 day can remove over 96% of the BOD<sub>5</sub> and almost all the RFA, with the benefits of biogas production of about 0.26 m<sup>3</sup> methane/kg COD removed and a very low sludge production.

The sludge yield by aerobic treatment for the CTMP effluent studied was found to be about 0.54 mg MLSS/mg BOD<sub>5</sub> removed, whereas that by anaerobic treatment only about 0.08. The kinetics and design parameters determined, as well as the favourable conditions obtained for both aerobic and anaerobic treatments, could be used to design a full scale two-stage treatment plant for the CTMP effluent studied.

In summary, the main contribution of the present research work is the formulation of the methods for both studying the behaviour (i.e., through the coupling of the kinetic models observed for both stages) and optimizing the design and operation of a two-stage anaerobic-aerobic treatment system (i.e., through the mathematical

expressions derived). The elucidation of the various mechanisms of the removal of resin and fatty acids during aerobic treatment is also an another important and valuable contribution of this research. The kinetic and design parameters found for the CTMP effluent studied also provide useful and valuable information for treatability studies of other CTMP effluents.

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**Key words :** CTMP effluent, anaerobic treatment, aerobic treatment, anaerobic-aerobic treatment, kinetics, system behaviour, optimization, BOD<sub>5</sub>, resin and fatty acids (RFA), mechanism

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## NOMENCLATURES

Remark : Symbols with a subscript 1 or 2 are referred to the anaerobic stage or the aerobic stage.

$a$	= Coefficient for oxygen required to oxidize substrate, mg $O_2$ /mg substrate removed
$A_o$	= Energy-related constant in Langmuir model, mg/g MLSS
ADT	= Air dried ton
$b$	= Coefficient for oxygen rate required for endogenous respiration, mg $O_2$ /mg MLSS oxidized/day
$B_o$	= Constant in Freundlich model
BLS	= Bleached low-yield sulfite
BK	= Bleached kraft
BOD	= Biochemical oxygen demand (general term), mg/L
$BOD_5$	= Biochemical oxygen demand measured after 5 days, mg/L
$C$	= RFA concentration in liquid phase or clarified liquid, mg/L or $\mu g/L$
$C_o$	= Initial value of $C$ , mg/L or $\mu g/L$
$C_o^*$	= RFA concentration in RAW CTMP effluent, mg/L or $\mu g/L$
$C_s$	= Concentration of RFA adsorbed onto sludge, mg/L or $\mu g/L$
$C_{sl}$	= RFA conc. in the liquid phase of thickened mixed liquor, mg/L or $\mu g/L$
$C_{so}$	= Concentration of RFA initially adsorbed onto sludge, mg/L or $\mu g/L$
CCD	= Central composite design (a factorial design)
COD	= Chemical oxygen demand, mg/L
CTMP	= Chemithermomechanical pulping
DHA	= Dehydroabietic acid
DO	= Dissolved oxygen, mg/L
DTPA	= Diethylenetriaminepenta-acetic acid

$E$	= Overall treatment efficiency or overall removal, %
$E_1, E_2$	= Treatment efficiency or removal, %
$E_{1o}$	= Treatment efficiency at the reference point $P_o$ , for sensitivity study, %
$E_{1(opt)}$	= Optimal value of $E_1$ , %
$\Delta E_{1o}$	= The change in $E_{1o}$
FA	= Long chain fatty acids, mg/L or $\mu\text{g/L}$
HRT	= Hydraulic retention time, days
HYS	= High-yield sulphite
$k$	= Rate constant of substrate removal (general term) involved in first order reaction model, $(\text{mg MLSS/L})^{-1} \cdot \text{d}^{-1}$
$k_1, k_2$	= Rate constant of substrate removal, $(\text{mg MLSS/L})^{-1} \cdot \text{d}^{-1}$
$K$	= Maximum specific rate constant of substrate removal involved in Monod model (general term), $\text{d}^{-1}$
$K_1, K_2$	= Maximum specific rate constant of substrate removal, $\text{d}^{-1}$
$K_L a$	= Overall oxygen transfer coefficient, $\text{h}^{-1}$
$K_{d1}, K_{d2}$	= Endogenous respiration rate coefficient, $\text{d}^{-1}$
$K_{s1}, K_{s2}$	= Half-velocity constant, mg/L
Kraft	= Kraft pulping - a chemical pulping process
LS	= Lignosulphnates, mg/L
LYS	= Low-yield sulphite
MLSS	= Mixed liquor suspended solids, mg/L
SOUR	= Specific oxygen uptake rate, $\text{mg O}_2/\text{mg MLSS day}$
$n$	= Constant relating the inter-attraction between molecules in Freundlich model
$P$	= Operating conditions ( $t_1, t_{s1}, X_1$ or $S_o$ )
$P_o$	= Value of $P$ at the reference point for sensitivity study
$\Delta P_o$	= The change of $P$ from $P_o$
$q$	= Amount adsorbed per unit mass of dry MLSS, mg/g MLSS
$q_m$	= Asymptotic saturation value of $q$ , mg/g MLSS
$Q_o$	= Feed flowrate, L/d

$Q_r$	= Flowrate of sludge recycle in general term, L/d
$Q_{r1}, Q_{r2}$	= Flowrate of sludge recycle, L/d
$Q_w$	= Flowrate of mixed liquor withdrawn from reactor, L/d
$Q_{w1}, Q_{w2}$	= Flowrate of mixed liquor withdrawn from reactor, L/d
$r$	= Correlation coefficient
$R$	= Sludge recycle ratio (general term)
$r_s$	= Rate of substrate removal, mg/L.d
$R_1, R_2$	= Sludge recycle ratio
RA	= Resin acids, mg/L or $\mu\text{g/L}$
RFA	= Resin and fatty acids, mg/L or $\mu\text{g/L}$
RMP	= Refiner mechanical pulping
$S_1, S_2$	= Effluent substrate concentration, mg/L or g/L
$S_o$	= Initial effluent substrate concentration, mg/L
$S_p$	= Parameter sensitivity, %
SGW	= Stone groundwood pulping
SRT	= Sludge retention time, days
Sulphite	= Sulphite pulping - a chemical pulping process
SVI	= Sludge volume index, mL/g MLSS
$t$	= Hydraulic retention time, in general, d
$t_1, t_2$	= Hydraulic retention time, d
$t_m$	= The minimum of $t_o$ , d
$t_o$	= Total treatment time or total hydraulic retention time, d
$t_{s1}, t_{s2}$	= Mean cell age, d
$t_s$	= Mean cell age, in general, d
$t_s^m$	= Minimal mean cell age, d
$T$	= Temperature, $^{\circ}\text{C}$
TKN	= Total Kjeldahl nitrogen, mg/L
TMP	= Thermomechanical pulping
TOC	= Total organic carbon, mg/L
TSS	= Total suspended solids, mg/L



UASB	= Up-flow Anaerobic Sludge Bed
UBK	= Unbleached kraft
UBLS	= Unbleached low-yield sulphite
V	= Reactor volume (general term), L
v	= Beaker volume, L
$V_1, V_2$	= Reactor volume, L
$v_o$	= Volume of raw CTMP effluent used in adsorption, L
$v_s$	= Volume of thickened mixed liquor, L
VFA	= Volatile fatty acids, mg/L
X	= MLSS concentration in reactor, in general term, mg/L
$X_1, X_2$	= MLSS concentration in reactor, mg/L
$X_e$	= TSS concentration in effluent from settling tank, in general term, mg/L
$X_{e1}, X_{e2}$	= MLSS concentration in effluent from settling tank, mg/L
$X_o$	= TSS concentration in feed, mg/L
$X_r$	= MLSS concentration in sludge recycle line, in general term, mg/L
$X_{r1}, X_{r2}$	= MLSS concentration in sludge recycle line, mg/L
$X_s$	= MLSS concentration in the thickened mixed liquor, mg/L
$X_T$	= Mass of microorganisms in reactor
$\Delta X$	= Mass of microorganisms removed each day
Y	= Sludge yield coefficient (general term), mg MLSS produced/mg substrate removed
$Y_1, Y_2$	= Sludge yield coefficient, mg MLSS produced/mg substrate removed
$\theta$	= Temperature coefficient

## INTRODUCTION

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### 1 Backgrounds

During the last two decades, the pressures from both the stringent environmental regulations and the energy and fibre resource shortages have been forcing the worldwide pulp and paper industry to explore pulping methods for minimizing pollution, saving energy and fibre materials, without reducing pulp quality and production. Consequently, since the early 1970s the most significant change has been the trend towards high yield pulping, in particular mechanical pulping in newsprint manufacture, with corresponding reductions in pollution loads and raw material consumption.

As a result, chemithermomechanical pulping (CTMP), a modification of thermomechanical pulping (TMP), was introduced to the pulp and paper industry in the early 1980s. Since then, CTMP has gained rapid development, especially in Canada. CTMP has now become a dominant process in Canada for manufacturing ultra-high yield pulps for newsprint and other paper products. The annual production of TMP/CTMP in Canada has increased from 2.4 metric tonnes in 1982 [1] to 9.2 metric tonnes (accounting for about 32% of the total pulps) in 1994 [2].

With the rapid growth of CTMP pulping, the effluent generated from the process, on the other hand, has become a serious concern from environmental protection viewpoint. Due to the severe pre-treatment of the wood chips used, compared to other mechanical pulping processes, CTMP still produces rather high pollution loads and a very toxic effluent although they are much lower than those from conventional low-yield sulphite processes. Loads of BOD<sub>5</sub> ranging from 35 to 65 kg/ADT [3-6] and very high concentrations, up to 560 mg/L, of resin and fatty acids

(RFA) [3], which have been identified as the principal source of the effluent toxicity to fish, have been reported. Such high BOD<sub>5</sub> loading and fish toxicity must be reduced to meet the more and more stringent effluent regulations.

The more and more stringent effluent regulations not only limit the discharge of BOD<sub>5</sub> loading but require detoxification of the effluent when discharging. The stringent effluent regulations, together with the worldwide rising energy price, require a treatment method to be both effective and economic when it is used to treat pulp and paper mill effluents.

Conventional aerobic biological processes, both aerated lagoon and activated sludge, have been found to be very effective for removing both BOD<sub>5</sub> and fish toxicity from pulp and paper effluents [7-14]; the costs of applying these methods, however, are elevated. Anaerobic processes have been proven in recent years to be applicable to the treatment of pulp and paper mill effluents [15-21], with economic benefits over aerobic processes [21-22]; anaerobic processes alone, however, have been found to be insufficient in most cases to detoxify pulp and paper mill effluents. To remove BOD<sub>5</sub> loading and detoxify the effluents, one of the effective and economic processes is a combination of anaerobic and aerobic processes. This combined two-stage process possesses the advantages of both anaerobic and aerobic processes and would be an ideal system for the treatment of CTMP effluents. From the view point of both economy and effluent detoxification, the two-stage process is thus studied in this research.

## **2 Objectives of this research**

The principal objectives of this research are :

- 1) Simulation and optimization of the two-stage anaerobic-aerobic system for a CTMP effluent;

- 2) Evaluation of the mechanisms of RFA removal by aerobic treatment.

The specific objectives of this research include :

- 1) Establishment of the favourable conditions for both aerobic and anaerobic treatments of a CTMP effluent;
- 2) Set-up of the kinetics of substrate ( $BOD_5$  and RFA) removal in both anaerobic and aerobic treatments, and evaluation of the kinetic and design parameters for the design of a full scale two-stage treatment process;
- 3) Simulation of the effects of operating parameters on the treatment behaviour of the two-stage process and verification of the simulation by experiments;
- 4) Development of an optimization method for the two-stage process and optimization of the process for the treatment of the CTMP effluent studied;
- 5) Determination of the mechanisms of RFA removal from CTMP effluent during aerobic treatment and evaluation of the effects of operating parameters on RFA removal by each mechanism.

This dissertation describes the present research in ten chapters.

Chapter 1 presents a literature review made on pulp and paper effluent regulations, CTMP production, effluent pollution loads and characteristics, and the state-of-the-art of biological treatment of CTMP effluents -- to justify the objectives of this research.

Chapter 2 presents the principles of anaerobic and aerobic treatment processes, the kinetic models employed, the basic equations, and the optimization method established for the two-stage treatment system studied in this research.

Chapter 3 describes the experimental methods and procedures used to attain the objectives set for this research.

Results and discussion are presented in Chapters 4 to 9. Chapter 4 presents the characterization of the pollutants in the various effluents collected from the CTMP mill studied, for the purpose of identifying the sources or origins of pollutants and selecting the effluent to be treated in this research.

Chapter 5 presents the experimental results and the discussion on the performances of anaerobic and aerobic treatments of the selected CTMP effluent. The favourable conditions obtained for each treatment are also presented.

Chapter 6 discusses the experimental kinetics and design parameters results for both anaerobic and aerobic treatments of the selected effluent under the favourable conditions obtained in Chapter 5.

In conjunction with the bio-kinetic parameters obtained in Chapter 6, Chapter 7 first demonstrates how to study (i.e., simulation) the behaviour of the two-stage system for the selected effluent, using the basic equations set-up in Chapter 2. It then presents how to optimize the two-stage system for the selected effluent, using the method developed in Chapter 2.

Chapter 8 reports the experiments conducted in the two-stage system, verifying the effects of operating conditions on the system behaviour predicted by the basic equations. The validity of the optimization method established for the two-stage system is also reported in this Chapter.

In Chapter 9, described is the experimental study on the RFA removal mechanisms by aerobic biological treatment. The effects of treatment variables on the removals by various mechanisms are also presented.

Chapter 10 summarizes the results of and presents the conclusions for the research.

## CHAPTER 1

### LITERATURE REVIEW

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#### 1.1 Pulp and paper mill effluent regulations

Pulp and paper is one of the principal industries in Canada. In 1994, about 145 paper mills in Canada produce a total of about 29 million tonnes of pulp and 20.6 million tonnes of paper & board [2]. The manufacture of pulp and paper, especially chemical pulping, requires large amounts of water. Fig. 1.1 presents the typical water consumption rates in various pulping processes used in Canada [3]. For example, a mill with a typical capacity of producing 1000 metric tonnes pulp normally consumes, upon the process used, 20,000 to over 100,000 m<sup>3</sup>/day of water. As the water leaves the mill, it has been contaminated by the organic and inorganic matter released from the manufacture process to form highly polluted and toxic mill effluent. Pulp and paper mill effluents have been proven toxic to fish and other sensitive organisms and, if directly discharged, would produce a serious pollution to water resources.

During the decade of the 1960s, human being began to recognize the importance of their environment protection. As a result, environmental concerns emerged across a wide range of issues in North America. The first Canadian federal effluent regulations were set in 1971 for new pulp and paper mills. Subsequently, the provincial governments also published their discharge limits for new mills. However, the former Canadian pulp and paper effluent regulations were only applicable to the mills started up after 1971 and did not apply to those existing prior to that time. Furthermore, as the paper industry developed rapidly during the last 20 years, environmental pollution caused by the paper industry has become more and more

serious, the regulations appeared to be not strict enough to protect our environment. In order to remedy this situation, the regulations were modified by tightening the discharge limits and widening their application to all paper mills. The new regulations [23-24] were thus proposed in 1991 and promulgated in 1992 (See Table 1.1).

According to the new Canadian Pulp and Paper Mill Effluent Regulations [23], the discharge limit of effluent BOD<sub>5</sub> is 7.5 kg/ADT by the end of 1995. A lower limit of 5 KG/ADT was set for the Québec mills by Québec Pulp and Paper Mill Regulations [24]. A major modification made is that the final effluents discharged have to be non-toxic to fish, according to the new federal and provincial regulations.

**Table 1.1.** The discharge limits of effluent BOD<sub>5</sub> and fish toxicity for Canadian and Québec pulp and paper mills

Pollutants	Federal limits [23]	Quebec limits [24]
	1992	1992
BOD <sub>5</sub> (Kg/ADT)	7.5	5.0 - 9.0*
Toxicity (96h LC <sub>50</sub> , v/v %)	Non-toxic (100%)	Non-toxic (100%)
Compliance date	Dec. 1995	Sept. 1995

\* - May be down to 5.0 in case of very efficient treatments.

## 1.2 Production of CTMP and its effluent pollution

### 1.2.1 Effluent pollution and pulping process development

Plant fibres, including wood and non-wood, are the principal materials used for paper manufacture. The fibre components are composed of three major chemical compositions : cellulose, hemicellulose and lignin, as well as extractives, such as resin

and fatty acids. Typical contents of these compositions in wood and non-wood materials are shown in **Table 1.2**. Among them, lignin possesses a high proportion, accounting for 25-33% for softwood, 16-24% for hardwood and 11-22% for nonwood.

**Table 1.2.** Chemical compositions of plant materials used for paper manufacture

Material	Cellulose	Hemicellulose	Lignin	Extractives
Softwood [25-27]	40-42	25-29	25-33	1-5
Hardwood [25-27]	43-47	35-35	16-24	2-3
Non-wood [27]	40-45	30-40	12-22	3-5

Note : All the contents in **Table 1.2** are expressed in % on dried material

Pulping is a process for separating either chemically or mechanically the cellulose fibres from the raw material to produce pulps for papermaking. A large amount of water is consumed in this process. During pulping process, a fraction of the lignin, and parts of hemicelluloses and extractives in the raw material, depending upon the process used, are removed and dissolve in the process liquor to form highly polluted and toxic pulping effluent which, if directly discharged, would produce a heavy pollution to water resources. There are two main types of pulping - chemical and mechanical.

#### 1.2.1.1 Chemical pulping

Chemical pulping technology employs inorganic chemicals to remove enough lignin at high temperature so that the cellulose fibres can be separated from one another, producing a pulp. At the same time, a portion of hemicelluloses are hydrolysed and dissolved in pulping liquor. Therefore, chemical pulping not only



produces a low yield pulp (**Table 1.3**), but generates heavy pollution loads in the untreated pulping effluent due to the removal of lignin and the losses of the hemicelluloses. Two major types of chemical pulping are currently used - kraft or sulphate and sulphite.

**Table 1.3.** Typical pulp yields for various processes [9]

Pulping process	Chemical pulping				Mechanical pulping			
	UBK	BK	LYS	HYS	SGW	RMP	TMP	CTMP
Yield, %	50-55	43-48	46-55	65-85	93-98	92-98	91-95	85-93

Kraft pulping : Kraft pulping (yield ranged from 43 to 55%), invented in 1870, employs sulphide and sodium hydroxide as cooking agents for delignification at high temperature, resulting a strong, dark coloured pulp suitable for the manufacture of many types of paper [25-26]. The development and practice in the period between 1928 and 1934 of the recovery system for chemicals and the non-fibrous wastes from kraft black liquor greatly reduce both the pollution loads generated from the pulping and the raw materials cost. Since the 1960s the production of kraft pulps has increased rapidly; mainly due to the efficient chemical recoveries as well as to a higher fibre strength of the pulp over that of a sulphite pulp. The introduction of effective bleaching technology enables kraft pulps to arrive at a high brightness, and the pre-hydrolysis of wood chips has made it possible to produce high grade dissolving pulps by kraft process. Kraft pulping is therefore by far the predominant chemical process and one of the major pulping processes used in worldwide paper industry.

Sulphite pulping : Conventional low-yield (46-55%) sulphite pulping, developed in 1866, employs salt sulphite under acidic conditions to remove lignin from the raw materials at elevated temperature, producing a weaker, but less coloured pulp

particularly suitable for printing grades of paper [28-29]. Recoveries of the non-fibrous wastes and cooking chemicals from the spent pulping liquor are rarely practised due to a combination of economic and technical factors. This creates a problem in controlling BOD discharge in many cases. Due to producing very high pollution loads together with low yield, the sulphite process has been gradually replaced since the late 1960s by high yield sulphite processes and in particular by mechanical pulping.

#### 1.2.1.2 Mechanical pulping

SGW and RMP processes : Mechanical pulp is manufactured through separating the cellulose fibres either by stone grinding or by refiner refining. In the oldest form of mechanical pulping, stone groundwood (SGW) developed by Keller in 1843 [30], wood logs are forced into contact with a revolving grindstone in the presence of water. In the late 1950s, disc refiners [30] were introduced as a variation of the SGW process. The advantage of refiner mechanical pulping (RMP) over the SGW process is that chips as well as wood residue generated from the forest product industry can be used as raw material instead of solid logs. As shown in Table 1.3, the pulp yield of either SGW or RMP is ultra-high (93-98%), correspondingly, the pollution loads generated are very low. However, the quality in particular the strength of the pulps made by either SGW or RMP is poor, due to a high content of shive and poor flexibility of the long fibres in the pulps [30]. The main use of the pulps is thus limited to newsprint manufacture [30].

In the late 1960s and the early 1970s, regulations to limit the discharge of pollutants in effluents from pulping and paper mills were promulgated in North American and countries over the world. Paper industry has thus been pressed by the environmental regulations. On the other hand, as the world demand for pulp and paper increases, the fibre resources diminish rapidly. The pressures from both the environmental regulations and the energy and fibre resource shortages forced the pulp and paper industry to look for pulping methods to minimize pollution, save energy and

fibre materials, without reducing pulp quality and production. Consequently, since the early 1970s the most significant change has been the trend towards high yield pulping, in particular mechanical pulping in newsprint manufacture, with corresponding reductions in pollution loads and raw material consumption. As a result, TMP [30] was developed as a modification of the original RMP process.

TMP pulping : In TMP pulping, the washed wood chips are pre-steamed in a pressurized vessel before defibering under pressure in a disc refiner. The thermal pre-treatment softens the lignin in the fibres to reduce damage of the long fibre component during mechanical defiberation [30], resulting in a substantially stronger and very high yield (91-95%) pulp with reduced content of shive and fines when compared with SGW and RMP. The pollution loads generated is also very low (Fig. 1.2) as compared with those by a sulphite process, and comparable to those produced by both SGW and RMP. The first TMP mill in Canada was started up at Donnacona, Quebec, in 1974. Since then, production of TMP has increased drastically (**Table 1.4**) while the sulphite has reduced readily. Although, the quality of the pulp produced by a TMP process has been improved considerably as compared with those of SGW and RMP, the pulp is still limited mainly to newsprint manufacture. Also, the energy consumption in a TMP process is high.

### 1.2.2 CTMP pulping and its production in Canada

To further improve the pulp quality, particularly the strength property, for expanding use, i.e., partially replacing chemical pulps, and to reduce the high energy consumption associated with TMP, a modified TMP process -- CTMP [30] was developed in Sweden in the middle 1970s. CTMP, in fact, a high-yield relative of TMP, refers to a family of processes which utilize a combination of chemical, thermal and mechanical treatments of fibre materials. With CTMP pulping, a small amount of chemical, usually 1 to 6% sodium sulphite [30], is added to the washed chips, either prior to or during the steaming of the chips, with first stage refining at an elevated

temperature of above 100 °C and any subsequent refining at atmospheric pressure. Except a slight decrease in yield, this slight chemical impregnation improves considerably the quality (except the opacity), in particular the strength property, of the produced pulp by increasing the flexibility of the long fibre fraction and reducing the shive content in the produced pulp. The improved quality, and about 10% increase in the overall pulp strength [30], makes CTMP pulps more suitable not only for newsprint, but for other products typically made from chemical pulps, such as tissue and disposable diapers [30-31]. To improve TMP quality, now most of TMP mills employ a small amount (0.5-2%) of sulphite in their processes. Due to this reason, the productions of TMP and CTMP are usually reported together.

**Table 1.4.** Productions, proportions and change rates of various pulps in Canada [1-2]

Pulps	1982		1994		% change rate (over 1982)
	Production (10 <sup>3</sup> tonnes)	Proportion (%)	Production (10 <sup>3</sup> tonnes)	Proportion (%)	
Kraft	7939	44.2	13305	45.6	67.6
Sulphite	1684	9.4	1340	4.6	-20.4
SGW	5111	28.4	4297	14.7	-15.9
RMP	262	1.5	200	0.7	-23.7
TMP/CTMP	2415	13.4	9253	31.7	283
<b>Total pulps</b>	<b>17978</b>	--	<b>29190</b>	--	62.4

Because of high yield, very interesting characteristics for expanding use, the adaptability to wide variety of wood species and less capital costs, CTMP pulping has gained rapidly development since the early 1980s, and has become the dominant

process in Canada for manufacturing ultra-high yield pulps for newsprint and other paper products. As shown in **Table 1.4**, the annual production of CTMP/TMP in Canada increased from 2.4 million metric tonnes (representing 13.4% of the total pulps) in 1982 [1] to 9.2 million metric tonnes (representing 31.7% of the total pulps) in 1994 [2]. In newsprint mills, CTMP has replaced the low-yield sulphite pulps which were produced without chemical recovery. It has been predicted [30] that CTMP is the future of pulping industry because the pulp has the superior properties similar to those of chemical pulps [30-31], with the ultra-high yield advantage of mechanical pulping.

### **1.2.3 CTMP effluent pollution loads and characteristics**

#### **1.2.3.1 CTMP effluent pollution loads**

With the rapid growth of CTMP pulping, the effluent pollution generated from the process, on the other hand, has become a serious concern from environmental viewpoint.

Due to the severe pre-treatment of wood chips, compared with other mechanical pulping processes, more organic matter as well as extractive are removed from the wood chips during a CTMP pulping. The process, therefore, produces higher pollution loads and more toxic matter as compared with other mechanical processes, as shown in Fig. 1.2. Loads of BOD<sub>5</sub> and COD generally range from 35 to 65 kg/ADT and 70-200 kg/ADT [3-6], respectively, depending on the wood species used and pulping process (non-bleaching and bleaching). Toxicity emission rate ranges from 1250 to 5900 TU<sub>m</sub><sup>3</sup>/ADT [3].

#### **1.2.3.2 CTMP effluent characteristics**

Due to the practice of extensive water recycling, the water consumption per

tonne of pulp in CTMP pulping is greatly reduced as compared with that in chemical pulping (Fig 1.1). The effluent generated thus has a very high concentration of BOD<sub>5</sub> as well as an elevated level of wood extractives such as resin and fatty acids; these acids have been identified to be very toxic to fish [32-37] and found to be the major source of fish toxicity of mechanical pulping effluents [8, 11, 36-39]. The concentrations of BOD<sub>5</sub> and RFA generally range from 1200 to 5000 mg/L [3] and from 26 to 65, and up to 560 mg/L [3], respectively. These concentrations significantly exceed those of other pulping effluents. The elevated RFA content renders CTMP effluent the most toxic among the various pulping process effluents, as shown in **Table 1.5**.

**Table 1.5.** Reported acute toxicity levels in various pulping effluents [3]

Pulping process	Acute toxicity (96h LC <sub>50</sub> , v/v %)
Unbleached kraft (UBK)	3-100
Bleached kraft (BK)	5-87
Unbleached sulphite (UBLS)	8-95
Bleached sulphite (BLS)	2-100
SGW	3-12
TMP	1.3-35.3
<i>CTMP</i>	<i>0.83-1.8</i>

In addition to organic pollutants, concentrations of other chemical compounds in CTMP effluent are also rather high as compared to those in other effluents. The sodium sulphite used in CTMP process results in sulphite contamination of the process effluent. The concentration of sulphite, reported as S, varies from 100 to up to 600 mg/L [3]. The concentration of sodium from sodium sulphite and sodium hydroxide

used in the process is also high, ranging from 700 to 1000 mg/L [3].

The concentration of residual hydrogen peroxide used in CTMP bleaching in the bleaching effluent ranges from 50 to 200 mg/L for Canadian mills and from 200 to 1000 mg/L for Sweden mills [3], which may be inhibitory or toxic to anaerobic bacteria in anaerobic systems.

Obviously, the effluent BOD<sub>5</sub> load is much higher than the new discharges limits set by either the federal or provincial governments, although it is much lower than those in sulphite pulping effluents. Such BOD<sub>5</sub> load and fish toxicity of CTMP effluent must be reduced to meet the new effluent regulations mentioned above. Since the concentration of organic matter is too dilute for straightforward evaporation and recovery, the effluent can be externally treated only to remove the BOD<sub>5</sub> loading and toxicity.

### **1.3 Present state of biological treatment of CTMP effluents**

In general, the methods applicable to the treatment of other types of pulp and paper mill effluents apply also to the removals of BOD<sub>5</sub> and toxicity from CTMP effluents. These methods include:

- 1) Chemical-physical treatment
- 2) Primary treatment
- 3) Secondary treatment

Chemical-physical method is able to remove most of the toxicants, such as resin and fatty acids (60-90% reduction), and 30-75% of BOD<sub>5</sub> from CTMP effluents [39-42] and other types of pulp and paper mill effluents [43-46]. However, since the method employs chemicals in the process, the cost of applying this method is very elevated. Since the volumes of pulp and paper mill effluents to be treated are usually

very large, the chemical-physical process is not an economic method for removing the pollutants from such quantity of effluents. This method is thus used only in pre- or advanced wastewater treatment.

Primary treatment processes, such as sedimentation, have been widely used in the treatment of pulp and paper wastewaters [9]. The function of primary treatment is primarily limited to removing the settleable portion of large particles, such as wood pulps, from mill effluents. Although primary treatment process removes also a very limited portion of the total  $BOD_5$  load (less than 10%) through adsorption mechanism [9], it can not produce high quality effluent to meet the stringent discharge regulations.

To reduce the  $BOD_5$  load and to remove the fish toxicity so as to respect the stringent effluent regulations, biological or secondary treatment is so far the most effective and economic method. Biological methods include aerobic, anaerobic, and a combination of anaerobic-aerobic treatments. Having high concentration of  $BOD_5$ , CTMP effluents may be treated using one of these biological methods.

### **1.3.1 Aerobic treatment of non-CTMP and CTMP effluents**

In aerobic biological processes, organic matter is oxidized to carbon dioxide and water by bacteria at the presence of oxygen. A fraction of organic matter removed is synthesized to new bacterial cells. Aerobic biological methods used in the treatment of CTMP and other mill effluents generally include : 1) the simplest aerated lagoon or stabilization basin; 2) conventional activated sludge.

#### **1.3.1.1 Aerated lagoon treatment**

Aerated lagoon, a low-rate aerobic biological process, is the oldest and simplest type of the engineered biological treatment systems to construct and operate.



Traditionally, it has long been widely employed in the treatment of non-CTMP effluents [9, 47-48], based on the experiences from municipal wastewaters which are generally quite different in characteristics from pulp and paper mill effluents. To produce a reliable high-quality effluent, this method generally uses a very long hydraulic retention time (HRT) of at least 5 days and up to 10 days [9, 49] and thus achieves a very high BOD<sub>5</sub> removal (85-95%) and effluent detoxification [9]. Extensive experiences of applying this method in the treatment of pulp and paper mill effluents are available. In both Canada and United States, most of the early constructed secondary treatment systems in pulp and paper mills are aerated lagoons, where available land space is not limited.

Aerated lagoon has also been in recent years used in the treatment of CTMP effluents to remove BOD<sub>5</sub> and toxicity. In Canada, several new CTMP mills [18, 47] have adopted this method for treatment of their effluents; they include the Whitecourt (10 day HRT), Taylor (10 day HRT), Gloden River Expansion (7 day HRT), Cascades in Port-Cartier [47] and a CTMP mill proposed by Albert Newsprint Company. In spite of the adoption of aerated lagoon process for these new CTMP mills, the system designs are based wholly on the experiences gained from the treatment of non-CTMP effluents, generally using a very long HRT of 7 to 10 days. This implies that very large land space is needed and the aeration power (operation cost) would be elevated. Reported studies on aerated lagoon treatment of CTMP effluents are rather limited, although it has been used for CTMP wastewaters.

One bench scale study [10] found that an HRT of 5 to 7 days is sufficient to detoxify a combined TMP/CTMP effluent. 90-98% reduction in BOD<sub>5</sub> was achieved. Wilson *et al*/ [50] has also shown that a combined NSSC/CTMP effluent was detoxified by a pilot scale aerated lagoon using an HRT of 7 days, and BOD<sub>5</sub> removal was over 95%. However, the results [51] from the full-scale aerated lagoon treatment of the Quesnel River CTMP effluent using an HRT of 5 to 7 days has shown that the treated effluent quality consistently exceeded the discharge limits including toxicity limit, due

to insufficient aeration capacity or treatment time. The main reason for this failure is that the design of the treatment system has been based on the experiences from the treatment of other pulp and paper mill effluents and domestic wastewaters. Since CTMP effluent has higher organic concentrations than other pulp and paper mill effluents, the HRT required for CTMP effluent treatment using an aerated lagoon should be longer than those for the other effluents.

It has been found that the major advantage of properly designed aerated lagoon is that it provides a better toxicity removal from pulp and paper mill including CTMP effluents than other high-rate treatment systems [9, 50]. Lagoons are generally able to detoxify pulp and paper mill effluents due to using a long HRT. Mainly due to this advantage, aerated lagoons have been universally accepted by the pulp and paper mills where the available land space is not limited. However, since the HRT in an aerated lagoon is very long, the required land space for constructing an aeration basin is very large, which is a major disadvantage of the method. In most mills, the available land space is usually limited, not allowing for the construction of an aerated lagoon. This led to the introduction of conventional activated sludge systems, which are high-rate biological processes and require much smaller land space, into the treatment of pulp and paper mill effluents.

#### **1.3.1.2 Conventional activated sludge treatment**

Conventional activated sludge, a high-rate biological process, is a process adapted largely from sanitary waste treatment. The principles of activated sludge treatment are the same as those involved in aerated lagoon. In an activated sludge process, however, there is a sludge settler following the aeration basin. The bacterial concentration in the aeration basin is maintained at a high level (2000 to 5000 mg/L) through returning a part of the settled sludge from the settler. Consequently, the required HRT for treating the same effluent is much shorter as compared to that in an aerated lagoon, and the required aeration basin size (land space) is, in turn, greatly

reduced.

Activated sludge treatment has also been used by the pulp and paper industry where the available land space is small and/or low treated effluent suspended solids concentrations are required. A large number of full-scale activated sludge systems have been operated in the United States [48] and several in Canada [9, 49] for the treatments of non-CTMP pulping effluents, achieving a very high BOD<sub>5</sub> removal (90-95%). However, similar to aerated lagoon systems, the designs and operations of these systems have been mainly based on the experiences from the treatments of other types of wastewaters, particularly domestic wastewaters.

This high-rate process has been in recent years employed in the treatment of CTMP effluents, mainly based on the experiences gained from the treatment of other types of pulp and paper mill effluents. Studies appearing in the literature on activated sludge treatment of CTMP effluent are very limited [14, 50, 52-55].

Results from bench scale or pilot scale studies [14, 52-53] have shown that activated sludge treatment is generally very effective for BOD<sub>5</sub> removal from CTMP effluents. Over 95% reduction in BOD<sub>5</sub> can be achieved.

RFA in the CTMP effluents can be easily removed by activated sludge treatment [14, 54]; the removal is generally very high (over 95%) which is quite similar to those observed in activated sludge treatment of other pulp and paper mill effluents [11, 13, 42, 49, 56-59]. The removal mechanisms are, however, unclear. Adsorption onto sludge might be one important removal mechanism, in addition to bacterial biodegradation. These limited studies show that activated sludge process is very effective for removing BOD<sub>5</sub> and RFA from CTMP effluents. The ability of the process to achieve a reliable degree of detoxification of CTMP effluents, however, remains somewhat uncertain.

Results from a lab- [55] and a full-scale [12] systems indicated that activated sludge treatment successfully detoxified the CTMP effluents studied. A bench scale testing also showed that activated sludge treatment was able to detoxify two TMP effluents when the HRT's were greater than 8 hours [13]. However, a 2.5-day HRT pilot-scale activated sludge treatment was unable to detoxify a combined NSSC/CTMP waste [50].

Some authors believe that detoxification of pulp and paper mill effluents is largely dependent on the aerobic retention time, and as such, aerated lagoons (with their long HRT's) are superior to activated sludge systems (with their short HRT's) [50]. However, the lack of the information about the effects of operating conditions on activated sludge treatment of CTMP effluents could also be one of the reasons for the insufficient detoxification of the effluents. Unfortunately, no study has been made on these effects. Properly designed and well operated activated sludge systems would be able to detoxify CTMP effluents.

In Canada, applications of full-scale activated sludge systems for CTMP effluents, to our knowledge, are still limited. Crofton's CTMP mill (Vancouver, B.C.) [12] has successfully upgraded its activated sludge system for the CTMP wastewater (originally designed for the TMP effluent) since 1989. The upgraded system can completely detoxify the CTMP effluent. In Québec, three activated sludge systems for CTMP effluents are being under construction : one for Témiscaming, Québec) [47], one for Kruger Inc. (Trois-Rivières, Québec) and one for Abitibi-Price Inc. (Beaupré and Kenogami, Québec) [55]. Today, many other types of activated sludge systems are under construction in Québec for TMP-based mills.

The elevated operating costs and the uncertainty of the ability to detoxify CTMP effluents may be the major reasons for the limited applications of activated sludge processes in CTMP effluent treatment. In addition, the frequent problem associated with sludge bulking in activated sludge treatment might be another reason,

although this problem might be controlled by the so-called anaerobic selector technology [60].

Although aerobic treatments, both aerated lagoon and activated sludge, have been found to be in general very effective for the removals of both  $BOD_5$  and toxicity from pulp and paper mill including CTMP effluents, the elevated operating costs of applying these methods are restricting their uses in pulp and paper mills. Mills look for other more economic alternatives to treat their effluents. One of the attractive methods is anaerobic treatment.

### **1.3.2 Anaerobic treatment of non-CTMP and CTMP effluents**

#### **1.3.2.1 Advantages and disadvantages of the treatment process**

Anaerobic process, which produces methane gas, occurs naturally in streams and ponds, and has been recognized since the 17th century as a means of producing combustible gas from the decomposition of organic matter. It is now widely recognized that anaerobic digestion of organic matter, unlike aerobic biodegradation, is a complex biological process occurred in the absence of oxygen by different groups of bacteria [61]. This process converts organic matter through a series of steps to methane and carbon dioxide as the main end products. Only a small fraction (less than 10%) of the degraded organic matter is converted into new bacterial cells. A detailed description of this process will be presented in Chapter 2.

Anaerobic digestion of municipal sewage sludge has been practised routinely since the 1930s. It has also been in recent decades widely applied to the treatment of agriculture and food industrial wastewaters, which are generally rich in biodegradable organic substrates [17]. Applications of anaerobic process to agriculture and food industries have demonstrated that this process, compared to aerobic treatment, generally possesses the following advantages :

- 1) Production of energy-rich biogas (theoretical methane yield is  $0.35 \text{ m}^3/\text{kg.COD}$  removed);
- 2) Lower sludge production (less than 10% of COD removed);
- 3) Lower energy demand since no aeration is needed in the process;
- 4) Lower nutrients requirements (i.e. nitrogen and phosphorus) since the biomass production is significant lower than that in aerobic treatment.
- 5) Ability to withstand extended period without feeding (months up to one year)
- 6) Ability to operate effectively at high temperature (up to  $55^\circ\text{C}$ ).

The first four advantages, especially the first one, can result in significant cost savings to an industry. The savings associated with the production of methane gas, for example, can offset part of the operational cost of the treatment plant. Approximately 1 KW of aeration power can be saved per 20 kg of  $\text{BOD}_5$  degraded anaerobically [62].

This technology also has some drawbacks. These drawbacks include :

- 1) Lower substrate removal rate, typically one-fourth to one-tenth of that obtained with aerobic treatment of similar substrate;
- 2) Sensitivity to changes in environmental conditions, such as pH, temperature, as well as to some inhibitory and toxic materials;
- 3) Very long first start-up period;
- 4) Difficulties to treat diluted effluents.

In the last three decades, efforts have been made to overcome or reduce these drawbacks. As a result, various high-rate anaerobic systems, as shown in Fig. 1.3, have been developed. The fourth drawback can be overcome by using the high-rate anaerobic processes, such as Up-Flow Anaerobic Sludge Blanket.

### 1.3.2.2 Principal types of anaerobic treatment systems

The low- and high-rate anaerobic processes currently used include :

- . Anaerobic lagoon
- . Anaerobic contact
- . Upflow anaerobic sludge blanket (UASB)
- . Anaerobic fluidized bed
- . Anaerobic fixed bed

Anaerobic lagoon (low-rate) : Anaerobic lagoon is the oldest anaerobic treatment process. It generally consists of a very large flow through basin where the sludge retention time (SRT) equals the HRT. To achieve a high treatment efficiency, the HRT is generally very long from 10 to over 30 days which is the major limitation of the system. Due to this limitation, anaerobic lagoons are limited mainly to the digestion of municipal sludge.

Anaerobic contact (high-rate) : Anaerobic contact process is the first high-rate anaerobic treatment system developed in the 1950s [63]. It is an outgrowth of the anaerobic lagoon, consisting of a fully mixed anaerobic reactor and a sludge settling tank, which is very similar to an activated sludge process. A portion of the sludge in the settling tank is returned to the contact reactor to maintain a high biomass concentration (from 3000 to over 10,000 mg/L) [19] in the reactor. As a result of this modification, SRT can be controlled to be much longer than the HRT. Separation of the sludge from the settling tank is the critical factor to maintain high biomass concentration and to operate the contact process. This system is suitable for treating concentrated effluents containing high concentrations of suspended solids. It can be operated at an organic loading from 2 to 6 kg COD/m<sup>3</sup>/day [19].

UASB process (high-rate): UASB process was developed by Lettinga and co-

workers in the Netherlands in the 1970s [64] and has been widely used there. This reactor operates entirely as a suspended growth system, and consequently does not contain any packing material. It contains a gas/liquid/solid separation device for separation of the biogas, treated effluent and suspended solids at the top surface of the reactor to minimize the losses of biomass. Influent is distributed into the bottom of the reactor and flows upward in the reactor.

In an UASB reactor, a very concentrated sludge bed, characterized by a dense granular sludge, develops at the bottom of the reactor. Above the sludge bed, a blanket zone of more diffuse growth with lower particle settling velocities develops. The up-flow influent and biogas produced in the sludge bed retain the sludge in the reactor in suspension. Formation of the granular sludge in the reactor is the most critical factor in process performance.

The SRT can be maintained to be extremely long up to 100 days, independent of the HRT. This feature makes the system possible to treat various concentrations from 250 to 24,000 mg/L of COD [65] of effluents, including pulp and paper mill effluents. Loading rate generally ranges from 6 to 12 kg COD/m<sup>3</sup>/day and can be up to 24 kg COD/m<sup>3</sup>/day [19]. At present, most of the full-scale high-rate anaerobic systems in use are UASBs [19, 21].

Fluidized bed process (high-rate) : In the fluidized process, influent flows upward through a medium, usually sand, in the reactor at a velocity sufficient to keep the medium in suspension. The process usually requires recycling of the effluent from the reactor to maintain the medium fluidized. Bacteria are grown on the surface of the medium. The expansion of the medium increases the surface area available for bacterial growth. The bacterial concentration developed can be five to ten times greater than that in a suspended growth system, resulting in significant reduction of HRT. The SRT in the reactor may be extremely long, comparable to an UASB reactor. Loading rate is in the range of 17 to 40 kg BOD/m<sup>3</sup>/day [19].



Fixed bed process (high-rate) : Fixed bed, also named fixed film or anaerobic filter, contains a packing material, usually a plastic material, with a large specific area. Bacteria grow on the surface of the packing material and in the void space between the surfaces. Influent may pass the bed up-flow or down-flow, resulting in up-flow fixed bed or down-flow fixed bed process. Loading rate ranges from 4 to 15 kg BOD/m<sup>3</sup>/day [19].

This type of process is suitable for the treatment of effluent containing low concentration of suspended solids. The state-of-the-art of this process has been updated in the literature reviews [66-67].

Modifications of these principal types of reactors have given rise to many other anaerobic reactor configurations. A comprehensive introduction to the high-rate anaerobic systems is provided by Van den Berg [68]. Excellent reviews on various anaerobic systems applied to pulp and paper industry have been available elsewhere [17-21].

#### **1.3.2.3 Recent progress in anaerobic treatment of pulp and paper mill effluents**

Theoretically, anaerobic technology may be also applicable to the treatment of pulp and paper mill effluents, and the advantages of the technology would also apply to the treatment of the effluents. However, the application of anaerobic technology to the treatment of pulp and paper wastewaters was quite limited before the 1980s. A combination of several factors was responsible for this lag in the application. The first reason was the lack of understanding the biochemistry and microbiology of the treatment processes. The second was that the characteristics of pulp and paper mill effluents are generally quite different from those of agricultural and food processing wastewaters. Most of pulp and paper mill effluents are usually not only diluted (300 to 2000 mg/L BOD<sub>5</sub>) which is not suitable for the conventional anaerobic processes such as anaerobic lagoon, but contain some toxic or inhibitory compounds which may

cause technical difficulties for the implementation of anaerobic treatment. The third reason was that before the 1970s most anaerobic systems in use were the conventional low-rate processes which are usually not suitable for the treatment of diluted effluent. The economic benefits associated with anaerobic treatment, however, have been always encouraging researchers to fully explore and overcome such limitations.

Research in the 1970s and the early 1980s resulted in significant advances in the state-of-the-art of anaerobic treatment technology, including both a much better understanding of the biochemistry and microbiology and the development of the high-rate anaerobic processes presented previously. These advances led to overcoming the above limitations and in turn to the successful application of full-scale anaerobic treatment systems in the pulp and paper industry. The first full-scale low-rate anaerobic lagoon treating paper mill effluents was successfully operated in the world in 1976 by an India kraft paper mill [69], and in North America in 1978 [70]. Development of the various high-rate anaerobic processes makes the economic benefit from anaerobic treatment more significant, which, again, increases the interest in the use of anaerobic technology for the treatment of pulp and paper mill effluents.

Since then, especially the middle 1980s, from the economic point of view, the use of anaerobic technology for the treatment of pulping and paper mill effluents, in particular CTMP effluents (due to their high  $BOD_5$  concentration), has become a subject of great interest to the worldwide pulp and paper industry because of its advantages over an aerobic treatment, although it also has some disadvantages as presented above. Consequently, a great number of studies on the subject have been made throughout the world for various pulp and paper mill effluents. They included : kraft mill effluent [71-72], kraft evaporator condensates [73-75], kraft bleachery effluent [76-78], peroxide bleachery waste and paper machine effluent [79], sulphite evaporator condensates [80-89], semi-mechanical or NSSC pulping wastewater [90-92], TMP effluents [75, 93-94] as well as newsprint waste [59]. These studies

focused mainly on either the treatability, or process development or applications of various high-rate anaerobic processes.

As a result of these studies, significant progress in the anaerobic treatment of pulp and paper mill effluents has been made. As evidences, to date, about 45 full-scale anaerobic treatment systems [19, 21] for various pulp and paper wastewaters have been operated or under construction in the world. Of which, there are about 30 UASB systems and 10 contact processes. Critical reviews on these full-scale anaerobic systems are available elsewhere [16, 19, 21]. In general, these systems can remove 75 - 85% of the BOD<sub>5</sub> and 55 - 65% of the COD [21]. The rates of methane production vary from 0.23 to 0.33 m<sup>3</sup>/kg. COD removed [21]. Sulphur compounds present in the effluents are thought to account for the low methane production rates [95]. However, these systems are generally unable to remove the fish toxicity [19, 59].

#### 1.3.2.4 Anaerobic treatment of CTMP effluent

Containing high concentrations of BOD<sub>5</sub>, CTMP effluent may be more suitable to anaerobic treatment than other pulp and paper wastewaters. However, CTMP effluent also contains high concentrations of some other compounds. The major compounds include wood extractives such as RFA, sulphur compounds, residual hydrogen peroxide and DTPA (in bleaching CTMP effluents). These compounds may induce inhibitory or toxic effects, depending on their concentrations, to methanogenic bacteria in anaerobic treatment systems, resulting in operational problems. Anaerobic treatment of CTMP effluent has, therefore, received particular attentions. Some laboratory and pilot studies on the subject have been made [50, 96-104], showing that CTMP effluents are anaerobically treatable.

**Effect of inhibitory compounds :** In some cases [99, 102-103], hydrogen peroxide, wood extractives, DTPA and sulphur compounds in CTMP effluent were

observed to inhibit the methanogenic activity.

Welander and Andersson [99] found that hydrogen peroxide at the concentration of 100 to 500 mg/L in a CTMP bleaching effluent seriously inhibited the methanogenic bacteria. They reported that a pre-stage prior to methanogenic reactor had successfully removed the hydrogen peroxide (up to 1200 mg/L). In the same study, the authors also found that methanogenic activity was initially completely inhibited by the presence of RFA (about 1000 mg/L reported as wood extractives) and DTPA. After several months of adaptation, methanogenic activity resumed, however, a shift in methanogenic species had occurred, implying that methanogens can acclimate to RFA. They reported that to avoid this initially inhibition effect, pre-treatment of the effluent to remove RFA and DTPA was necessary. A mixture of aluminum, ferrous iron, and calcium was shown to be an optimum combination to remove wood extractives from the effluent in a detoxification tank before the methanogenic reactor.

Pichon *et al* [102-103] found that the presence of high levels (700-800 mg/L) of sulphur compounds hinders anaerobic treatment of softwood CTMP effluent. They reported that the methanogens can acclimate to these levels after a certain period of adaptation.

Sulphur compounds inhibit methanogenic activity in effect through hydrogen sulphide. In anaerobic treatment, sulphur compounds are reduced to hydrogen sulphide which is a strong inhibitor of methanogenic activity. Although it has been recommended that the tolerable limit of hydrogen sulphur is about 200 mg/L for anaerobic systems [105], it is now well established that methanogenic bacteria can acclimate to a much higher hydrogen sulphur concentration up to 800 mg/L (reported as S) [106-107]. In addition, several methods have been developed to successfully control hydrogen sulphide toxicity in anaerobic treatment, which will be presented in Chapter 2.

Most of the studies on anaerobic treatment of CTMP effluents did not find the toxic effects of these compounds. Some authors [20] believe that the inhibitory effects of these compounds on methanogenic bacteria are affected by several factors such as the biomass growth history (acclimated or non-acclimated), effluent compositions, design and type of the reactor used. This point will be discussed in Chapter 2.

**Treatment efficiencies :** Anaerobic treatment generally removes about 70 to 85% of the BOD<sub>5</sub> [50, 96-102] and 50 to 60% of the COD from CTMP effluents [96-104], which are quite similar to those observed from other pulp and paper wastewaters [19, 21]. This level of BOD<sub>5</sub> removal can not meet the stringent BOD<sub>5</sub> discharge limits, requiring further removal of BOD<sub>5</sub> from the anaerobically treated effluents.

Anaerobic treatment alone is unable to detoxify CTMP effluents [50, 96-100] (other pulp and paper mill effluents as well [59]), which can not meet the non-toxic to fish regulation. In all the cases, aerobic post treatment was needed to remove toxicity.

Unlike aerobic treatment (both aerated lagoon and activated sludge), anaerobic treatment generally produces a poor removal (less than 60%) of RFA from CTMP effluent [103] and other pulp and paper wastewaters [59, 108]. The poor removal of RFA appears to be one of the important reasons for insufficient detoxification of CTMP effluents by anaerobic treatment alone, since RFA concentrations in CTMP effluents are elevated.

**Application of full scale systems :** To date, there have been at least nine full-scale anaerobic treatment systems in the world used for the treatment of CTMP effluents : four UASB systems in Canada [19, 51, 109-110], two contact reactors in Sweden [111-112], one contact reactor in the United States [113], one UASB reactor

in Finland [19] and one two-stage anaerobic system (UASB/Polyurethane Carrier reactor) in New Zealand [104]. None of these systems can detoxify CTMP effluents.

Therefore, anaerobic treatment can be only used as a pre-treatment for highly toxic CTMP effluent. In fact, all the full scale anaerobic systems currently used for the treatment of pulp and paper mill including CTMP effluents have been used as the pre-treatment processes. To produce a non-toxic effluent, a post aerobic polishing stage following the treatment is always needed. Two-stage anaerobic-aerobic processes have thus been introduced to the treatment of CTMP and other pulp and paper mill effluents.

### **1.3.3 Two-stage anaerobic-aerobic treatment of CTMP effluent**

#### **1.3.3.1 The process and its advantages**

Two-stage anaerobic-aerobic process consists of an anaerobic stage (usually a high-rate system) followed by an aerobic stage (an aerated lagoon or activated sludge). The idea of using this process for the treatment of pulp and paper mill effluents is : 1) using anaerobic treatment as pre-treatment (first stage) to convert most of the  $BOD_5$  in the effluent to methane gas; 2) using aerobic treatment as post-treatment (second or polishing stage) to remove the fish toxicity and to further increase the  $BOD_5$  removal. This two-stage process should be effective for the removals of both  $BOD_5$  and toxicity from pulp and paper mill effluents.

The gas methane generated in the anaerobic stage can be useful. Since  $BOD_5$  has been mostly removed in the anaerobic stage, the hydraulic retention time required for the post aerobic treatment is thus greatly reduced, as compared with that required for a single stage aerobic treatment for a fixed removal of  $BOD_5$ . Consequently, the operating costs related to the aerobic stage are greatly reduced. This two-stage process, as compared to single stage aerobic process, would be more cost effective,

as shown in Fig. 1.4 [18], in particular for CTMP effluent which contains high concentration of  $BOD_5$  (3000 mg/L, on an average). Therefore, two-stage treatment should be both effective and economic for CTMP effluent. It is thus used in this research to treat the CTMP effluent studied.

#### 1.3.3.2 Treatment of CTMP effluents

Using this two-stage process, numerous studies have been made on the treatment of CTMP effluents [50-51, 98, 110-112, 114] and other pulp and paper wastewaters [71-72, 76, 78, 85, 88, 94]. All of them were in effect made on the first stage, focusing on the treatability of the effluents by anaerobic treatment and on the development of treatment techniques as presented in section 1.3.2. No study was made on how to combine the anaerobic and aerobic stages together.

This two-stage process has been used in not too many mills to remove  $BOD_5$  and toxicity from CTMP [19, 21] and other pulp and paper mill effluents [19, 21]. All the existing full-scale treatment systems with anaerobic reactors presented in the above for pulp and paper mill effluents are in effect two-stage anaerobic-aerobic processes.

It is believed that the design and operation of the full-scale anaerobic-aerobic treatment systems for CTMP effluents have been based not on the theoretical criteria but on the knowledge and experiences from single stage anaerobic and aerobic treatments of other pulp and paper mill effluents and other types of wastewaters, because no study has been made on either the kinetics or the design parameters for either aerobic or anaerobic treatment of CTMP effluents. Thus, at least no optimization has been made on the design and operation of each stage in the process. It is therefore necessary to determine the kinetic and design parameters for both anaerobic and aerobic treatments of CTMP effluents.

Theoretically, for a two-stage treatment process, there should have an optimum combination between the stages at which the design of the process is optimal. For instance, for a fixed overall treatment efficiency, what should be the HRT in the anaerobic stage for the treatment switching from this stage to the aerobic stage so that the total treatment time required is minimal? The design and operation of each stage in existing two-stage systems for CTMP effluents and for other pulp and paper wastewaters have been, however, based wholly upon experiences, since no methods have been available for the designs. It is therefore quite necessary and valuable to establish optimization methods for the design and operation of this two-stage process.

Although aerobic treatment has been found to be very effective for fish toxicity removal from CTMP and other pulp and paper mill effluents, the removal mechanisms of RFA by the treatment are unclear. Understanding the mechanisms would be useful for optimizing the treatment to detoxify CTMP effluents.

The present research, with the objectives as presented previously in the Introduction of this thesis, was therefore carried out to study how the operating conditions would affect the treatment behaviour of this process through simulation, how to optimize this process for CTMP effluent treatment, and how the RFA which relate to fish toxicity are removed by aerobic treatment.



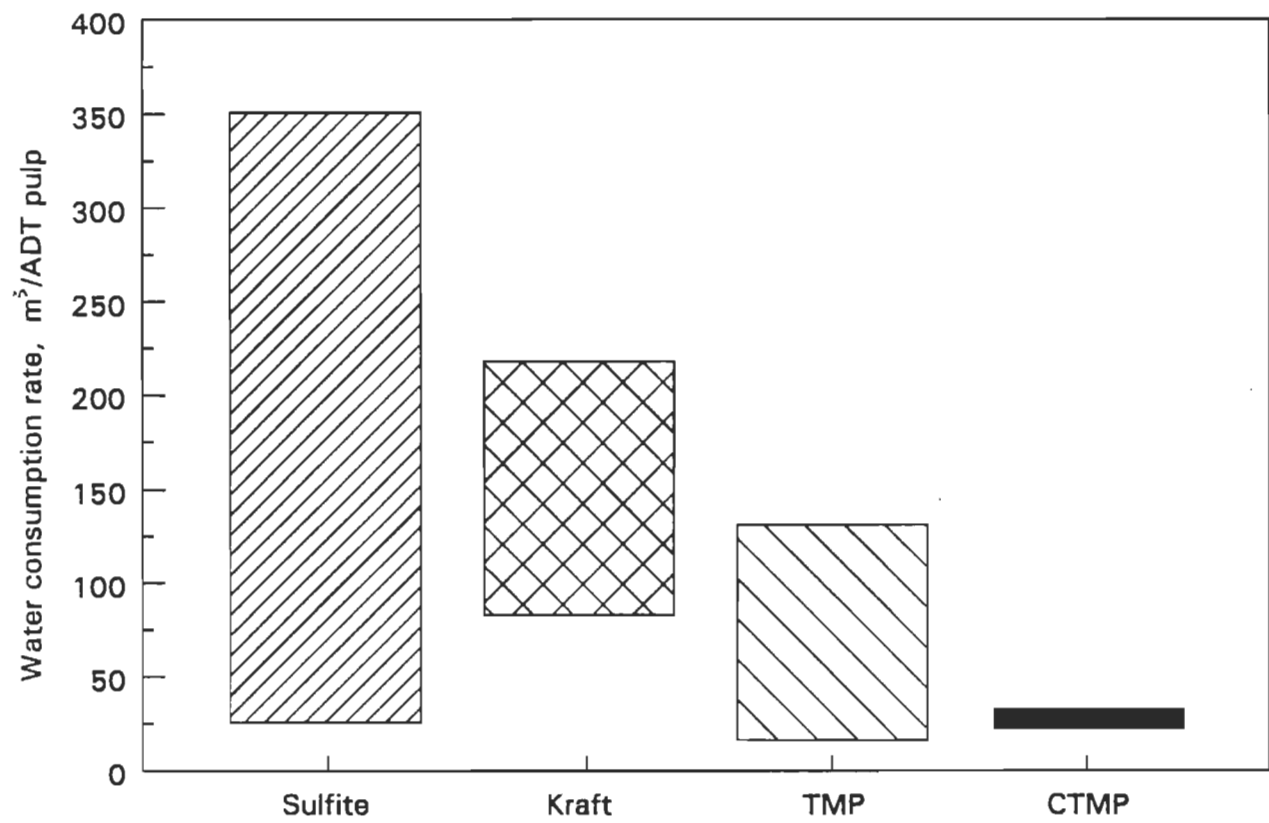


Fig. 1.1 Typical water consumption rate of various pulping processes used in Canadian mills

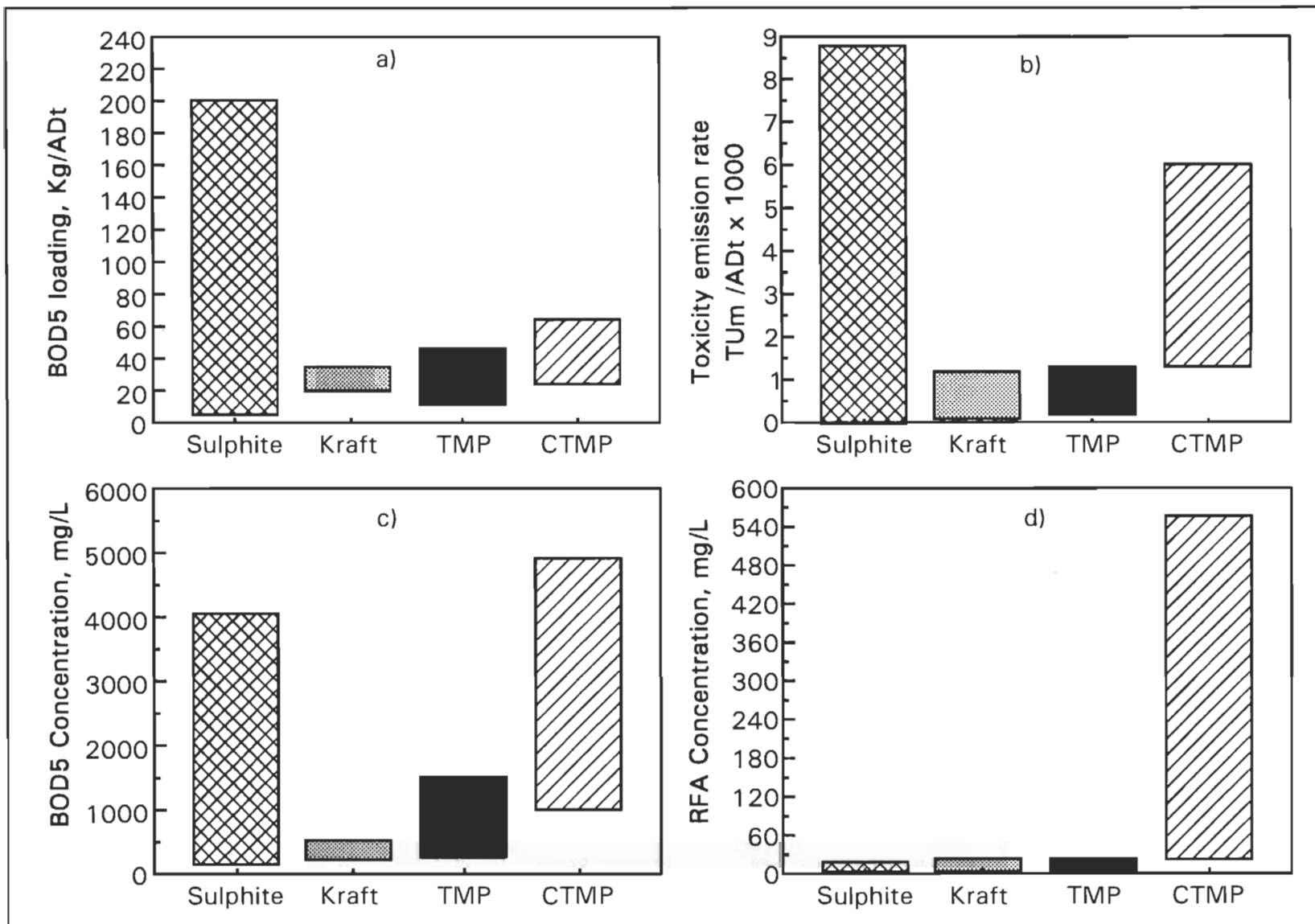


Fig. 1.2 Approximate characteristics of the effluents from various pulping processes: Sulphite, Kraft, TMP and CTMP [3].

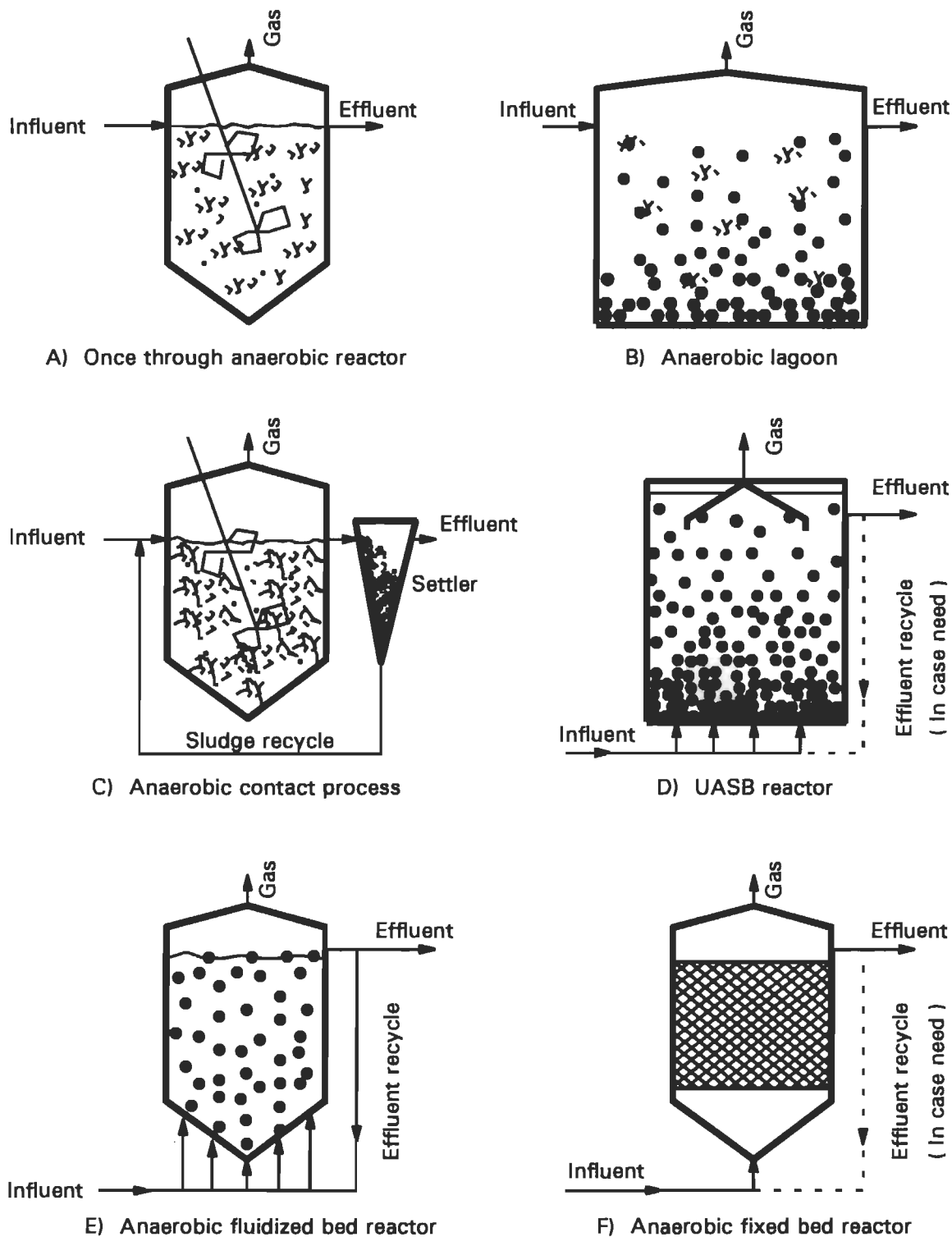


Fig. 1.3 Principal types of anaerobic treatment processes

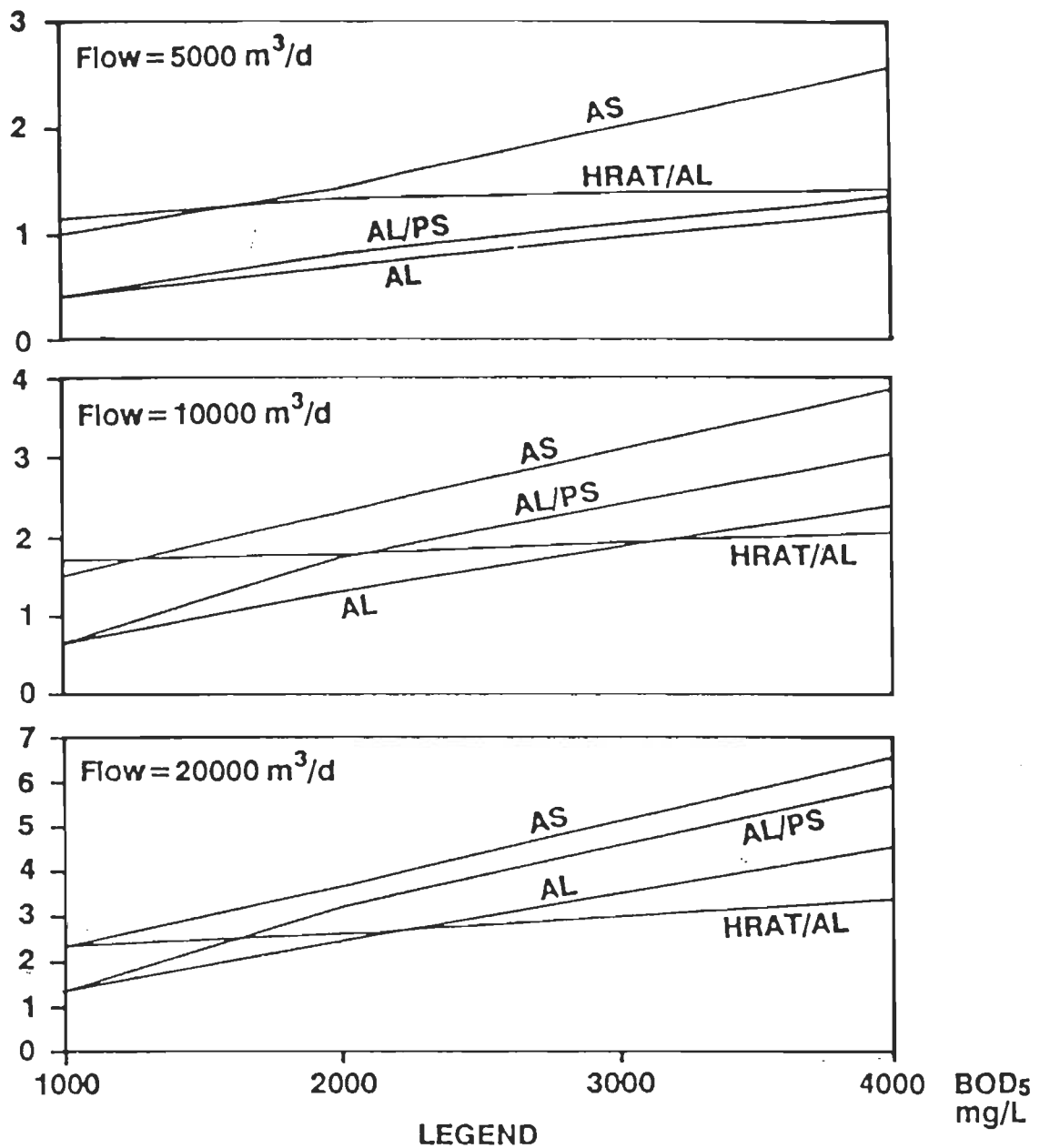


Fig. 1.4 Total annual cost comparison between four biological treatment processes for CTMP effluents [ref. 18]

## CHAPTER - 2

### THEORETICAL

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Since the two-stage process consists of a stage of anaerobic digestion and a stage of aerobic bio-oxidation, the principles applied to the single stage, either anaerobic or aerobic, treatment should be applicable to the corresponding stage in the process.

#### 2.1 Anaerobic digestion

##### 2.1.1 General description of the process

Anaerobic digestion of complex organic wastes is a multi-step process consisting of series and parallel biochemical reactions and has been in general described as the four-step process [19], as illustrated in Fig. 2.1. In this process, complex organic compounds are sequentially converted to methane and carbon dioxide as main end products. The four steps are : 1) hydrolysis, 2) fermentation, 3) acetogenesis and dehydrogenation, and 4) methanogenesis.

1) *Hydrolysis* : In the first step, complex high molecular weight organic matter (i.e. carbohydrates, protein, and lipids) is first hydrolysed by extracellular enzymes to soluble product of low molecular weight organic compounds (i.e. simple sugars, amino acids, fatty acids, and glycerol) which can pass through the cell membrane.

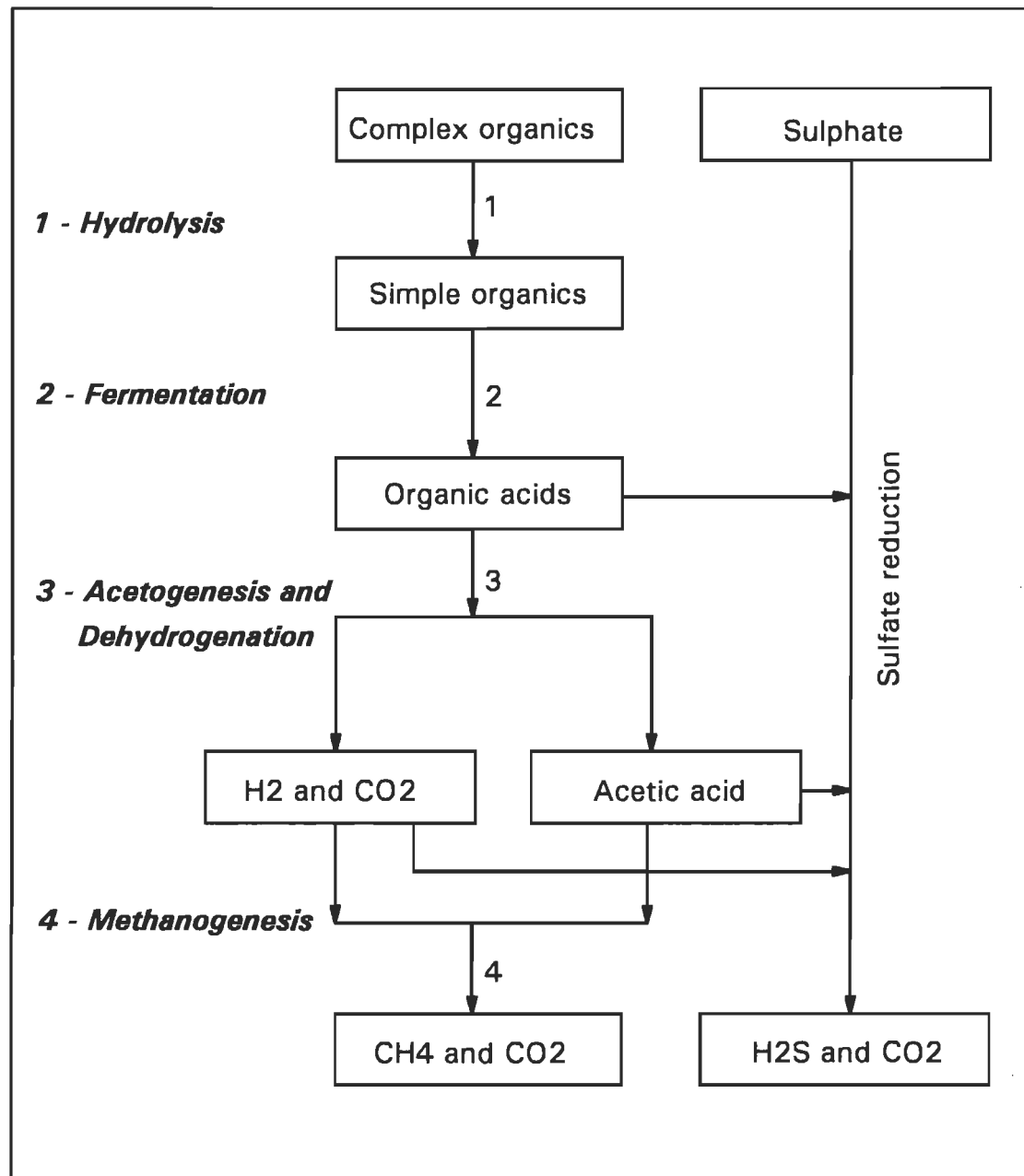
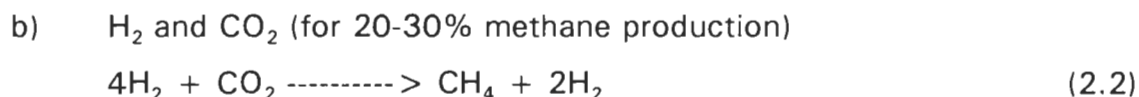
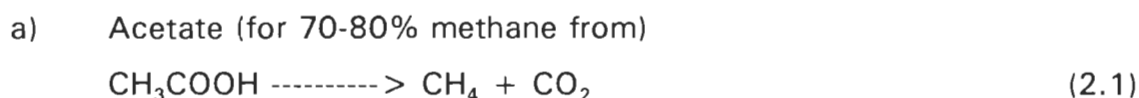


Fig. 2.1 The principal steps of anaerobic digestion of complex organic wastes containing sulphur compounds [19]

2) *Fermentation* : These relative simple organics produced from hydrolysis are then converted to short-chain fatty acids, and to acetic acid, alcohol, carbon dioxide, hydrogen, and ammonia by acidogenic bacteria.

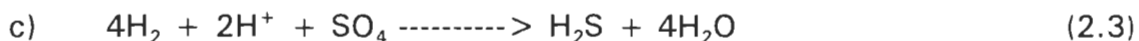
3) *Acetogenesis and dehydrogenation* : The short-chain fatty acids (other than acetate) are subsequently converted to acetic acids, hydrogen and carbon dioxide by acetogenic bacteria.

4) *Methanogenesis* : The methanogenic bacteria finally metabolize and convert acetate, methanol, carbon dioxide and hydrogen to methane according to the following reactions:



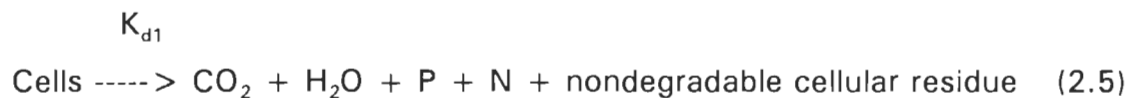
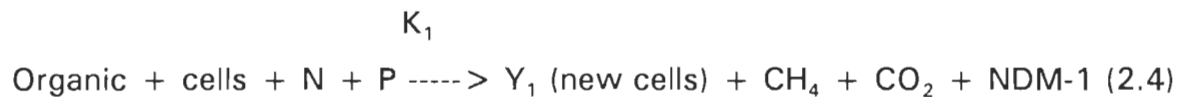
The methanogenic bacteria are strict anaerobes and require a highly reduced environment with optimal redox condition of less than -51 MV [115]. Therefore, in this step, the system must be absolute oxygen-free. Three principal methanogenic bacteria are responsible for reactions (a) and (b); they are methano-bacterium, methanosarcina and methanococcus.

In reaction b),  $\text{CO}_2$  is an electron ( $\text{H}_2$ ) acceptor. Sulphur compounds are also electron ( $\text{H}_2$ ) acceptors. If sulphur compounds are present in the process, they also consume the  $\text{H}_2$  and are reduced by sulphate-reducing bacteria, Dessulfovibrio (19), to both highly toxic and corrosive hydrogen sulphide ( $\text{H}_2\text{S}$ ), as represented by the following reaction c), reducing methane production.



Reaction c) accounts for the odour and low methane production from anaerobic treatment of paper mill wastes in particular CTMP effluents in which sulphur compounds are present. At pH 7, about 20% of the  $H_2S$  produced dissolves in the liquor phase in the treatment system; the other 80% exists with  $CO_2$  and  $CH_4$  in the biogas.

In the whole process, only a small fraction of organic matter removed is converted to new bacterial cells. The cells undergo, at the same time, progressive auto-oxidation of their cellular mass; reactions involved in this process are much more complicated than the ones presented above, and not always clearly defined. However, if one has no interest to study the reaction mechanisms involved in this process, the overall process of an anaerobic digestion may be represented approximately by the following equations :



Where NMD-1 is the non-degradable organic matter by anaerobic digestion.

In equ. (2.4),  $Y_1$  is the fraction of organic matter removed that is synthesized to biomass of anaerobic bacteria. The value of  $Y_1$  is normally very low and less than 0.1, (i.e. less than 10% of the  $BOD_5$  removed is converted to new anaerobic biomass), which is one of the major advantages of anaerobic treatment.  $K_1$  is the overall removal rate of the organic matter by anaerobic digestion. While  $K_{d1}$  in equ. (2.5) is the fraction of anaerobic biomass endogenously oxidized per day.



### **2.1.2 Environmental conditions affecting the process**

Anaerobic processes are generally very sensitive to the variation of the environmental conditions. Stable operation of an anaerobic system requires a strict control of the environmental conditions. The environmental conditions affecting anaerobic treatment include : temperature, pH and alkalinity, volatile acids, nutrients and micronutrients, inhibition and toxicity, etc.

#### **2.1.2.1 Temperature**

Temperature is an important environmental condition affecting the growth rate of anaerobic bacteria. Optimum temperature for mesophilic bacteria lies between 30 and 38 °C and for thermophilic bacteria between 50 and 60 °C [19, 116-117]. Considering the relatively high temperature (50 to 70 °C) of many pulp and paper mill effluents, operation of anaerobic systems in the optimum range of 55 to 60 °C has been investigated [19]. The temperature in the thermophilic optimum range, however, has not been found to be effective for pulp and paper mill effluents. It is recommended to operate anaerobic treatment at temperature around 35 °C. All of the full-scale anaerobic systems currently treating pulp and paper mill effluents are operating in the mesophilic temperature range (32 to 36 °C) [19].

#### **2.1.2.2 pH and alkalinity**

pH is a critical environmental condition in anaerobic treatment. In an anaerobic system, the methanogenic bacteria require more strict pH condition than the acidogenic bacteria. The optimal pH for the methanogenic bacteria growth ranges from 6.8 to 7.5 [19, 116-117], although the methane production is possible in the pH range of 6.0 to 8.5. Methanogenic bacteria growth will be inhibited when pH is below 6.5 or above 9, resulting in a lower methane production. Acidogenic bacteria are still very active at pH below 4.5 [21].

Alkalinity in anaerobic system must be sufficient to neutralize the volatile acids produced during the process to maintain an optimum pH (6.8 to 7.5). Bicarbonate alkalinity is the primary buffer for this end. Bicarbonate alkalinity in the range of 1000 to 5000 mg/L (as  $\text{CaCO}_3$ ) normally is adequate to maintain an optimum pH [116]. CTMP effluent usually contains high level of alkalinity so that very little additional caustic should be required for pH control [3, 51].

#### 2.1.2.3 Volatile fatty acids

The concentration of volatile fatty acids (VFA) is an useful parameter for monitoring and controlling an anaerobic process. The concentration of VFA in a well operated anaerobic system should not exceed 5 - 10 meq/L or 300 - 600 mg/L (as  $\text{CH}_3\text{COOH}$ ) [118]. If the methanogenic bacteria are not able to convert the VFA as rapidly as they are produced by the acidogenic bacteria, the VFA will accumulate in the system and cause a depression in the system pH. If this is allowed to continue, the pH will be depressed outside the optimum range and poor system performance will result. VFA can be toxic by virtue of their acidity above 2000 mg/L, if adequate pH conditions are not maintained [19].

#### 2.1.2.4 Nutrients and micronutrient

Biomass synthesis in all biological process require nitrogen and phosphorus as nutrients. For anaerobic treatment, a ratio of  $\text{BOD}_5/\text{N}/\text{P}/ = 100/1/0.5/$  or  $\text{COD}/\text{N}/\text{P} = 100/0.4/0.2$  is required [21, 51, 118]. For pulp and paper mill effluents, additions of inorganic nitrogen and phosphorus are required to obtain this necessary food to nutrients ratio.

In addition to nitrogen and phosphorus, several other inorganic elements are also required in trace quantities for optimizing anaerobic processes. These micronutrients and their required concentration are presented in Table 2.1 [118]. The

most important micronutrients are iron, nickel, cobalt, molybdenum and selenium. Pulp and paper mill effluents normally contain most of the micronutrients in sufficient quantities, as a result of piping and equipment corrosion.

**Table 2.1.** Required minimum concentration of some micronutrients for anaerobic digestion [118]

<i>Micronutrient</i>	<i>Required minimum concentration (mg/L)</i>
Aluminium	0.01
Calcium	50.0
Cobalt	0.09
Copper	0.01
Iron	0.06
Magnesium	3.6
Manganese	0.05
Molybdenum	0.01
Nickel	0.03
Potassium	7
Selenium	0.03
Zinc	0.07

#### 2.1.2.5 Inhibition and toxicity of toxicants

Methanogenic bacteria in anaerobic systems are generally very sensitive to the presence of toxic compounds, which is one of the major limitations of anaerobic treatment. The toxic or inhibitory effects of toxic compounds may result in operational problems in anaerobic systems. It is impossible to list all the toxic or inhibitory compounds. The inhibitory or toxic compounds that are of potential concern in anaerobic treatment of pulp and paper mill effluents include :

- . Inorganic sulphur compounds (sulphate, sulphite and sulphide);
- . Oxidants such as residual hydrogen peroxide used in pulp bleaching;
- . Wood extractives, including RFA;
- . Organic additives, such as DTPA, a strong chelating agent;
- . Volatile organic acids;
- . Heavy metals.

**Table 2.2.** Toxic or inhibitory effects of some compounds on anaerobes

Compounds	Concentration (mg/L)	Effect
NH <sup>+</sup>	1500-2000	Toxic
Ammonium (NH <sub>3</sub> )	50-80	50% inhibitory
Sulphur	> 200	Toxic
Sulphate	2200-10000	50% inhibitory
Sulphite	150-250	50% inhibitory
Sulphide (S <sup>=</sup> )	20-250	50% inhibitory
Sulphide (H <sub>2</sub> S)	50	40% inhibitory
	200-250	Toxic
H <sub>2</sub> O <sub>2</sub>	50-200	Strong inhibitory
Sodium (Na <sup>+</sup> )	7600-10000	50% inhibitory
Potassium (K <sup>+</sup> )	6100	50% inhibitory
Calcium (Ca <sup>2+</sup> )	4700	50% inhibitory
Magnesium (Mg <sup>2+</sup> )	1930	50% inhibitory
Long chain fatty acids	500-1250	50% inhibitory
Resin acids	55-115	50% inhibitory
Monomeric tannin	940-3200	50% inhibitory

**Table 2.2** lists the concentrations of some compounds that produce inhibitory effects on methanogenic bacteria [118]. It should be mentioned that the values of

these inhibitory concentrations listed in **Table 2.2** can be different due to different experimental conditions, such as biomass growth history, temperature, pH etc.

**Sulphur compounds :** Small amounts of sulphur compounds are essential for the growth of anaerobic bacteria. However, at high concentration sulphur compounds may inhibit anaerobic bacterial growth. Inhibitions by sulphite [106, 119] and dithionite [119] are observed at 100 mg/L and by free hydrogen sulphide at about 50 - 100 mg S/L [105, 120-123]. Free hydrogen sulphide inhibits also propionate oxidizers, which may cause even more serious problems for the anaerobic process than inhibition of the acetotrophic methanogens [124]. However, after acclimation methanogens may tolerate sulphate and hydrogen sulphide at concentration up to 1600 mg S/L [120] and 200 mg S/L [105], respectively. Sulphate inhibition of anaerobic treatment of CTMP softwood effluents [102-103] have also been reported. Different experimental conditions may account for these different inhibition results.

As presented previously, in anaerobic systems sulphur compounds are reduced to hydrogen sulphide which is a strong inhibitor to methanogenic bacteria. Therefore, it appears that, in anaerobic treatment, the most relevant sulphur inhibitor is the free hydrogen sulphide produced from the reduction of sulphur compounds. In anaerobic treatment of pulp and paper mill effluents, sulphur inhibitions are of most concern and should be minimized. Several methods are available to reduce hydrogen sulphide inhibition to anaerobic treatment systems :

- . Biomass acclimation/adaptation, long sludge retention time;
- . Removal of sulphur compounds from the feed;
- . Metal precipitation of hydrogen sulphide;
- . Hydrogen sulphide stripping and reactor biogas recirculation;
- . pH control at values of 8 or above to reduce free hydrogen sulphide;
- . Maintaining COD:SO<sub>4</sub> -S ratio in excess of 100:1 to prevent sulphide inhibition. Ratio as low as 10-12:1 has also been claimed to achieve this

end [103];

- . Two-stage anaerobic systems in which sulphur is reduced to hydrogen sulphide and removed in the first stage.
- . Diluting feed.

All these methods have been successfully used in anaerobic treatment of pulp and paper mill including CTMP effluents which usually contain sulphur compounds [19].

**Hydrogen peroxide :** Methanogenic bacteria are strict anaerobes, requiring a highly reduced environment. Hydrogen peroxide, a very strong but unstable oxidizer, is very toxic to methanogenic bacteria that have no catalase enzyme to decompose it. Hydrogen peroxide at concentration about 200 mg/L has been found to inhibit the methanogenic activity in anaerobic treatment of CTMP effluents [99-100]. However, hydrogen peroxide is not toxic to facultative and aerobic bacteria that possess catalase enzyme. On this principle, physical separation of acidogenic and methanogenic phases of anaerobic treatment into two sequential stages is one method of peroxide detoxification. Other methods for removing hydrogen peroxide include 1) decomposition by chemical reaction with reduced compounds; 2) detoxification in a pre-stage by aerobic sludge. All these methods are very effective for decomposition of hydrogen peroxide and have been successfully used in anaerobic treatment of pulp and paper mill effluents [19].

**Wood extractive, RFA and DTPA :** Wood extractives including RFA at high concentration, and DTPA are toxic to anaerobic organisms [99, 125-128]. 50% inhibitory concentrations for resin acids and fatty acids range from 55 to 115 mg/L and from 523 to 1250 mg/L, respectively (**Table 2.2**) [116]. The concentration of resin acids in some CTMP effluents would fall in the range and could be of concern for anaerobic treatment of the effluents. DTPA has also been found to be inhibitory to anaerobic bacteria [99].

These organic toxicants can be removed by precipitation with aluminum, iron, and calcium salts [39-46, 99, 129]. Adaptation of the methanogens to RFA and DTPA at certain concentrations is also possible.

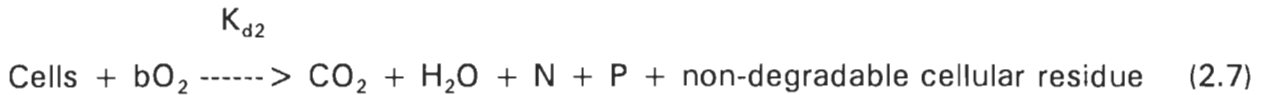
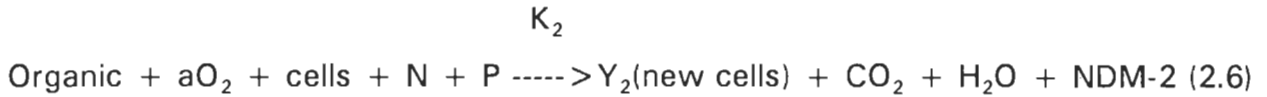
**VFA :** VFA can be toxic by virtue of their acidity approximately above 2000 mg/L, if optimum pH condition is not maintained [116]. As long as the VFA are neutralized, higher level can be tolerated after bacteria acclimation, until the soluble cations become inhibitory at levels exceeding 4000 to 7000 mg/L [116].

**Heavy metal :** Heavy metals at high concentrations can be toxic to anaerobic bacteria by reacting with enzymes to block metabolism. They are however, are not of concern in anaerobic treatment of pulp and paper mill effluents since they precipitate in the presence of sulphide. Iron and nickel, in fact, are two metals that frequently must be added to obtain the necessary micronutrient.

In summary, if toxic compounds present at high concentrations are inhibitory to anaerobic systems, they must be removed prior to anaerobic treatment. General approaches include removal of toxic compounds from process stream before anaerobic treatment, addition of antagonistic compounds, dilution to nontoxic concentrations, and acclimation of the biomass.

## 2.2 Aerobic oxidation

In aerobic treatment, organic matter is directly bio-oxidized to gaseous end product,  $\text{CO}_2$ , and water by microorganisms and new cell mass is synthesized, with the consumption of oxygen. In the deficiency of organic matter, some cells undergo progressive auto-oxidation (endogenous decay) of their cellular mass. The above processes occur simultaneously and can be represented by the following two equations :



Where NDM-2 is the non-degradable organic matter by aerobic oxidation

In equ. (2.6),  $K_2$  is the constant of the overall removal rate of organic matter by aerobic bacteria, and  $a$  is the coefficient for the oxygen required to bio-oxidize the organic matter by the bacteria.  $Y_2$  is the fraction of the organic matter removed that is synthesized into aerobic biomass. Generally, the value of  $Y_2$  is very high, ranging from 0.4 to 0.6 (i.e., 40 to 60% of the  $\text{BOD}_5$  removed is converted to new aerobic biomass).  $K_{d2}$  in equ. (2.7) is the fraction of aerobic biomass auto-oxidized per day and  $b$  is the coefficient for oxygen rate required for endogenous decay of the aerobic biomass.

Unlike anaerobic processes, aerobic processes do not require strict environmental conditions. Aerobic microorganisms are not sensitive to the compounds that are toxic to anaerobic bacteria. The compounds that are toxic to anaerobic bacteria are usually not toxic to aerobic microorganisms. The environmental conditions that affect aerobic processes are much less severe than those for anaerobic processes; they include temperature, pH and concentration of dissolved oxygen. Optimum environmental conditions may be different from effluent to effluent to be treated, and must be investigated for the effluent to be treated.



## 2.3 Kinetic models and design equations

As described previously, both anaerobic and aerobic biodegradations of organic matter essentially involve several biochemical reactions that degrade the organic matter to end products. For any biological treatment process, reaction kinetics plays a central role in the design, optimization, and operation of the process. To study the performance behaviour and design optimization of the two-stage anaerobic-aerobic process with the use of the selected CTMP effluent in the research, the parameters mentioned above, i.e., ( $K_1$  and  $K_2$ ), ( $K_{d1}$  and  $K_{d2}$ ), ( $Y_1$  and  $Y_2$ ), and ( $a$  and  $b$ , for aerobic process only) are needed and must be determined experimentally.

### 2.3.1 Kinetic models for biological processes

The rate of substrate (organic matter) utilization by microorganisms in a biological process usually follows a certain kinetic model. A number of kinetic models are available for biological processes. Among the available models, the first order reaction kinetics and Monod model [130], as expressed by eqs. (2.8) and (2.9), respectively, have been successfully applied in describing the rate of substrate removal in both steady state anaerobic and aerobic treatments of most wastewaters [131-134]. These two models are also simple in form and thus easy to use, which is very important in practical treatment. They are thus used to study the kinetics of substrate removal (in terms of  $BOD_5$  and RFA) in both the anaerobic and aerobic treatments of the CTMP effluent studied.

First order reaction model :

$$r_s = -kXS \quad (2.8)$$

Monod model :

$$r_s = \frac{KXS}{K_s + S} \quad (2.9)$$

### 2.3.2 Equation for sludge yield

For a completely mixed system, the specific net yield rate of sludge is given by :

$$\frac{\Delta X}{X_T} = \frac{1}{t_s} - Y \frac{S_o - S}{Xt} - K_d \quad (2.10)$$

### 2.3.3 Equation for oxygen utilization

For an aerobic process, another very important design parameters are the oxygen utilization coefficients. The following equation [131] is used to determine these parameters :

$$SOUR = a \frac{S_o - S}{Xt} + b \quad (2.11)$$

## 2.4 Basic equations for the two-stage anaerobic-aerobic system

For simplification, the two-stage system is shown schematically in Fig.3.1c. As shown, the system consists of two CFSTR's in series with sludge recycle, in which the first stage is for anaerobic treatment and the second for the post aerobic treatment. Both stages are assumed to operate under steady state conditions. To control the mean cell age in each stage, the wastage of sludge is withdrawn directly from the stage.

To study the behaviour of the system and to optimize the design and operation of such system for the CTMP effluent studied, the basic equations for each stage in the system are first set-up by coupling the kinetic models observed for the two stages. If the substrate removal rates in both stages follow a first order reaction kinetics (equ. (2.8)), or Monod model (equ. (2.9), or any combination of the two, then the corresponding models are used to set-up the basic equations for the system studied. In the following, the basic equations for each stage are presented, as an example, on the basis of first order reaction model, providing that the substrate removal rates for both stages follow this model.

#### 2.4.1 Basic equations for the anaerobic stage

**Mass balance of substrate :** A mass balance for substrate around the reactor yields:

$$[Q_o S_o + Q_{r1} S_1] - [(Q_o + Q_{r1} - Q_w) S_1 + Q_w S_1] - [r_{s1} V_1] = 0 \quad (2.12)$$

Insertion of equ. (2.8) into equ. (2.12) gives, after rearrangement :

$$\frac{Q_o(S_o - S_1)}{V_1} = k_1 X_1 S_1 \quad (2.13)$$

The hydraulic retention time  $t_1$  in the reactor is given by:

$$t_1 = \frac{V_1}{Q_o} \quad (2.14)$$

From equs. (2.13) and (2.14), one obtains the following equation :

$$\frac{(S_o - S_1)}{t_1} = k_1 X_1 S_1 \quad (2.15)$$

The solution of equ. (2.15) for  $S_1$  gives :

$$S_1 = \frac{S_o}{k_1 X_1 t_1 + 1} \quad (2.16)$$

The treatment efficiency in terms of removal  $E_1$  of the stage is expressed as :

$$E_1 = \frac{(S_o - S_1)}{S_o} 100\% \quad (2.17)$$

**Mass balance of microorganisms and mean cell age :** A mass balance for microorganisms around the stage including the settling tank results in :

$$[Q_o X_o] - [Q_{wl} X_1 + (Q_o - Q_{wl}) X_{el}] + [r_{gl} V_1] = 0 \quad (2.18)$$

The net growth rate of microorganisms is given by :

$$r_{gl} = Y_1 r_{sl} - K_{dl} X_1 = Y_1 k_1 X_1 S_1 - K_{dl} X_1 \quad (2.19)$$

Neglecting  $X_o$  and inserting equ. (2.19) into equ. (2.18) yields, with the  $r_{s1}$  in equ. (2.8):

$$\frac{Q_{wl} X_1 + (Q_o - Q_{wl}) X_{el}}{V_1 X_1} = Y_1 k_1 S_1 - K_{dl} \quad (2.20)$$

The mean cell age  $t_{s1}$  for the stage has been defined as :

$$t_{s1} = \frac{V_1 X_1}{\Delta X_1} = \frac{V_1 X_1}{Q_{wl} X_1 + (Q_o - Q_{wl}) X_{el}} \quad (2.21)$$

One thus obtains from equs. (2.20) and (2.21) :

$$t_{s1} = \frac{1}{Y_1 k_1 S_1 - K_{dl}} \quad (2.22)$$

From equs. (2.15) and (2.22), an expression for  $X_1$  as a function of  $t_1$ ,  $t_{s1}$ ,  $S_o$  and  $S_1$  is obtained :

$$X_1 = \frac{t_{s1}}{t_1} \frac{Y_1(S_o - S_1)}{1 + K_{d1}t_{s1}} \quad (2.23)$$

For calculation purpose, equ. (2.22) is rearranged to yield another expression for the substrate concentration  $S_1$  in the anaerobic stage :

$$S_1 = \frac{1 + K_{d1}t_{s1}}{Y_1k_1t_{s1}} \quad (2.24)$$

Expressions (2.16), (2.17) and (2.24) are the basic equations for studying the treatment behaviour of the anaerobic stage.

#### 2.4.2 Basic equations for the aerobic stage

For the aerobic stage, the basic equations are the same as those just presented above, except for the symbols.

**Mass balance of substrate :**

$$\frac{(S_1 - S_2)}{t_2} = k_2 X_2 S_2 \quad (2.25)$$

$$S_2 = \frac{S_1}{k_2 X_2 t_2 + 1} \quad (2.26)$$

$$E_2 = E + \frac{(S_o - S_2)}{S_o} 100\% \quad (2.27)$$

**Mass balance of microorganisms and mean cell age :**

$$t_{s2} = \frac{1}{Y_2 k_2 S_2 - K_{d2}} \quad (2.28)$$

$$X_2 = \frac{t_{s2}}{t_2} \frac{Y_2 (S_1 - S_2)}{1 + K_{d2} t_{s2}} \quad (2.29)$$

$$S_2 = \frac{1 + K_{d2} t_{s2}}{Y_2 k_2 t_{s2}} \quad (2.30)$$

Where :  $t_2 = V_2 / (Q_o - Q_{w1})$ .

Expressions (2.26), (2.27) and (2.30) are the basic equations for studying the overall behaviour of the treatment system, in terms of the BOD<sub>5</sub> and RFA concentrations in the final effluent and their overall % removals.

Following the same approaches, the basic equations for the two-stage system can also be set-up on the basis of the Monod model or any combination of first order reaction kinetics and Monod model. Table 2.3 lists the basic equations set-up for the system on the basis of the Monod model.

**Table 2.3.** Basic equations set-up for the two-stage anaerobic-aerobic system on the basis of Monod model

Basic equations for the anaerobic stage	Basic equations for the aerobic stage
$\frac{(S_o - S_1)}{t_1} = \frac{K_1 X_1 S_1}{K_{s1} + S_1} \quad (2.31)$	$\frac{(S_1 - S_2)}{t_2} = \frac{K_2 X_2 S_2}{K_{s2} + S_2} \quad (2.36)$
$S_1 = \frac{S_o - K_{s1} - K_1 X_1 t_1 + \sqrt{(S_o - K_{s1} - K_1 X_1 t_1)^2 + 4 K_{s1} S_o}}{2} \quad (2.32)$	$S_2 = \frac{S_1 - K_{s2} - K_2 X_2 t_2 + \sqrt{(S_1 - K_{s2} - K_2 X_2 t_2)^2 + 4 K_{s2} S_1}}{2} \quad (2.37)$
$t_{s1} = \frac{K_{s1} + S_1}{Y_1 K_1 S_1 - K_{d1} (K_{s1} + S_1)} \quad (2.33)$	$t_{s2} = \frac{K_{s2} + S_2}{Y_2 K_2 S_2 - K_{d2} (K_{s2} + S_2)} \quad (2.38)$
$X_1 = \frac{t_{s1}}{t_1} \frac{Y_1 (S_o - S_1)}{(1 + K_{d1} t_{s1})} \quad (2.34)$	$X_2 = \frac{t_{s2}}{t_2} \frac{Y_2 (S_1 - S_2)}{(1 + K_{d2} t_{s2})} \quad (2.39)$
$S_1 = \frac{K_{s1} (1 + K_{d1} t_{s1})}{t_{s1} (Y_1 K_1 - K_{d1}) - 1} \quad (2.35)$	$S_2 = \frac{K_{s2} (1 + K_{d2} t_{s2})}{t_{s2} (Y_2 K_2 - K_{d2}) - 1} \quad (2.40)$

## 2.5 Derivation of optimization method for the two-stage treatment system on the basis of first order reaction model

As mentioned previously, from the view point of both economy and effluent

detoxification, the use of two-stage anaerobic-aerobic process for the treatments of CTMP effluent and other pulp and paper wastewaters has recently become a subject of great interest to the pulp and paper industry. However, the design and operation of not too many full-scale anaerobic-aerobic treatment systems for CTMP effluents [19, 21] and other pulp and paper wastewaters [19, 21] have been wholly based on the knowledge and experiences from single stage aerobic and anaerobic treatments of other pulp and paper mill effluents and other types of wastewaters. Although one can obtain the expected removal efficiency from the two-stage system, the reactor volumes used in both stages might be over-sized due to that the design has not been optimized. An optimization method for determining the hydraulic retention time in, or the reactor volume of, each stage is necessary and useful for the design of such two-stage system.

Since the two-stage system consists of two bioreactors in series, there should exist a best combination of the treatment times in the two stages so that the system design is optimal. Theoretical optimization of two-stage-in-series aerobic processes have been studied in earlier work [131, 135] using kinetic models including first order reaction and Monod models. In these studies, optimization was made in terms of the maximization of the overall treatment efficiency (total  $BOD_5$  removal) for a given total hydraulic retention time. In one case [131], the kinetic constants in both stages are assumed to be identical. The overall treatment efficiency is maximum when the treatment times in, or reactor volumes of, both stages are identical. In the other case [135], the overall treatment efficiency can be maximised, when the kinetic constants in the two stages being non-identical.

However, in practice, when designing a two-stage biological treatment system to meet the pollutant discharge limit, an overall treatment efficiency, such as 98%  $BOD_5$  removal, is usually given on the basis of effluent regulations. The parameters to be determined are the HRT's in both stages and the corresponding reactor volumes required to achieve the desired efficiency. If the total hydraulic retention time required



for a fixed overall treatment efficiency can be minimized and if the corresponding reactor volume ratio between the two stages can be determined, then the system design can be optimized. Based on the above, optimization of the two-stage anaerobic-aerobic treatment system was thus carried out in this research.

In a two-stage anaerobic-aerobic treatment, due to the use of different groups of microorganisms in different environment existing in each treatment stage, the kinetic parametric values in one stage are therefore different from the other. Usually, the substrate removal rate in anaerobic treatment is much lower than that in aerobic treatment. To achieve similar treatment efficiency, the required quantity of microorganisms in anaerobic treatment is 3 or 4 times of that in aerobic treatment. For this reason, anaerobic treatments are usually operated with high concentration of microorganisms. If an anaerobic treatment process is combined with an aerobic process to form a two-stage-in-series system, according to the theory of reactor design, there would exist an HRT  $t_1$  in the anaerobic stage, for which the required total HRT  $t_o = t_1 + t_2$  is minimal for a fixed overall treatment efficiency  $E$ .

Providing that both removal rates follow a first order reaction kinetics (equ. (2.8)), to optimize the two-stage system shown in Fig. 3.1c, the expression for  $t_o$  is thus first set-up by the rearrangement and combination of equs. (2.15) and (2.25).

$$t_o = t_1 + t_2 = \frac{(S_o - S_1)}{k_1 X_1 S_1} + \frac{(S_1 - S_2)}{k_2 X_2 S_2} \quad (2.41)$$

Insertion of equs. (2.17) and (2.27) into equ. (2.41) yields an expression for  $t_o$  as a function of  $E_1$ :

$$t_o = t_1 + t_2 = \frac{E_1}{k_1 X_1 (1 - E_1)} + \frac{E - E_1}{k_2 X_2 (1 - E)} \quad (2.42)$$

### 2.5.1 Minimization of total hydraulic retention time $t_o$ for a fixed overall removal $E$

To minimize mathematically the total HRT  $t_o$  for a fixed overall removal  $E$ , equ. (2.42) was differentiated with respect to  $E_1$  to yield :

$$\frac{\partial(t_1+t_2)}{\partial E_1} = \frac{1}{k_1 X_1 (1-E_1)^2} - \frac{1}{k_2 X_2 (1-E)} \quad (2.43)$$

If  $t_o$  has a minimum value  $t_m$ , the second derivative of  $t_o$  with respect to  $E_1$  must be positive, i.e.,  $\partial^2 t_o / \partial E_1^2 > 0$ . Differentiating equ. (2.43) again with respect to  $E_1$  yields :

$$\frac{\partial^2(t_1+t_2)}{\partial E_1^2} = \frac{2}{(1-E_1)^3 k_1 X_1} > 0 \quad (2.44)$$

Since the value of  $E_1$  is always smaller than 1, therefore, the term on the right side of equ. (2.44) is always positive, implying that the required total treatment time  $t_o$  can be minimized with respect to  $E_1$ . To establish an expression for the optimal  $E_1$  at which the required  $t_o$  is minimal, we set equ. (2.43) to equal zero and then solve for  $E_{1opt}$  :

$$E_{1opt} = 1 - \sqrt{\frac{k_2 X_2 (1-E)}{k_1 X_1}} \quad (2.45)$$

Because  $E_{1opt}$  is the treatment efficiency of the anaerobic stage, its value should be positive. In order to have a positive  $E_{1opt}$  on the left hand side of equ. (2.45), the following inequality must be hold :

$$\frac{k_2 X_2}{k_1 X_1} (1-E) < 1 \quad (2.46)$$

which after rearrangement gives :

$$\frac{X_1}{X_2} > \left(\frac{k_2}{k_1}\right)(1-E) \quad (2.47)$$

Equ. (2.47) is the necessary condition for  $E_{1opt}$  to have a real value.

### 2.5.2 Optimal reactor volume ratio $V_1/V_2$ for a fixed overall removal $E$

From Fig. 3.1c, the volume  $V_1$  of the anaerobic stage is equal to  $t_1 Q_o$  and that  $V_2$  of the aerobic stage equal to  $t_2(Q_o - Q_{w1})$ . The ratio of the two is given by :

$$\frac{V_1}{V_2} = \frac{t_1}{t_2} \frac{(Q_o - Q_{w1})}{Q_o} \quad (2.48)$$

In anaerobic treatment, since the sludge yield is normally very low (around 5-10% of the  $BOD_5$  removed) and some of the sludge flows out the reactor together with the treated effluent, to maintain a high biomass concentration in the reactor, the sludge produced is almost not wasted from the system and the mean cell age  $t_{s1}$  is normally kept very long (usually longer than 30 days).  $Q_{w1}$  is therefore very small as compared with  $Q_o$  and thus can be neglected from equ. (2.48). Equ. (2.48) is then reduced to :

$$\frac{V_1}{V_2} = \frac{t_1}{t_2} \quad (2.49)$$

The optimal volume ratio corresponding to the  $t_m$  required for a fixed overall removal,  $E$ , can be calculated, for constant  $S_o$ ,  $X_1$  and  $X_2$ , using equ. (2.49), in cooperation with equs. (2.45), (2.17), (2.15), (2.27) and (2.25).

### 2.5.3 Optimization equations derived on the basis of the various combinations of first order reaction kinetics and Monod model

Equations (2.45), (2.47) and (2.49) were established on the basis of first order

reaction kinetics for the optimal design of the two-stage system, providing that this kinetics is applicable to both stages. However, following the same approach presented above, optimal design equations can also be developed if the removal rate kinetics for each stage follows other model, such as Monod model, etc. Table 2.4 presents the optimal design expressions for the two-stage anaerobic and aerobic system, developed on the basis of the various combinations of first order reaction and Monod models. From the theory of reactor design, it should be mentioned that the expressions required to maximize the overall substrate removal for a given total HRT are exactly the same as those developed for the minimization of the total HRT for a fixed overall substrate removal for a two-stage-in-series system. Therefore, the expressions presented in **Table 2.4** can be used to maximize the overall  $\text{BOD}_5$  removal for a given total HRT.

To conclude, treatment process kinetics plays critical roles in simulation study of the effects of operating conditions on the system behaviour and in optimization of the two-stage system. Process kinetics and the kinetic parameters must be first determined prior to optimization of the system.

**Table 2.4.** Equations developed for optimal design of the two-stage anaerobic-aerobic system, on the basis of various combinations of first order reaction model and Monod model

Kinetics followed		Equations for optimal design		
Anaerobic stage	Aerobic stage	Optimal removal in anaerobic stage, $E_{1opt}$	Necessary condition	Total treatment time, $t_o$
First order	First order	$E_{1opt} = 1 - \sqrt{\frac{k_2 X_2}{k_1 X_1} (1-E)}$ (2.45)	$\frac{X_1}{X_2} \geq \left(\frac{k_2}{k_1}\right)(1-E)$ (2.47)	$t_o = \frac{E_1}{k_1 X_1 (1-E_1)} + \frac{(E-E_1)}{k_2 X_2 (1-E)}$ (2.42)
Monod	First order	$E_{1opt} = 1 - \sqrt{\frac{k_2 X_2 K_{s1} (1-E)}{K_1 X_1 - k_2 X_2 S_o (1-E)}}$ (2.50)	$\frac{X_1}{X_2} \geq \left(\frac{k_2}{K_1}\right)(K_{s1} + S_o)(1-E)$ (2.51)	$t_o = \frac{[K_{s1} + (1-E_1)S_o]E_1}{(1-E_1)K_1 X_1} + \frac{E-E_1}{k_2 X_2 (1-E)}$ (2.52)
First order	Monod	$E_{1opt} = 1 - \sqrt{\frac{K_2 X_2}{k_1 X_1} \frac{(1-E)}{K_{s2} + (1-E)S_o}}$ (2.53)	$\frac{X_1}{X_2} \geq \left(\frac{K_2}{k_1}\right) \frac{(1-E)}{K_{s2} + (1-E)S_o}$ (2.54)	$t_o = \frac{E_1}{k_1 X_1 (1-E_1)} + \frac{(K_{s2} + (1-E)S_o)(E-E_1)}{(1-E)K_2 X_2}$ (2.55)
Monod	Monod	$E_{1opt} = 1 - \sqrt{\frac{K_2 X_2 K_{s1} (1-E)}{K_1 X_1 [K_{s2} + (1-E)S_o] - K_2 X_2 S_o (1-E)}}$ (2.56)	$\frac{X_1}{X_2} \geq \left(\frac{K_2}{K_1}\right) \frac{(K_{s1} + S_o)(1-E)}{K_{s2} + (1-E)S_o}$ (2.57)	$t_o = \frac{[K_{s1} + (1-E_1)S_o]E_1}{(1-E_1)K_1 X_1} + \frac{[K_{s2} + (1-E)S_o](E-E_1)}{(1-E)K_2 X_2}$ (2.58)

## CHAPTER 3

### EXPERIMENTAL

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This Chapter describes the experimental methods and procedures used for the biological treatment of the selected CTMP effluent. Unless specified, the methods and procedures presented are applied throughout this research.

#### 3.1 CTMP effluents studied and their characteristics

The effluent from the washing of CTMP in an integrated pulp and paper mill was used in the work reported in Chapter 5 and Chapter 6 of this thesis, since it has been identified, in the first part of the experimental work (Chapter 4), as the major source of BOD<sub>5</sub> and RFA in this particular mill -- which produces CTMP for newsprint and coated paper from a chip mixture containing about 90% black spruce and 10% eastern hemlock. The average characteristics of this effluent are presented in **Table 3.1**.

Unfortunately, due to a considerable modification in the CTMP pulping operation in the above selected mill, the characteristics of the effluent studied in Chapter 4 and used in the work reported in Chapter 5 and Chapter 6 had changed drastically at the moment of starting the experimental work of Chapter 8. After modification of operating conditions, the concentrations of the BOD<sub>5</sub> and COD in the effluent were reduced from about 3000 and 6200 to 1000 and 2500 mg/L, respectively. Since the BOD<sub>5</sub> concentration in the effluent was too low for anaerobic treatment; thus, this effluent

could not be used in the experiments to be run (Chapter 8). A new concentrated CTMP effluent was collected from another CTMP mill and used in the experiments. The new mill utilized a similar chip mixture as used in the first mill. The average characteristics of the new CTMP effluent are also presented in **Table 3.1**.

**Table 3.1.** Average characteristics of the first and new CTMP effluents studied

Characteristics	First effluent		New effluent
	Modification of operating conditions		
	Before	After	
BOD <sub>5</sub> , mg/L	3000	1000	2800
COD, mg/L	6200	2500	7000
RFA, mg/L	45	23	65
Lignosulphonates (LS), mg/L	2300	-	-
Colour, C.U.	5000	-	-
pH	5.5 - 6	-	6.6-7
Total sulphur, mg/L	89	-	125
TKN, mg/L	64	-	65
Total phosphor (as PO <sub>4</sub> ), mg/L	24	-	22

### 3.2 Effluent collection and feed preparation for biological treatment

During the experimental period, 1000 litres of effluent sample were collected from the mill every two weeks and stored in a plastic storage tank at ambient temperature. Sub-sample of 100 litres was withdrawn from the storage tank for each feed preparation. The raw effluent collected usually contained large fibres and other

kinds of particles. The sub-sample was thus first filtered with a 500-mesh plastic screen to remove large suspended solids then transferred to the feeding reservoir. Nutrients (potassium dihydrogen phosphate and ammonium chloride) were then added to the feed according to  $BOD_5/N/P = 100/5/1$  for aerobic treatment and 100/1/0.5 for anaerobic treatment. The pH in feed was finally adjusted to around 7 using sodium bicarbonate.

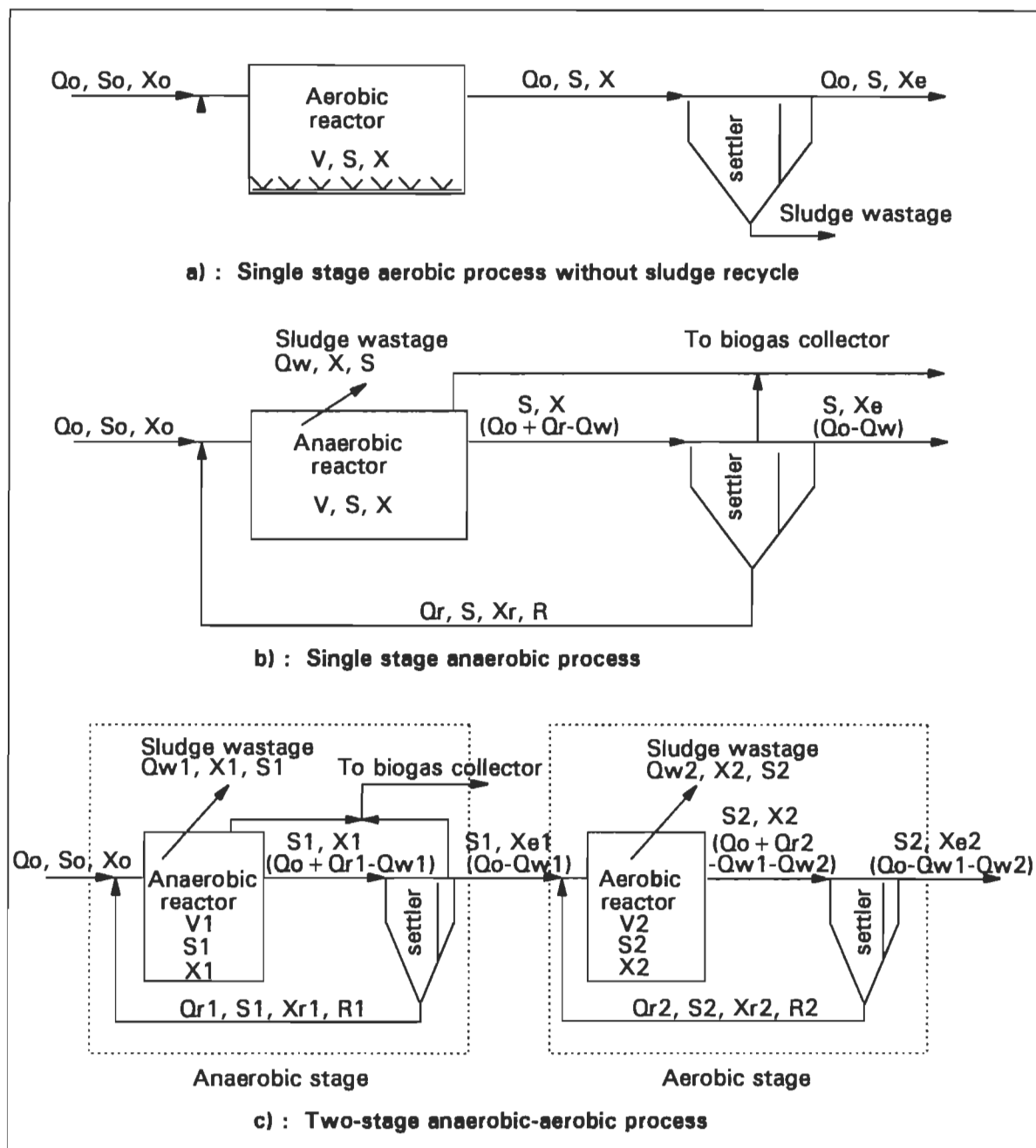
### 3.3 Treatment systems and their operations

**Treatment systems :** Three conventional continuous treatment systems were used in this research, as shown schematically in Fig. 3.1. The single stage aerobic system without sludge recycle (Fig. 3.1a) was used to study the effects of operating conditions on, and to evaluate the kinetics and design parameters for the aerobic biological treatment of the first CTMP effluent (Table 3.1). The single stage anaerobic process (Fig. 3.1b) was employed to determine effects of operating conditions, kinetics, and design parameters for treatment of the first CTMP effluent. With the new CTMP effluent (Table 3.2), optimization of the two-stage CTMP effluent treatment was carried out using the system shown in Fig. 3.1c . Each stage consisted of three major components : a fully mixing bioreactor, a funnel-shaped settler of which the conical section had a slope of 60°, and peristaltic pumps used to supply feed, to recycle sludge, and to add  $NaHCO_3$  solution to control the pH in the bioreactor; and to recycle biogas as well as to provide internal recirculation of liquid in the case of anaerobic bioreactor.

#### 3.3.1 Single stage aerobic treatment

**Feed :** The first CTMP effluent was used as the feed for single stage aerobic treatment.





**Fig. 3.1 Treatment systems used in the research**

**Bioreactor :** Single stage aerobic treatment was carried out in the system presented in Fig. 3.1a. Six identical cylindrical aerated bioreactors (of 25 litres each and made of transparent acrylic plastics) and settlers were used in the experiments and operated in parallel. Each bioreactor had an adjustable side overflow tube, used to adjust the effective mixed liquor volume in the bioreactor and to discharge the treated effluent to the settler. The effective reactor volume was controlled at 15 litres.

**Seeds and their acclimation :** The mixed liquor taken from a municipal wastewater treatment plant was used as seeds for the treatment. Each aerated bioreactor was initially filled with the mixed liquor. Nutrient added CTMP effluent was then gradually fed to the bioreactor to acclimatize the microorganisms in the mixed liquor. During the acclimation period, the concentrations of COD and the MLSS in the bioreactor were measured once every two days. Microscopic observation of the microbial populations was made daily. Seed acclimation was considered accomplished when the COD and MLSS concentrations in the bioreactor were quite constant. Our experimental results indicated that seed acclimation was generally accomplished within two weeks.

**pH and temperature control :** The pH and temperature in each bioreactor were controlled automatically, using on-line pH controller (Model : 5997-20, Cole-Parmer Ins. Co.) and temperature controller (Dyna-Sense : 02158-02, Reg TM Scientific Instruments Inc.), respectively.

**DO, mixing and anti-foaming :** The dissolved oxygen required for the growth, reproduction, and decay of microorganisms in each bioreactor was provided by passing regulated, filtered and metered compressed air through a circular diffuser fixed onto the bottom of the bioreactor along the perimeter. The air diffuser was made of a perforated polyethylene tube with i.d. = 9.5 mm and o.d. = 12.5 mm. Action of the air bubbling provided perfect mixing of the bioreactor content. Foaming in the bioreactor was controlled by adding a small given amount of Dow Corning antifoam-B

(dispersed in water in a volume ratio of about 1 : 100) to the bioreactor, using a timer controlled peristaltic pump (Masterflex No. 7014) with a frequency of six seconds per minute.

**Microorganisms concentration and sludge age control :** For single stage aerobic process without sludge recycle, the concentration of microorganisms in the bioreactor at stable state would be auto-fixed by the treatment conditions, and the sludge age equals the HRT in the bioreactor.

### 3.3.2 Single stage anaerobic treatment

**Feed :** Since no hydrogen peroxide was present in the first CTMP effluent and since the RA and FA concentrations were far below their inhibitory levels (see **Table 2.2**), the effluent was not pre-treated prior to entering the bioreactor that contained acclimatized seeds. Effluent conditioning took place in the feeding reservoir as well as in the storage tank; some of the sulphur compounds present in the raw effluent were reduced to hydrogen sulfide and escaped to the atmosphere during storage at room temperature.

**Bioreactor :** Single stage anaerobic treatment was conducted using the system shown in Fig. 3.1b. A 15-litre Microferm-100 fermenter (New Brunswick Scientific Inc.) was used as the bioreactor. This fermenter possesses a variable speed agitator and an automatic control system for liquor level, temperature, pH and anti-foam. The effective mixed liquor volume in the bioreactor was also controlled at 15 litres. The funnel-shaped settler, made of 316 stainless steel, had a total volume of 30 litres and was sealed with a cover made of transparent acrylic plastics. On the cover, five holes with plug each were made for sampling, collecting biogas, and inserting a thermometer for temperature control. For temperature control, the settler was wrapped along its outside perimeter with several turns of flexible heating tape and insulated with fibre glass. Inside the settler, a baffle was installed near the effluent outlet to prevent the

carryover of floating sludge from the settler.

**Seeds and their acclimation :** The seeds used for the treatment were taken from a full-scale UASB reactor treating the CTMP wastewater of the Bathurst mill of Stone Container, located in Bathurst, New Brunswick. They have been already acclimatized to that particular CTMP effluent. The seed sludge was in form of black granules. The acclimation of those seeds to the first CTMP effluent studied was carried out in the bioreactor, using a very long hydraulic retention time of 6 days. During acclimation, the biogas production and effluent COD concentration were monitored. The seeds were considered acclimatized to the CTMP effluent when both the rate of biogas production and the effluent COD concentration were quite stable. Experimental results showed that, since the seeds used have been already acclimatized to a CTMP effluent, the seeds acclimated to the CTMP effluent studied within about two weeks.

**pH, temperature and mixing :** The pH and temperature in the bioreactor were controlled automatically through the control system. Mixing was realized with the variable speed agitator turning at 200 RPM.

**Microorganisms concentration and sludge age control :** The concentration of microorganisms in the bioreactor was controlled through recycling the sludge from the settler to the bioreactor with a recycle ratio, **R**, determined by the following equation:

$$R = \frac{Q_r}{Q_o} = \frac{(t_s - t) X}{(X_r - X) t_s} \quad (3.1)$$

The control of sludge age was realized through removing a given volume of mixed liquor, two or three times per day, directly from the bioreactor according to the following equation :

$$Q_w \propto \frac{V}{t_s} \quad (3.2)$$

**Biogas collection and hydrogen sulphide (H<sub>2</sub>S) removal :** The biogas produced from both the bioreactor and the settler was collected together in a 20-litre gas collector as shown in Fig. 3.2, using the method of water displacement. To prevent H<sub>2</sub>S and CO<sub>2</sub> dissolving in water, the water in the gas collector was acidified with H<sub>2</sub>SO<sub>4</sub> to pH  $\approx$  1 prior to biogas collection. To reduce the potential toxicity inhibition of H<sub>2</sub>S to the treatment, collected biogas was pumped continuously through 3N NaOH solution in a 3-litre Erlenmeyer flask to remove its H<sub>2</sub>S content, and then recycled to the bioreactor so as to purge the H<sub>2</sub>S produced.

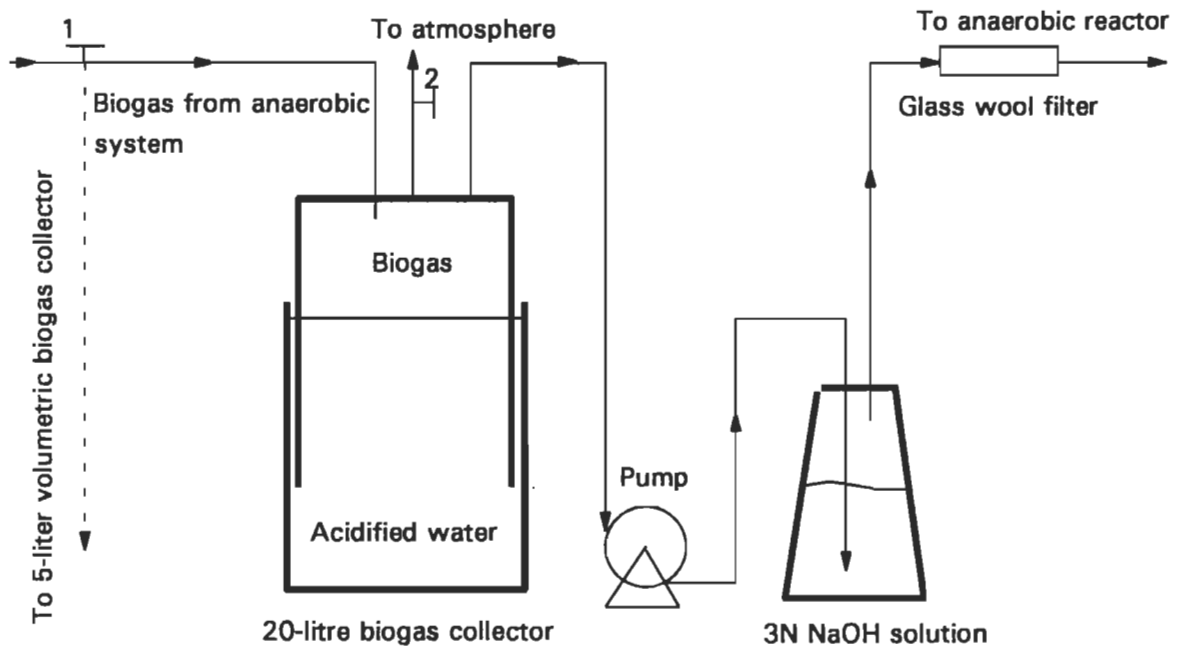
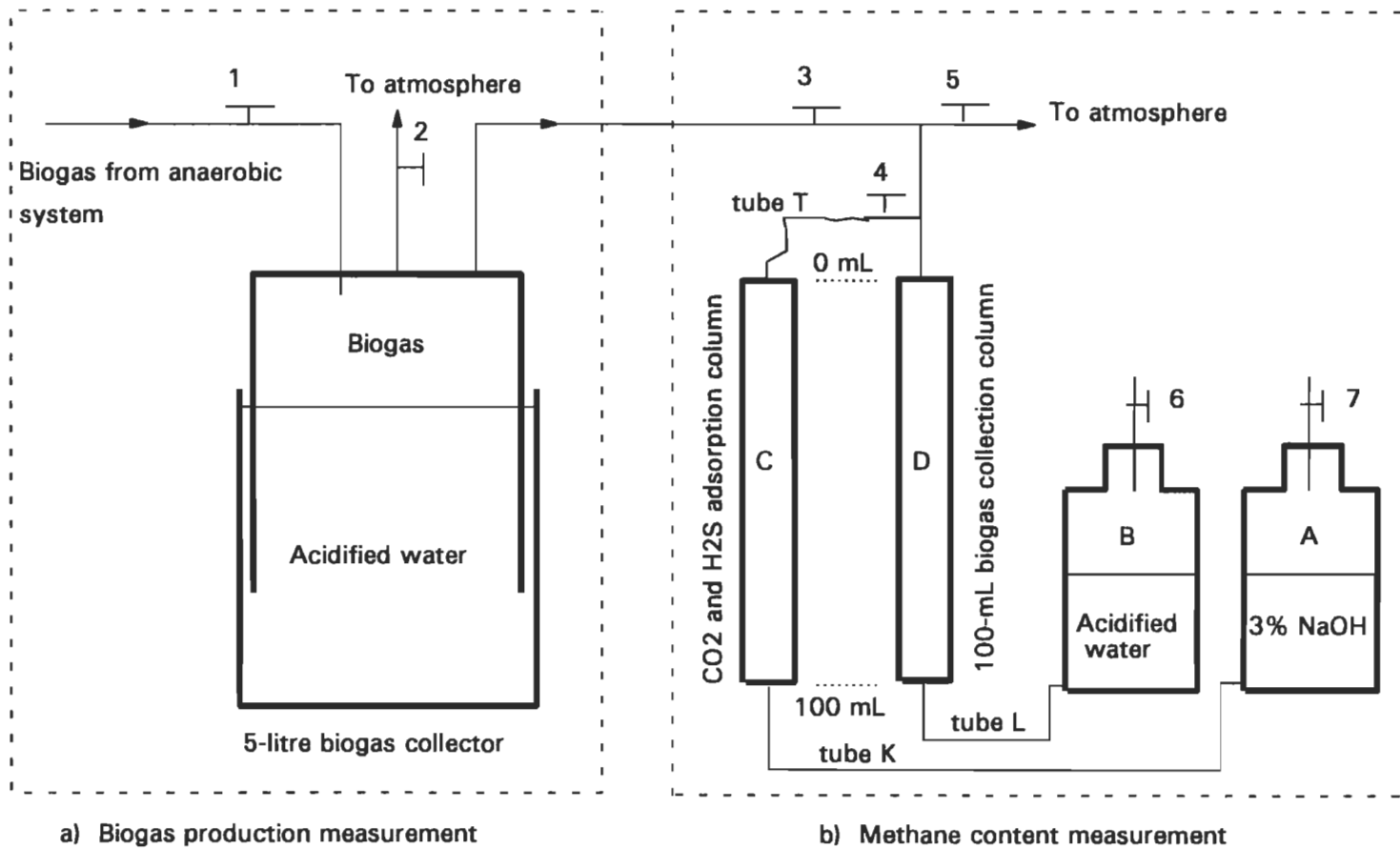


Fig. 3.2 Biogas collection and recycle to anaerobic reactor

**Production and methane content of biogas :** When measuring the biogas production, the collection of biogas in the 20-liter collector and recycling of biogas to the reactor were discontinued for a few hours. By means of three-way valves, the biogas produced in both the bioreactor and the settler was collected in a smaller 5-liter gas collector shown in Fig. 3.3a. The increase in volume of gas in this collector was measured for a given period of time. The methane content of biogas was measured with the apparatus shown in Fig. 3.3b. The measurement was made by following the procedures described below :

- 1) Filling column C with 3N NaOH solution to the 0 mL level line :  
With valves 2 and 3 closed and 4, 5 and 7 opened, raising bottle A upward until the liquid level in the bottle aligning with the 0 mL level line; then closing valve 4 and lowering bottle A.
- 2) Filling column D with acidified water ( $\text{H}_2\text{SO}_4$ ,  $\text{pH} \approx 1$ ) to the 0 mL level line :  
With valves 2 and 3 closed and 5 and 6 opened, raising bottle B upward until the liquid level in the bottle aligning with the 0 mL level line, then closing valve 5 and lowering bottle B.
- 3) Filling column D with 100 mL of biogas at atmospheric pressure :  
Opening valves 3 and 7 to fill the column with biogas to the 100 mL level line by lowering bottle B until the liquid level in the bottle aligning with the 100 mL level line, then closing valves 3 and 7.
- 4) Absorbing  $\text{H}_2\text{S}$  and  $\text{CO}_2$  in the biogas by NaOH solution :
  - a) Opening valve 4 and raising bottle B upward until the liquid level in the bottle aligning with the 0 mL level line, so as to transfer all the biogas from column D to column C, then closing valve 4;
  - b) Clipping tube T with a clamp at the 0 mL level line;



Where : 1, 2 .. 7 = valve

Fig. 3.3 Apparatus for biogas production and methane content measurements

- c) Disconnecting tube T from valve 4 and lowering column C vertically so as to fill the column with about 10 mL of NaOH solution from bottle A;
  - d) Gripping tube K tightly with right hand;
  - e) Dismounting column C, followed by holding and repeatedly (about 25 times) shaking the column with upside-down and downside-up actions until the gas volume absorbed by NaOH solution being constant, then releasing the grip of tube K;
  - f) Mounting column C and raising bottle A upward until the liquid level in the bottle aligning the liquid level in the column.
- 5) Recording the gas volume in column C.

### 3.3.3 Two-stage anaerobic-aerobic treatment

**Feed :** The new CTMP effluent presented in **Table 3.1** was the feed to the first stage anaerobic bioreactor. The treated effluent from the settler after the anaerobic bioreactor was the feed flowing directly to the aerobic stage.

**Treatment system :** To have a very good control of the microbial granules concentration at the desired level in the anaerobic bioreactor, for the validity verification study of the optimization method developed in Chapter 2, the 15-litre Microferm-100 fermenter used in the single stage anaerobic treatment was modified and used as the first stage to carry out the experiments. One disadvantage of a conventional fully mixed laboratory scale anaerobic reactor with biosolids recycling is the difficulty of having a very good control of the biosolids concentration in the reactor. To overcome this disadvantage, some modifications in operation of the anaerobic bioreactor were made. These modifications are :

- 1) Adjusting and controlling the agitator speed at very low RPM, about 50, so as to make the microbial granules suspended just within 1/2 to 2/3 of the reactor



volume so that the liquid phase in the upper part of the reactor (about 1/3 reactor volume) is almost free from microbial granules. This modification made the microbial granules in the reactor suspended below the upper liquid phase.

- 2) To increase the contact between the microbial granules and the liquid in the reactor, a large quantity (recycling rate : about 15 L/hour) of the liquid in the upper part of the reactor was recycled and recirculated through three circular liquid distributors, made of Teflon tube, i.d. = 5 mm and fixed onto the bottom of the reactor.
- 3) Biogas was recycled, with a proper flowrate, from the gas collector (volume : 20-litre) back to the reactor through two circular gas diffusors mounted on the reactor bottom. Biogas recycling also provided a better contact between the microbial granules and the liquid inside the reactor.
- 4) Feed was fed to the reactor through a circular plastic distributor fixed onto the reactor bottom. Prior to leaving the reactor, the treated effluent first passed through a circular liquid-solids separator remove the not too much suspended microbial granules, if any, in the upper liquid phase, and then flew out of the reactor into the settler.

These modifications made the microorganisms concentration in the reactor be well controlled at the desired level, while the microbial granules and the liquid in the reactor were kept in good contact. When measuring the MLSS concentration and performing sludge wastage from the reactor, the content in the reactor was fully mixed by introduction of nitrogen with a high flowrate for 1 to 2 minutes. Other operation procedures were identical to those as described in above. The operation of the second stage corresponded to that of the single stage aerobic treatment with the addition of sludge recycle. Two such two-stage systems were operated in parallel.

**Microorganisms concentration in the bioreactor of the second stage and sludge age control :** The concentration of microorganisms in the bioreactor was controlled through the recycle of sludge from the settler to the bioreactor with a recycle ratio,  $R_2$ , determined by the following equation :

$$R_2 = \frac{Q_{r2}}{(Q_o - Q_{w1})} = \frac{(t_{s2} - t_2) X_2}{(X_{r2} - X_2) t_{s2}} \quad (3.3)$$

Sludge age was controlled through the removal of a given volume of mixed liquor directly from the bioreactor, two or three times per day, according to the following equation :

$$Q_{w2} = \frac{V_2}{t_{s2}} \quad (3.4)$$

### 3.4 Sampling and analyses

For each set of treatment conditions, once the single-stage or two-stage system reached its steady state, sampling was made and continued for about two weeks. Samples were taken directly from the bioreactors. Analyses of the sample were made immediately after sampling.

**Table 3.2.** Parameters to be analyzed and frequency of analysis

<i>Parameters for performance assessment</i>	<i>Frequency of analysis</i>
BOD <sub>5</sub>	once every two days, 5-6 per set of conditions
COD	once every two days, 5-6 per set of conditions
RFA	once every four days, 2-3 per set of conditions
Lignosulphonates	once every four days, 2-3 per set of conditions
Colour	once every four days, 2-3 per set of conditions
MLSS	corresponding to BOD <sub>5</sub> or COD measurements
SVI	corresponding to MLSS measurements
Microbial population	twice a week
Biogas production	once every two days
<i>Parameters for process control</i>	
VFA	almost daily
Alkalinity	almost daily
Total sulphur	optional

#### 3.4.1 Performance parameters to be analyzed

The performance parameters to be analyzed and the frequency of their analyses

are presented in **Table 3.2**. Selections of these parameters were based either on their importance in effluent regulations, or on their roles in process control. Effluent regulations [23-24] impose that the loadings of many pollutants in an effluent have to be reduced below their allowed limits before discharge. Among them, effluent BOD<sub>5</sub> and fish toxicity are the most important pollutants to be controlled. Because we do not have the facilities for running fish toxicity assay and because RFA, notably RA, have been identified to be the principal source of CTMP effluent toxicity to fish, the effluent toxicity was thus estimated in this research using RFA concentration. Thus, these two pollutants (BOD<sub>5</sub> and RFA) were analyzed to assess the performance of the single stage and the two-stage treatment systems. COD is also an important characteristic of an effluent and it is easily determined. In some countries in Europe, it has been suggested to limit COD discharge loading. Thus, this pollutant was also measured in this research. It is well known that lignin is principally responsible for the colour of pulp and paper effluents. Lignosulphonates (LS) and colour in the untreated and treated effluents were therefore determined. Biogas production was an useful parameter for assessing the performance of an anaerobic process and thus monitored.

MLSS concentration and sludge volume index (SVI) are the two major parameters for sludge characteristics. MLSS concentration is also an important parameter for a biological treatment. Concentrations of VFA and alkalinity in the anaerobic reactor are the two key variables for controlling anaerobic treatment. These four parameters were measured in this research.

### 3.4.2 Methods of analysis and measurement

**BOD<sub>5</sub>, COD, MLSS, TSS and colour :** These five parameters were determined according to the standard methods [H1, H2, H3.p, H.3p, H.5p] of CPPA.

**Sludge characteristics :** Measurement of MLSS concentration was made using the CPPA standard method. SVI, for sludge settleability evaluation, was determined

following the standard method 2710C specified by the American Public Health Association [136]. Microbial species and populations in the sludge were examined microscopically.

**RFA :** RFA in an effluent sample were identified and determined in comparison with RFA standards (Helix Biotech Corporation, Vancouver, B.C. Canada) according to the GC-FID method [137], using a computer controlled gas chromatography (Varian 3600) and a DB-5 glass Megabore column of 30m by 0.53mm (Chromatographic Specialties Inc.). In the RFA extraction step, a modification in the amount of solvent used was made. A larger ratio of solvent/sample = 1.5/1, instead of an equal amount of each as recommended by the method, was used in the extraction step in order to ensure a complete extraction of the RFA. In Comparison with other methods, the modified method has two advantages : no foam formes during extraction and no isomerization of resin acids would occur due to the extraction being carried out at high pH of 9. Adsorbed RFA were first extracted from the sludge sample (sample size : 0.3 - 0.4 g) in a Soxhlet extraction tube for 12 hours, with a mixture of acetone/methanol in a ratio of 88/12 (V/V) in the presence of hydrochloric acid [138]. The extract collected in the flask was then evaporated in a rotary evaporator to dryness. The RFA in the extract was then analyzed by the GC-FID method.

**Lignosulphonates :** Lignosulphonates concentration was evaluated spectrophotometrically (Model PM2D, Zeiss) at 280 nm, using an absorptivity of 11.5 L/g.cm [139], according to the following equation :

$$\text{LS concentration, mg/L} = [ (\text{Absorbance})_{280\text{nm}} \times \text{dilution factor} ] / 11.5 \quad (3.5)$$

The real absorptivity of the LS in the CTMP effluent may not be equal to 11.5 L/g.cm. However, this value had no influence on the percentage removal since it is a relative value.

**VFA and alkalinity** : VFA concentration and alkalinity were analyzed by chemical analysis, following the standard method 5560 of the American Public Health Association [136], expressed in mg  $\text{CH}_3\text{COOH/L}$  and mg  $\text{CaCO}_3/\text{L}$ , respectively. The composition of the VFA was not analyzed.

**Biogas and methane** : Biogas yield, expressed in  $\text{m}^3/\text{kg}$  of COD removed, was determined using the increase in volume of gas in the 5-litre gas collector (Fig 3.3a) measured for a given period of time and the corresponding quantity of COD removed during this period. Typically, biogas from anaerobic treatment consists of methane as well  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{N}_2$ , and  $\text{H}_2$ . Since the amounts of  $\text{N}_2$  and  $\text{H}_2$  are normally quite small and can be neglected, the methane content was thus estimated by removing  $\text{CO}_2$  and  $\text{H}_2\text{S}$  from a given volume (100 mL) of biogas through 3 N NaOH solution (Fig. 3.3b). The content, as percentage, was calculated by subtracting the gas volume absorbed from the 100 mL biogas.

### 3.5 System performance and experimental conditions

#### 3.5.1 System performance

System performance was assessed using the following criteria:

- Treatment system stability,
- Removals of pollutants ( $\text{BOD}_5$ , COD, LS and colour),
- Removal of toxicity, in terms of RFA removal,
- Sludge characteristics (sludge volume index, microbial species and population),
- Biogas production and methane content (for anaerobic treatment).

Since the principal objective of this research is to optimize the two-stage treatment system for the CTMP effluent studied, particular interest will focus on

pollutants and RFA (toxicity) removals by the treatments. Thus, the removals of pollutants, particularly BOD<sub>5</sub>, and RFA (toxicity) are the major criteria in this research. Optimization of the two-stage system was made on the basis of these two criteria.

### 3.5.2 Experimental conditions

Experimental conditions will be presented in the section on "Results and Discussion" for each treatment (single stage and two stages) in late chapters.

## 3.6 Mechanisms of RFA removal

### 3.6.1 Materials

About 100 litres of the first CTMP effluent (**Table 3.1**) were filtrated and used as the source of RFA. It was stored at 4°C for about one week before use. As shown in **Table 3.1**, the RFA concentration in the effluent was about 45 mg/L.

The mixed liquor used in all the experiments was taken from an aerobic biological reactor used to treat the effluent, with the conditions listed in **Table 5.1**, ensuring that the microorganisms in the sludge were already acclimated to the effluent sample to be tested. That reactor, operated at steady-state with a long hydraulic residence time of 5 days and a mean sludge age of around 20 days, continuously generated and provided uniform mixed liquor for use in this study. Before use, the withdrawn mixed liquor was thickened. The RFA concentration in the liquor phase of the mixed liquor was, on an average, very low (less than 0.5 mg/L) and that adsorbed onto the thickened sludge varied between 1.38 and 1.78 mg/g.

### 3.6.2 Static air oxidation of RFA

Without the presence of microorganism and in the presence of light, sterilized

untreated effluent containing no nutrients was aerated with air in a 3-litre clean beaker. The top of the beaker was covered with a plastic film with a hole to minimize the effect of water evaporation, if any. At each pre-selected aeration time, a 100 mL sample of the aerated effluent was withdrawn from the beaker. The RFA concentration in the aerated effluent sample, without centrifugation and filtration, was determined to evaluate the RFA removal by the air oxidation mechanism.

### 3.6.3 Static adsorption of RFA onto sludge

For determining the static adsorption of RFA onto sludge, no biooxidation and air oxidation should take place. Before use, the pH of the untreated effluent was adjusted to 7 and the thickened mixed liquor was aerated with  $N_2$  for one hour to remove completely the dissolved oxygen in the mixed liquor. Experiment was conducted in the same 3-litre clean beaker. According to calculated ratio, untreated effluent was well mixed with the thickened mixed liquor in the beaker using a magnetic stirrer. To ensure that no air entering into the beaker, a small amount of nitrogen was continuously fed through a diffuser fixed onto the bottom of the beaker, and the top of the beaker was covered with a plastic film. No nutrient was added to the effluent.

At each pre-selected time, a 100 mL sample of the mixed liquor was withdrawn from the beaker. The liquid and the sludge in the sample were separated through filtration. To eliminate the residual liquid trapped in the sludge layer formed during filtration, the sample was first centrifuged in a 150 mL centrifuge glass tube at 1500 rpm for 10 minutes to separate the liquid and the sludge. After carefully collecting the upper layer clarified liquid, the sludge at the tube bottom was completely transferred to a glass fibre filter by washing the sludge and the tube with 100 mL of distilled water and filtered to remove the residual liquid and the washing water. After filtration, the sludge together with the filter was then subjected to solvent extraction for RFA in a Soxhlet extraction apparatus. RFA concentration in the upper layer clarified liquid and that in the extract were determined.



#### 3.6.4 Dynamic adsorption of RFA onto sludge

The term "dynamic adsorption " used in the study refers to the adsorption of RFA onto sludge during aerobic biological treatment. It is used to distinguish with the "static adsorption" of RFA where only adsorption takes place. The amount of dynamic adsorption of RFA onto the sludge was directly determined by analyzing the RFA content in the sludge sample taken from biotreatment. The experimental procedure followed is the same as that for the biooxidation of RFA, which will be described thereafter. The preparations of the clarified liquid and sludge samples followed the same procedures as those used in the static adsorption study (Sub-section 3.6.3). The amount of adsorbed RFA in the sludge sample was determined. The amount of the untreated effluent RFA adsorbed onto the sludge by dynamic adsorption was the difference between the amount of RFA adsorbed and the RFA adsorbed initially onto the sludge.

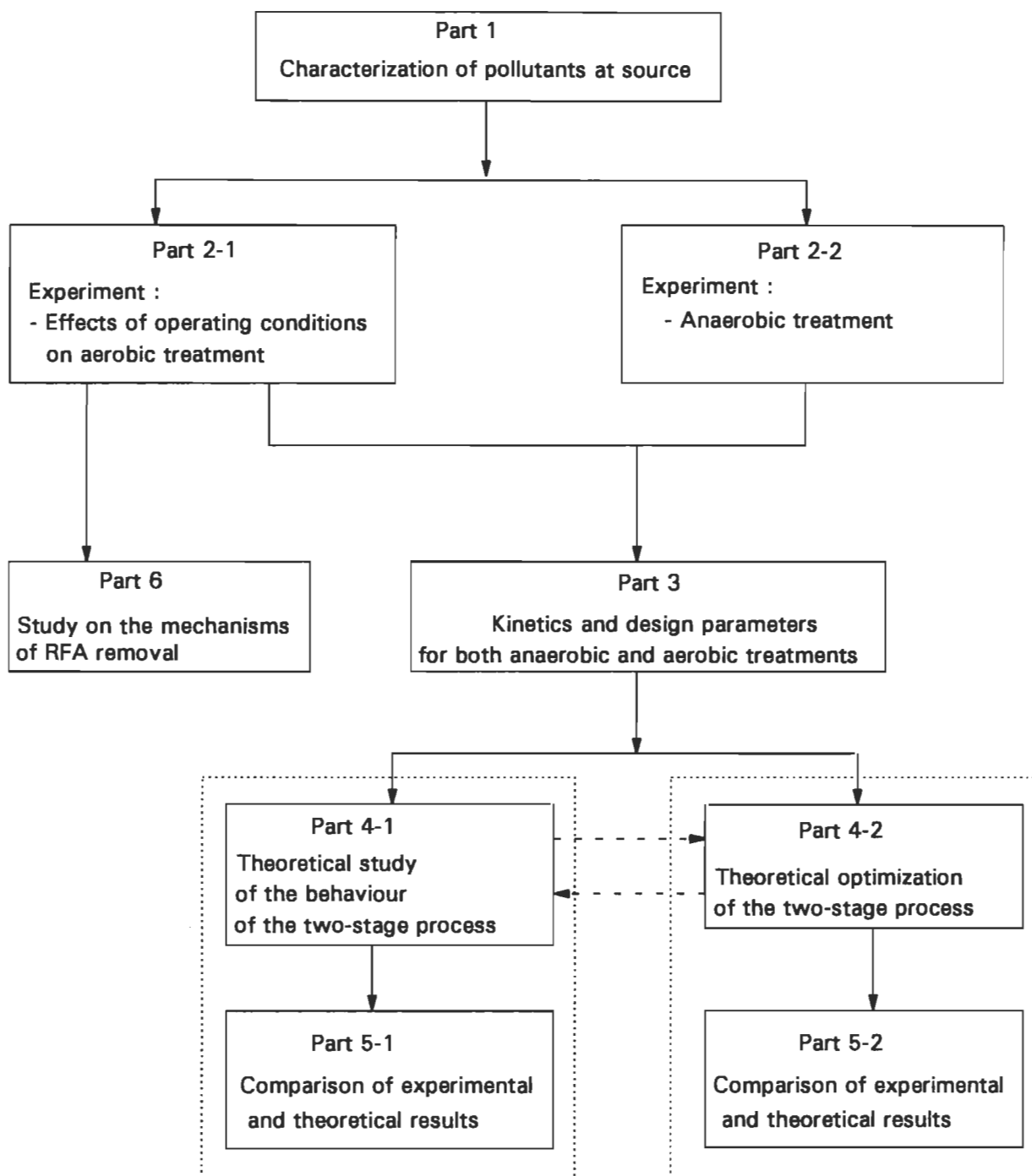
#### 3.6.5 Bio-oxidation of RFA

In the same 3-litre clean beaker, untreated effluent, nutrients ( $\text{BOD}_5/\text{N}/\text{P} = 100/5/1$ ) and the thickened mixed liquor were mixed. At the rate of 0.224 L air/min L reactor, compressed air was introduced into the beaker through a circular diffuser fixed at the bottom of the beaker. The action of air bubbling provided the dissolved oxygen for the growth and synthesis of microorganisms and supplied good mixing for the content of the beaker. At each pre-selected treatment time, a 100 mL sample of mixed liquor was sampled. Sample preparations of clarified liquid and sludge have been described in the Sub-section 3.6.3. The content of RFA in the clarified liquid and that onto the sludge were then determined immediately, for the evaluations of both the overall RFA removal by the treatment and the amount by the dynamic adsorption onto the sludge. The biooxidation of RFA was estimated by subtracting the removals by both dynamic adsorption and static air oxidation from the overall removal.

### 3.7 Research work program

For better understanding the research work conducted in the study, the complete program is presented in Fig. 3.4. The sequence of the works follows the arrow.

To evaluate the main sources of pollutants for the mill and to select the effluent to be treated, characterization of pollutants at source was first made in Part-1 (Chapter 4) prior to other studies. Consequently, treatments of the selected effluent by single stage aerobic and anaerobic processes were conducted in Part-2 (Chapter 5) to determine the favourable operating conditions for the removals of substrates. The kinetics and design parameters for both treatments were then determined in Part-3 (Chapter-6). On the basis of the removal kinetics observed, the effects of the main operating conditions on the behaviour of the two-stage treatment system for the CTMP effluent studied were firstly simulated in Part-4 (Chapter 7), using the basic equations presented in Chapter 2 and the kinetic parameters obtained in Part-3 (Chapter 6). Optimization of the two-stage treatment system was then carried out, using the method developed in Chapter 2. In part 5 (Chapter 8), the effects of operating parameters on the behaviour of the two-stage system and the validity of the optimization method were verified by experiments for the CTMP effluent studied. In Part-6 (Chapter 9), the mechanisms of RFA removal by aerobic treatment were studied.



**Fig. 3.4** Research program followed in the thesis

## CHAPTER - 4

### CHARACTERIZATION OF POLLUTANTS AT SOURCE FOR THE CTMP MILL STUDIED

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#### 4.1 Introduction

The reported characteristics and pollution loads of CTMP effluents in literature are usually obtained from lab- or pilot-scale simulations of CTMP operations. Little attention, however, has been paid to the sources or origins of the pollution loads and toxicants within a full-scale CTMP mill operation. Information on the sources, is however, useful for pollution control and for treatment of the mill effluents. From the economic point of view, the effluents from the origins with low loads of pollutants may not be necessary to receive an external treatment and can be recycled within the mill, and only those with high loads are treated. As such, the effluent volume to be treated will be greatly reduced.

This work investigated the sources or origins of the pollutants and toxicants within the integrated pulp and paper mill studied. The mill produces 600 t/d of CTMP for newsprint and coated paper with a chip mixture containing about 90% black spruce and 10% eastern hemlock. To characterize pollutants at each source and to evaluate the main sources of pollutants generated from the mill for selective treatment of the effluents, effluents from different sources were collected for characterization of pollutants during a two month period.

## 4.2 Experimental

**Sources :** Seventeen sources in the mill as listed in **Table 4.1** were selected. They represent the major effluent sources in the mill.

**Table 4.1.** Seventeen effluent sources selected in the mill studied

Code	Source	Code	Source
S <sub>1</sub>	White water surplus	S <sub>10</sub>	CTMP refiners 1 and 2
S <sub>2</sub>	Paper machine (PM) No.1	S <sub>11</sub>	CTMP refiner 3
S <sub>3</sub>	Paper machine (PM) No.2	S <sub>12</sub>	CTMP washing
S <sub>4</sub>	Paper machine (PM) No.3	S <sub>13</sub>	Clear filtrate from vacuum disc filter (VDF)
S <sub>5</sub>	Paper machine (PM) No.4	S <sub>14</sub>	Cloudy filtrate from VDF
S <sub>6</sub>	Coating machine	S <sub>15</sub>	Dilution water
S <sub>7</sub>	Paper machine (PM) No.7	S <sub>16</sub>	Primary clarifier inlet
S <sub>8</sub>	Boiler condensate	S <sub>17</sub>	Primary clarifier outlet
S <sub>9</sub>	Main sewer		

**Sampling and determinations of pollutants :** One sample was taken at intervals of eight hours, three from the effluent were grabbed at each source in the same day, once every ten days with a two month period. These three samples, kept at 4°C, were then mixed to form a composite. The concentrations of pollutants (BOD<sub>5</sub>, COD, TSS, and RFA) in each composite were determined the next day in quadruplicate.

**Loadings of pollutants :** During sampling, the corresponding effluent flow rate was also measured. Pollutant loading was calculated by multiplying the pollutant concentration with the corresponding effluent flow rate. The concentration as well as the loading of each pollutant reported was the average of the results determined from the analysis of six composites at each source within a two month period.

### 4.3 Results and discussion

In effluent regulations, the major pollutants regulated are effluent BOD<sub>5</sub>, TSS and toxicity. RFA have been identified as the major source of the toxicity of mechanical pulping effluents [8, 11, 36-39]. Thus, concentrations and loadings of BOD<sub>5</sub>, TSS and RFA as well as those of COD were determined. Results are listed in Table 4.2 and presented in Figs. 4.1, 4.2, 4.3, 4.4 and 4.5.

**Table 4.2.** Concentrations and loadings of pollutants at source

Source	BOD <sub>5</sub>		COD		RFA		TSS	
	Conc. mg/L	Loading t/d	Conc. mg/L	Loading t/d	Conc. µg/L	Loading Kg/d	Conc. mg/L	Loading t/d
S <sub>1</sub> *	720	9.8	1200	16.3	981	13.38	300	4.1
S <sub>2</sub>	450	3.8	760	6.6	744	8.63	650	5.6
S <sub>3</sub>	260	1.5	310	1.8	1644	0.99	380	2.2
S <sub>4</sub>	370	0.4	1300	1.5	676	11.68	470	0.5
S <sub>5</sub>	800	0.3	600	0.2	3345	0.99	1000	0.3
S <sub>6</sub>	740	1.8	1100	2.6	4742	11.68	6400	15.8
S <sub>7</sub>	1000	5.1	1600	7.8	2034	1.04	350	1.7
S <sub>8</sub>	100	0.1	400	0.2	580	1.05	300	1.1
S <sub>9</sub> *	800	56.3	1030	72.9	2220	157.41	630	21.6
S <sub>10</sub> *	650	1.8	1300	3.8	4810	45.10	514	1.4
S <sub>11</sub> *	1300	3.5	2800	6.5	10100	85.33	951	3
S <sub>12</sub>	3040	222.2	6200	453.4	44900	3249.7	2500	184
S <sub>13</sub>	3000	216.8	5800	424.0	13926	1580.88	430	32
S <sub>14</sub>	2900	211.7	5500	403.0	15456	1128.8	490	36
S <sub>15</sub>	2900	214.1	5400	396.3	16288	1189.59	1030	76
S <sub>16</sub>	850	65.3	900	68.9	3200	246	680	52
S <sub>17</sub>	550	38.0	700	53.7	3420	261	100	7.5

\* --- These sources send their effluents directly to the primary clarifier.

#### 4.3.1 Concentrations and loadings of BOD<sub>5</sub>, COD and TSS

The results in Figs. 4.1 and 4.2 show clearly that the concentrations and loadings of BOD<sub>5</sub> and COD generated from four sources: S<sub>12</sub>, washing effluent; S<sub>13</sub>, clear filtrate from VDF; S<sub>14</sub>, cloudy filtrate from VDF and S<sub>15</sub>, dilution water, are extremely high, compared with other sources. The washing effluent also contains a very high concentration and loading of TSS. The concentrations and loadings of pollutants generated from other sources, except for the main sewer (S<sub>9</sub>), are very low as seen in Figs. 4.1 and 4.2. Concentrations of BOD<sub>5</sub> and COD in the effluents from the seventeen sources vary in rather wide ranges, from 300 to 3000 mg/L for BOD<sub>5</sub> and from 500 to 6200 mg/L for COD. Figs 4.1 and 4.2 also indicate that the function of primary clarifier not only removed TSS (about 85%) but part of the BOD<sub>5</sub> and COD of the receiving water.

A good correlation, with a *r* value of 0.98, between the concentrations of BOD<sub>5</sub> and COD in the seventeen source effluents has been found, as shown in Fig. 4.3. The ratio of BOD<sub>5</sub>/COD in each source effluent was found to be about 0.5.

#### 4.3.2 Resin and fatty acids

The concentrations of RFA in samples collected from the 17 sources varied in a very wide range from 0.6 to 45 mg/L (Fig. 4.4). As identified in other paper mill effluents [10-11, 13, 39], major resin acids: pimaric, sandaracopimaric, isopimaric, levopimaric, palustric, abietic, dehydroabietic and neoabietic acids, and three fatty acids: oleic, linoleic and linolenic acids were found in all the effluent samples tested. Dehydroabietic acid is the dominant resin acid, accounting for about 37% of the total as shown in Fig. 4.5. Other resin acids present at significant levels are abietic (22%), levopimaric/palustric (16%) and isopimaric acid (10%). Of the fatty acids, linoleic (52%) and oleic (39%) acids were the dominant species. These proportions of the acids are quite similar to those reported for two TMP mill effluents [13]. In contrast

to the concentrations of RFA, the relative proportions of the individual resin and fatty acids present in the seventeen effluents showed a little variability, as shown in Fig. 4.5, which agrees well with the findings obtained for two TMP mill effluents [13].

As seen in Fig. 4.4, concentrations and loadings of RFA generated from the four sources ( $S_{12}$ ,  $S_{13}$ ,  $S_{14}$  and  $S_{15}$ ) mentioned previously are also extremely high, compared with other sources. Both the concentration (45 mg/L) and loading (3.3 t/d) in the washing effluent are the highest among the four sources, which are comparable to those measured in an untreated Canadian CTMP effluent [10], but much lower than those reported by Bennett *et al* [39] for a CTMP effluent.

From **Table 4.2**, it can be seen that the effluent from CTMP washing is the major producer of pollutants, in terms of  $BOD_5$  (217 t/d), COD (453 t/d) and RFA (3.3 t/d). The four sources ( $S_{12}$ ,  $S_{13}$ ,  $S_{14}$  and  $S_{15}$ ) do not send directly any pollutant loading to the clarifier, because the effluents from these sources are recycled inside the mill. The approximate amounts sent to the receiving water from the clarifier ( $S_{17}$ ) are  $BOD_5$ : 38 t/d (63.3 Kg/ADT); COD: 54 t/d (90 Kg/ADT) and RFA: 0.26 t/d (0.43 Kg/ADT), which are similar to those reported for other CTMP/TMP effluents [4-6, 101-102].

#### 4.3.3 Material balance of pollutant loading

Among the seventeen sources, four sources:  $S_1$ , white water surplus;  $S_9$ , main sewer;  $S_{10}$ , CTMP refiner 1 and 2, and  $S_{11}$ , CTMP refiner 3, send their effluents directly to the primary clarifier. For estimating the total loadings of major pollutants ( $BOD_5$ , COD, RFA and TSS) into the primary clarifier, the sum of the contribution of each pollutant in these four effluents was calculated. A material balance on each pollutant around the clarifier inlet was made.

The calculated total loadings of  $BOD_5$  and RFA were 71.4 and 0.3 t/d, respectively, in comparison with 65.3 and 0.25 t/d as determined at the clarifier inlet.



The errors of estimation for these two pollutant loadings were about 9% and 20%, respectively. The calculated total loadings of TSS and COD were 30 and 99.6 t/d, respectively, compared with 51.9 and 68.9 t/d as determined at the clarifier inlet. The errors of estimation for these loadings were about 43%. An error with such a magnitude might be induced by errors in flow rate measurements of the four influents to the clarifier.

#### 4.4 Conclusions

- 1) For the mill investigated, there are four sources of effluents containing very high concentrations of BOD<sub>5</sub>, COD and RFA. They are the CTMP washing effluent, clear and cloudy filtrates from vacuum disc filter, and dilution water. Among these effluents, the CTMP washing effluent has the highest concentrations and loadings of pollutants and thus was selected for biological treatment in this research.
- 2) The mill discharges about 38 t/d (63.3 Kg/ADT) BOD<sub>5</sub>, 0.26 t/d (0.43 Kg/ADT) RFA, 54 t/d (90 Kg/ADT) COD and 7.5 t/d (12.5 Kg/ADT) TSS from its primary clarifier to the receiving water.
- 3) The ratio of BOD<sub>5</sub>/COD in each source effluent is about 0.5, which is quite constant.
- 4) The relative proportions of individual resin and fatty acids in the seventeen source effluents are quite constant with a little variability. Among the resin acids, dehydroabietic acid is the dominant specie, accounting for about 37% of the total amount.

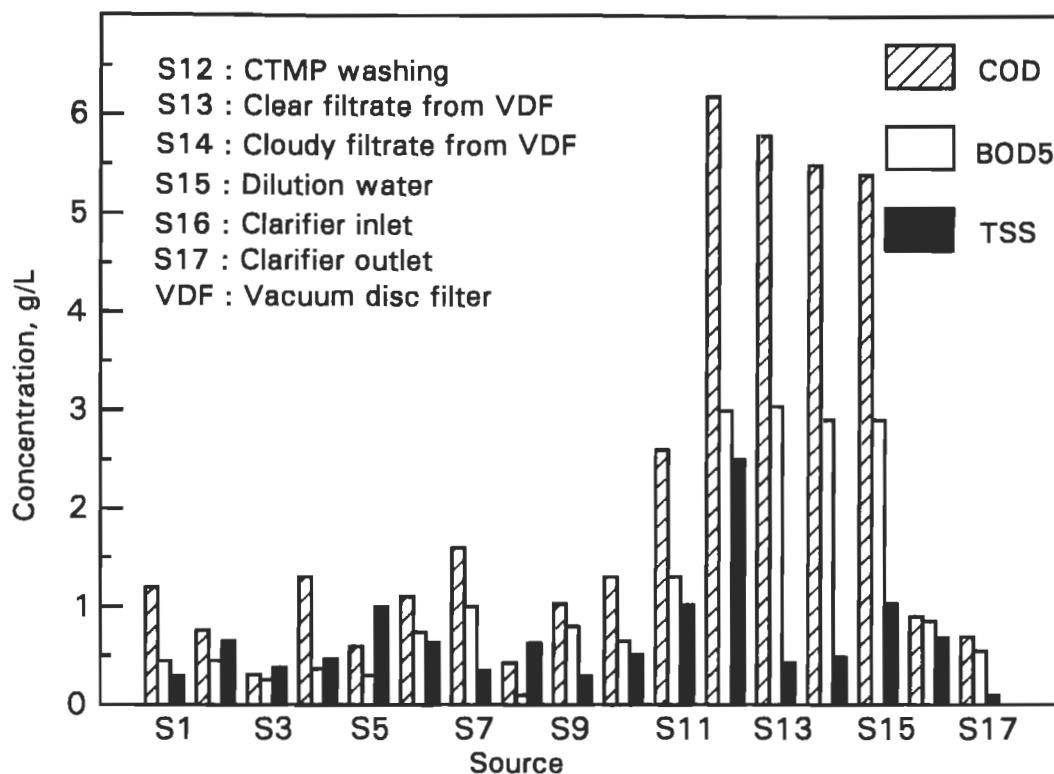


Fig. 4.1 Concentration of pollutants (COD, BOD5 and TSS) at source

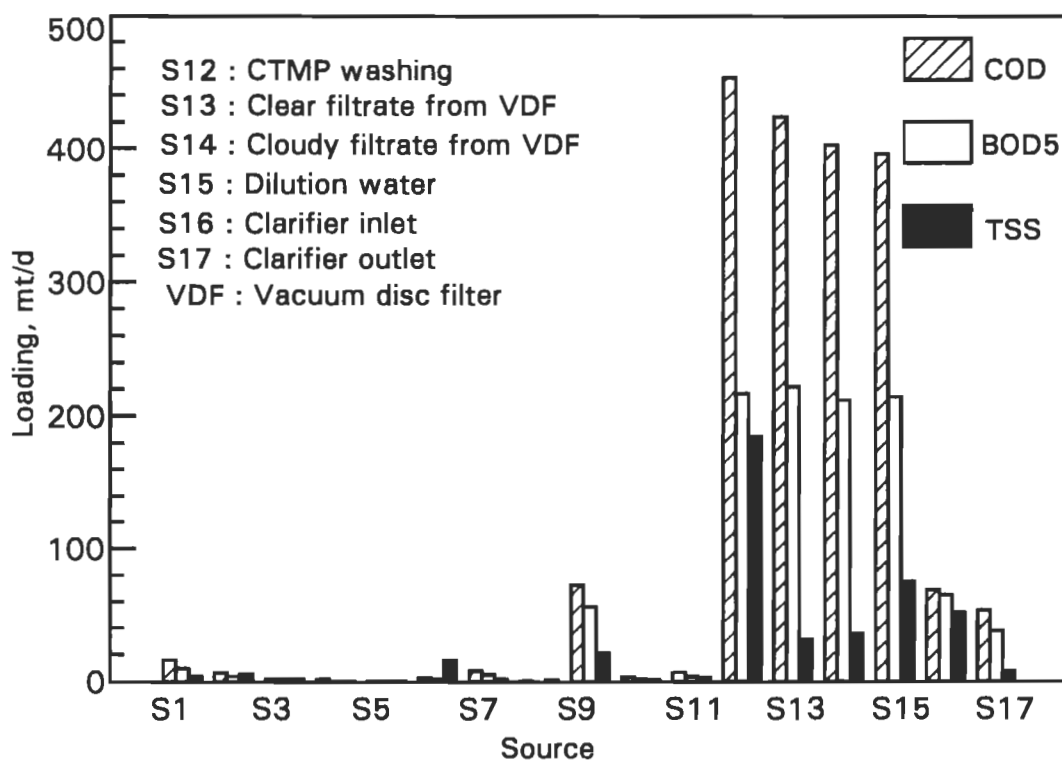


Fig. 4.2 Loading of pollutants (COD, BOD5 and TSS) at source

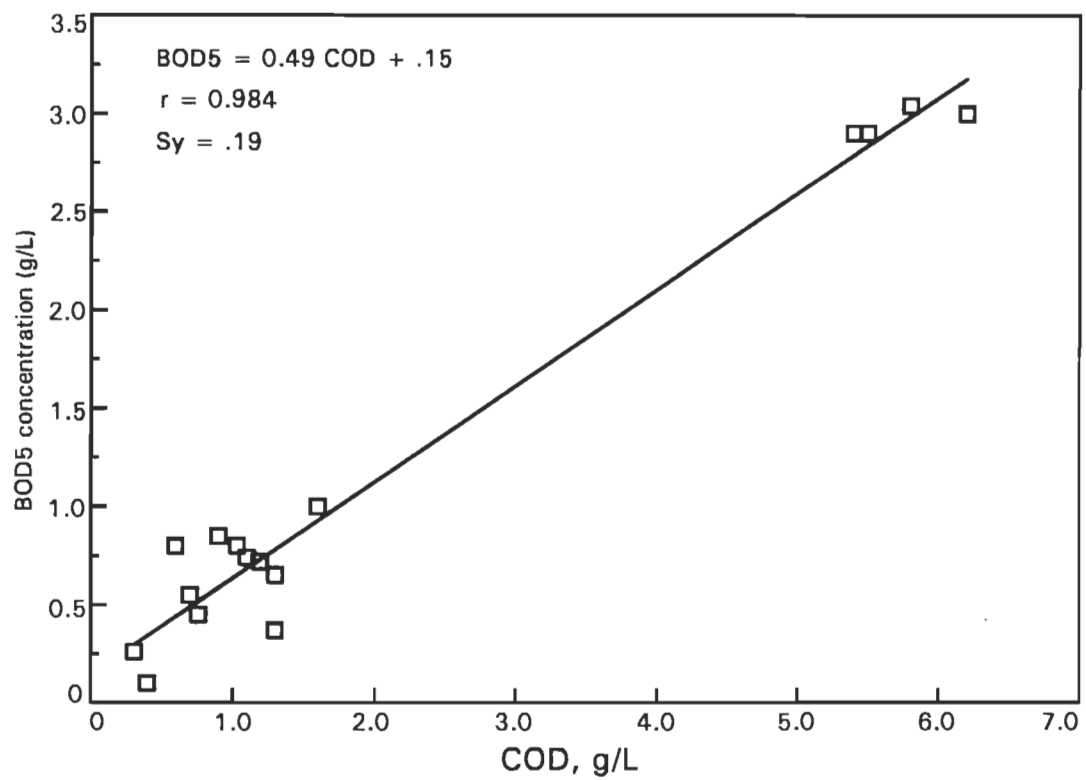


Fig. 4.3 Correlation between the concentrations of BOD5 and COD

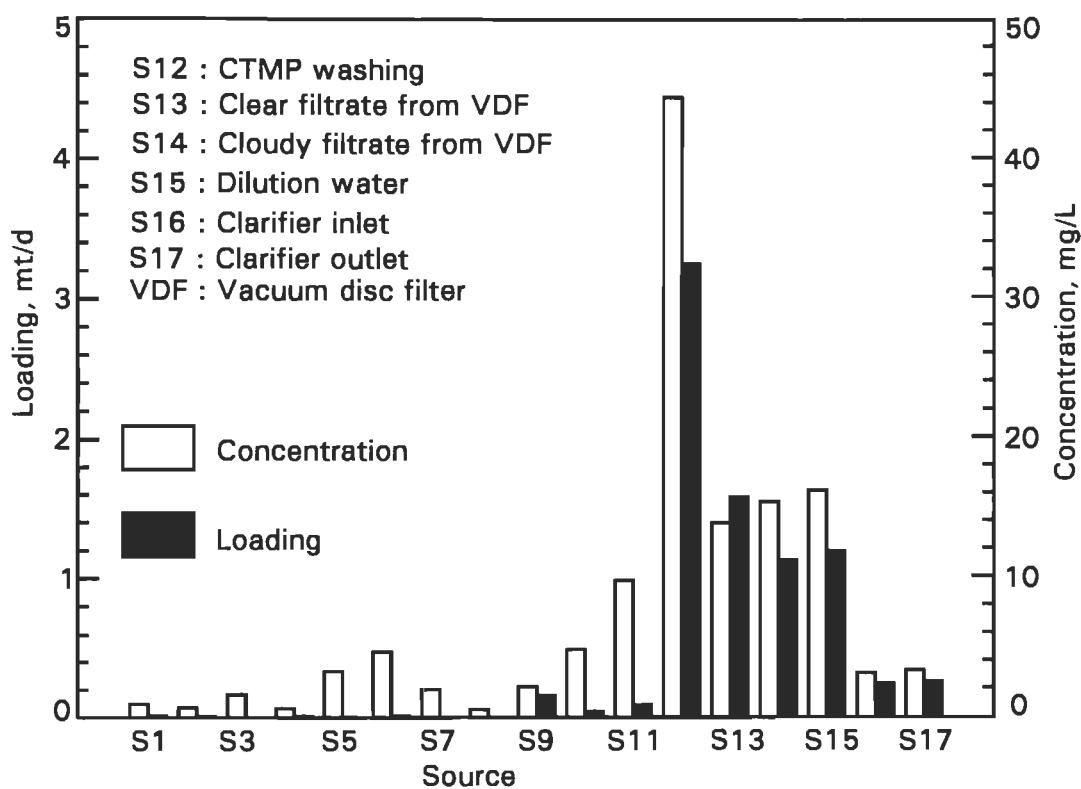


Fig. 4.4 Concentration and loading of RFA at source

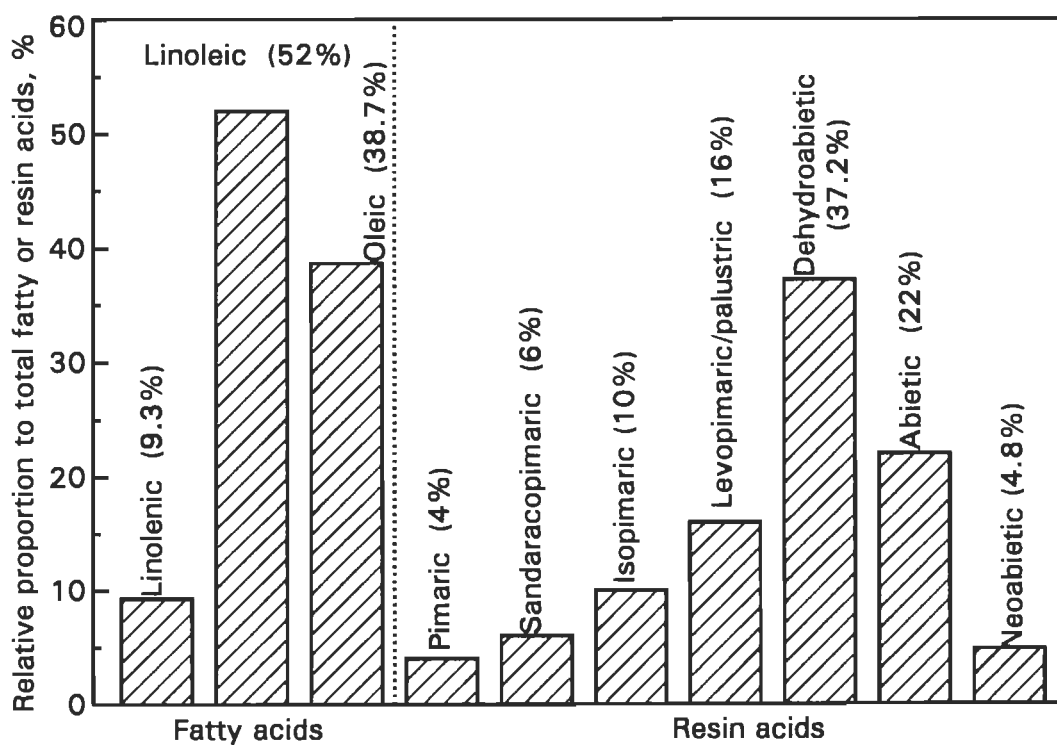


Fig. 4.5 Relative proportions of individual resin and fatty acids in the seventeen source effluents

## CHAPTER 5

### AEROBIC AND ANAEROBIC TREATMENTS OF A CTMP EFFLUENT

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#### 5.1 Introduction

Based on the results presented in Chapter 4, the CTMP washing effluent in the mill was selected for biological treatment in this research. The average characteristics of the effluent were shown in **Table 3.1**.

In this chapter, the effects of operating parameters (pH, hydraulic retention or treatment time, level of dissolved oxygen, and temperature) on biodegradation of the effluent were investigated under a very wide range. The objectives of this work were : 1) to study the effects of operating parameters on both aerobic and anaerobic treatments; 2) to determine the favourable conditions to be used in the two-stage anaerobic-aerobic treatment of the effluent and the kinetics and design parameters for both treatments.

#### 5.2 Experimental

##### 5.2.1 Treatment system

The experiments for aerobic treatment were conducted using the system shown in Fig. 3.1a. Six such systems were operated in parallel. The anaerobic treatment set-up has been illustrated in Fig. 3.1b. The experimental procedures for both treatments have been described in Chapter 3.

### 5.2.2 Experimental conditions

**Aerobic treatment** : The experimental conditions for the aerobic treatment are presented in **Table 5.1**.

**Table 5.1.** Effects of operating parameters on aerobic treatment of the CTMP effluent ---- Experimental conditions and results

Exp. run No.	Experimental conditions				Experimental results						
	pH	HRT	T	DO	BOD <sub>5</sub>	COD	RFA	LS	Colour	MLSS	SVI
		days	°C	mg/L	%*	%*	%*	%*	%*	mg/L	L/g
AE-1	5	3	20	7-8	96.6	70.1	96.2	43.4	54.2	1160	60
AE-2	6	3	20	7-8	97.6	72.9	97.9	49.5	57	1430	68
AE-3	7	3	20	7-8	98.1	79.1	99	52.3	58	1730	138
AE-4	8	3	20	7-8	98	74.4	98.1	51.2	66	1530	102
AE-5	7	0.5	20	7-8	86.7	62.3	96.2	36.3	35.4	1310	90
AE-6	7	1	20	7-8	93.4	68.2	98	40	41.7	1420	106
AE-7	7	2	20	7-8	98	79.6	98	49.2	52.5	1800	122
AE-8	7	3	20	7-8	98.9	29.4	99	52	56.8	1730	138
AE-9	7	5	20	7-8	98.9	78.7	99.2	48.1	50.3	1600	128
AE-10	7	3	10	7-8	92	73.8	96	54	55	1250	120
AE-11	7	3	20	7-8	98.9	79.7	99	52.3	56.6	1730	138
AE-12	7	3	30	7-8	96.2	73.6	99.3	45.7	49.2	1450	80
AE-13	7	3	40	7-8	90.5	69.5	97.9	36.9	44	1400	40
AE-14	7	3	50	7-8	79.4	46	96.2	5	10	620	98
AE-15	7	3	20	2.5	93.5	69.7	96	46.2	30	480	36
AE-16	7	3	20	3.5	95.1	73.8	97	50.7	39	550	27
AE-17	7	3	20	5	95.4	74.3	97	51.4	52	570	28
AE-18	7	3	20	6.2	97.1	75	98	54.6	56	930	50
AE-19	7	3	20	7.2	96	77.6	98	55.3	60	960	58
AE-20	7	3	20	8.2	97.8	79.7	99	60.5	69	980	110

\* - % removal

**Anaerobic treatment** : As described previously in Chapter 2, methanogenic bacteria require strict, uniform and stable environmental conditions. It is well established that the optimal environmental conditions for anaerobic treatment of most wastewaters are almost the same; they are : pH = 6.8 to 7.5; temperature 33 to 38 °C (mesophilic range) or 50 to 60 °C (thermophilic range), and absolute oxygen-free. Based on the above, the effects of pH and temperature on the treatment were therefore not investigated in this work. The mesophilic temperature 35 °C and pH 7 were used throughout this study for the treatment experiments. Other conditions for the treatment were 1) HRT : 0.5 to 4 days and 2) MLSS concentration : 5 g/L.

### 5.3 Results and discussion

#### 5.3.1 Aerobic treatment

##### 5.3.1.1 Effect of HRT

**Removals of pollutants** : Fig. 5.1a shows the effect of HRT on treatment efficiency for the fixed conditions (i.e., pH : 7; temperature : 20°C and DO : 7-8 mg/L) studied as shown in **Table 5.1**. The HRT studied ranged from 0.5 to 5 days. As seen, both BOD<sub>5</sub> and COD removals improve significantly as HRT increases from 0.5 to 2 days; a further increase in HRT does not affect any more removals of the pollutants. Under the conditions studied, almost 98% of BOD<sub>5</sub> and about 80% of COD can be removed with an HRT of two days. Very high removals of BOD<sub>5</sub> (88%) and RFA (96%) can be achieved even with an HRT of only 0.5 day, where the F/M was very high (about 4.5 kg BOD<sub>5</sub>/kg.MLSS.d).

As seen in Fig. 5.1a, increase of HRT from 0.5 to 3 days augments the LS removal from 36 to 52%. It is surprising to see that up to 52% of the LS in the effluent was removed. Being high molecular weight compounds, lignin in wood

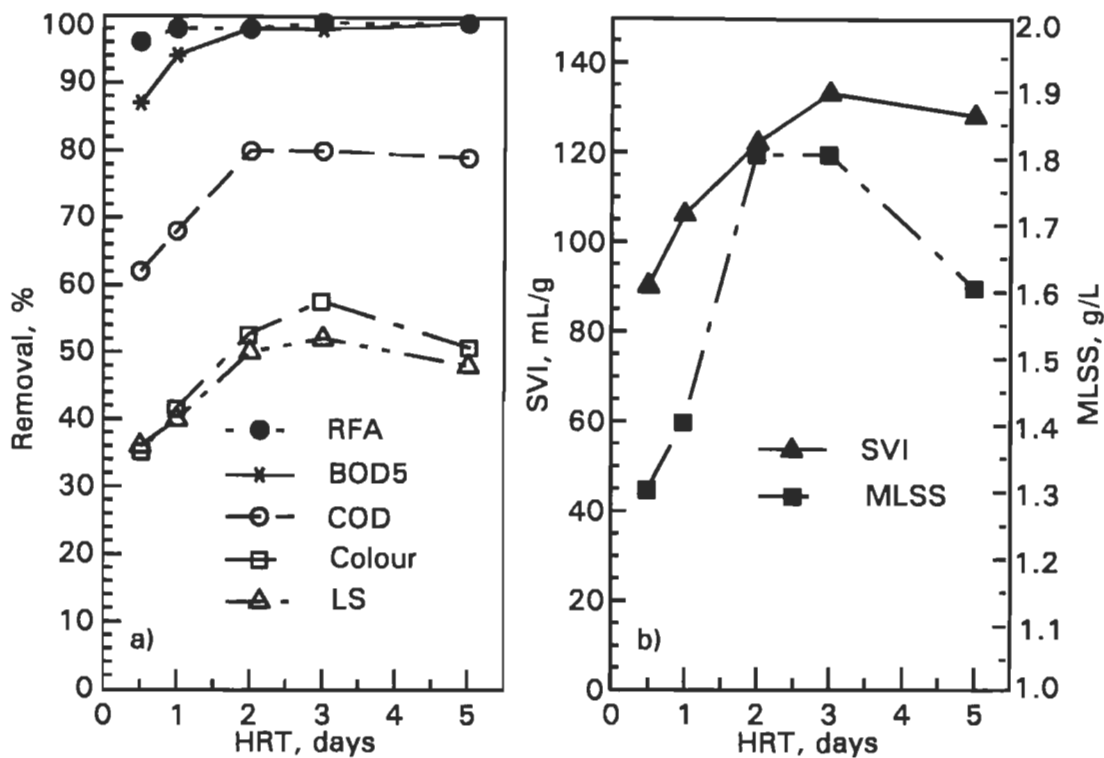


Fig. 5.1 Effect of HRT on aerobic treatment performance

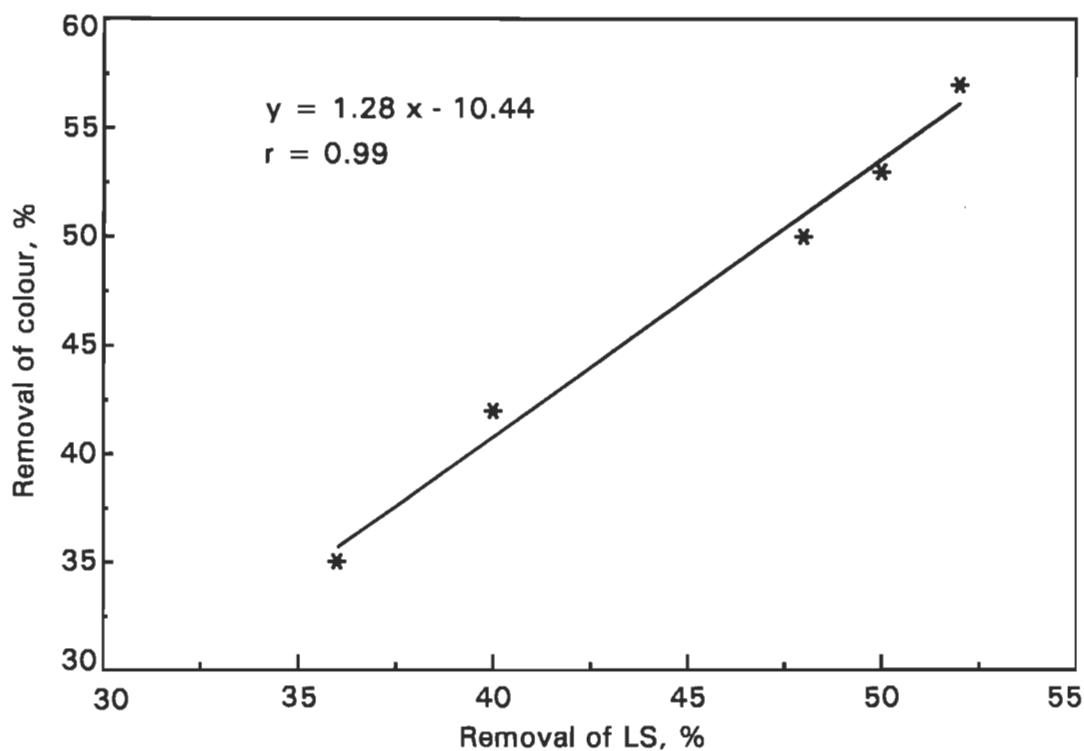


Fig. 5.2 Correlation of removals of LS and colour for the HRT's studied



components [140] and the LS in spent sulphite liquor [137] are normally difficult to biodegrade. In order to elucidate the mechanisms by which the LS were removed, the possibility that the LS was removed by adsorption onto the biosolids in the treatment system was assessed. The results indicated that only about 0.9 to 1.4% of the LS in the effluent was adsorbed onto the sludge. Thus, the removal of the rest of the LS was due to biodegradation. It is speculated that the LS released during chemithermomechanical pulping contain a large fraction of low-molecular-weight compounds readily attacked by aerobic microorganisms. It is thought that the comparatively high removal of the LS might be one reason for the high removal of COD.

The reduction of colour ranged between 35 and 57%, and the corresponding removal of the LS ranged from 43 to 52%. It has been well known that lignin is a highly colour producer. To see if the colour reduction is related to the LS removal, the removal of the LS and that of colour was correlated. It was found that there was a linear relationship between these two removals, with a correlation coefficient of 0.99, as shown in Fig. 5.2, which strongly indicates that the reduction in effluent colour was caused by the removal of the LS.

**RFA removal :** Removal of effluent toxicity has become a mandatory issue in new pulp and paper effluent regulations. According to the Canadian [23] and Québec [24] Pulp and Paper Mill Regulations, the final effluents discharged from the pulp and paper mills have to be non-toxic to fish. During the experimental period, we did not have facilities for testing the acute toxicity to fish of the effluents before and after treatment. However, since it is well known that the toxicity of mechanical pulping effluents is mainly coming from RFA, notably the resin acids [8, 11, 36-39], an attempt was thus made to judge the degree of effluent detoxification by monitoring the removal of RFA. The 96-h  $LC_{50}$  of resin acids has been reported to be, on an average, 1.3 mg/L [141].

Fig. 5.1a indicates that the RFA in the effluent to be treated is very readily and

almost completely removed by aerobic biological treatment, even at a short HRT of 0.5 day. No significant difference in RFA removal indicates an insignificant effect of HRT on the removal. The removal of RFA equals about 98% for all the HRT's studied, with the result that the RFA concentration in the treated effluents was about 0.9 mg/L. This value is well below the lethal concentration limit of 1.3 mg/L, implying that the treated effluents obtained for all the HRT's studied would be non toxic to fish.

Fig. 5.3 presents the responses of individual resin and fatty acids in the effluent to aerobic treatment at each HRT studied. No significant differences in reductions of resin acids were found for all the HRT's studied. The resin acids were almost completely removed from the effluent. The removals of fatty acids, especially oleic acids, were lower in comparison with those of the resin acids.

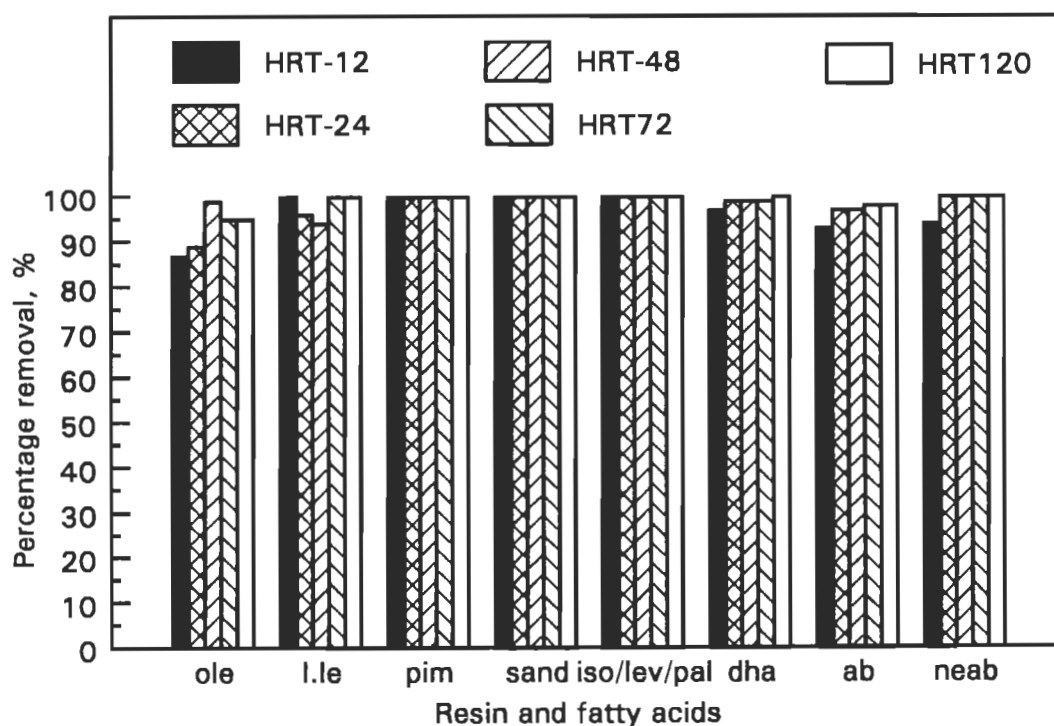


Fig. 5.3 Removals of individual RFA by aerobic treatment at several HRT's

It has been generally thought that biodegradation is responsible for the removal of RFA through aerobic treatment [3]. However, other removal mechanisms may exist, such as adsorption onto the biosolids in the treatment system and air oxidation. Results from the extraction of RFA adsorbed onto the sludge samples from aerobic treatment with a mixture of methanol/acetone (12/88 : V/V) for 12 h showed that the adsorption was a very important mechanism for the RFA removal. A complete study of these mechanisms will be presented in Chapter 9 of this thesis.

**Sludge characteristics :** As shown in Fig. 5.1b, the MLSS concentration increased from 1.3 to 1.8 g/L when the HRT was increased from 0.5 to 2 days, remaining nearly constant with a further increase of the HRT to 3 days. Extending the HRT from 3 to 5 days induced a decrease in the MLSS concentration from 1.8 to 1.6 g/L. These results were due to the three phases of microorganism growth.

With the sludge age (mean cell age), which equals HRT for the treatment, between 0.5 to 2 days (the sludge was equal to corresponding HRT in this treatment), the microbial populations in the bioreactor were in the exponential growth phase. In this phase, the supplies of food and nutrients to the bioreactor were in excess, and the growth rate of the microorganisms was much higher than the death rate of old cells. Therefore, an increase in cell age induced an increase in the MLSS concentration. Between the age of 2 and 3 days, the populations were in the stationary growth phase. The supplies of food and nutrients were just adequate for the growth of cells. The growth of new cells was offset by the death of old cells. Thus, an increase in age produced no effect on the MLSS concentration. When the age was older than 3 days, the populations entered into the endogenous respiration phase. The amounts of food and nutrients were limited for the cell growth, and the microorganisms were forced to metabolize their own protoplasm without replacement. The death rate of old cells exceeded the production of new cells. Therefore, an increase of cell age led to a drop in the MLSS concentration.

Good sludge settling has been observed for all the HRT's and even for very high F/M (4.5 kg BOD<sub>5</sub>/kg.MLSS.d), as indicated by the SVI's ranging between 90 and 130 mL/g, as shown in Fig. 5.1b, which are well below the upper limit (150 mL/g) for easily settled sludge. Excellent sludge settling at F/M ratios in excess of 2 kg BOD<sub>5</sub>/kg.MLSS.d has been also observed [142].

Microscopic observations revealed that the microbial populations in the sludge samples were composed mainly of bacteria as well as of representative protozoa and metazoa. No filamentous microorganisms were found in the samples, even if the system was operated at very high F/M of 4.5 kg BOD<sub>5</sub>/kg.MLSS.d, which was the reason for good sludge settling obtained for all the HRT's.

#### 5.3.1.2 Effect of pH

**Removal of pollutants :** Four pH levels of 5, 6, 7 and 8 were studied with other fixed conditions (i.e., HRT : 3 days; temperature : 20°C; and DO : 7-8 mg/L) as presented in Table 5.1. As shown in Fig. 5.4a, more than 96% of BOD<sub>5</sub> can be removed under each pH studied; an increase in pH from 5 to 8 does not induce effect on the removal of BOD<sub>5</sub> (97 to 98%). Thus, the treatment system can tolerate a change in pH between 5 and 8 without inducing effect on BOD<sub>5</sub> removal; and this pollutant can be readily biodegraded for the fixed conditions investigated.

As illustrated in fig. 5.4a, the removal of COD increases from 70 to 80% when pH increases from 5 to 7; then decreases to 74% as pH increases further to 8. Therefore, pH has a significant influence on COD removal.

As in the case of HRT effect, up to 52% of the LS was removed from the effluent. An increase in pH from 5 to 7 improved the LS removal from 44 to 52% (Fig. 5.4a). No more removal of the LS was observed as pH increased further from 7 to 8. The effluent colour was reduced by 54 to 66% as pH increased from 5 to 8.

Also, a similar linear relationship between the removals of the LS and colour, as in the case of HRT effect, was found.

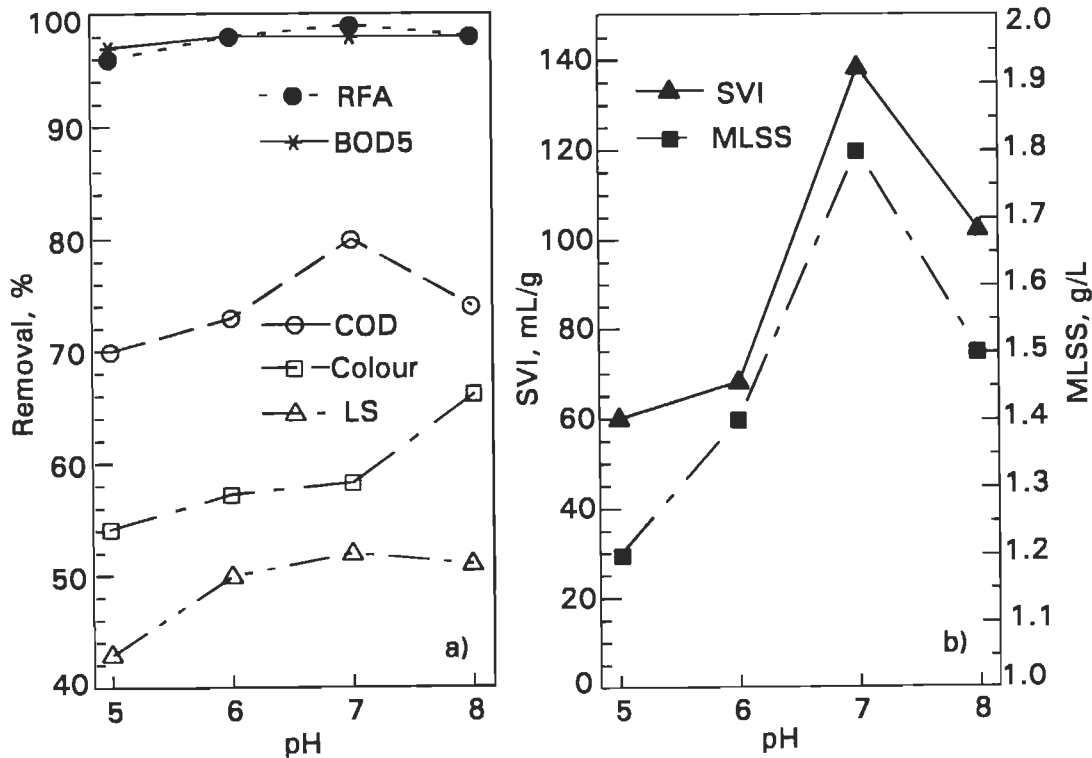


Fig. 5.4 Effect of pH on aerobic treatment performance

**RFA Removal :** As seen in Fig. 5.4a, pH does not have influence on RFA removal. Almost 98% of RFA in the effluent can be readily removed at all the pH levels investigated. The concentrations of RFA in the treated effluents were below 1 mg/L. Thus, the treated effluent obtained at all the pH levels studied would be expected to be non toxic to fish.

**Sludge characteristics :** Generally, the optimum pH for bacteria growth lies between 6.5 and 7.5 [134]. Fig. 5.4b shows that the concentration of bacteria developed at pH 7 (1.8 g/L) is much higher than those at other pH values (1.2 to 1.5

g/L). Good sludge settling has been observed for the pH range studied, as indicated by SVI ranging from 60 to 138 mL/g; they are well below the upper limit for easily settled sludge.

As in the case of HRT effect, microscopic observations of sludge samples revealed no significant differences in microbial populations, which consisted mainly of bacteria, representative protozoa, and metazoa, for all the pH values studied. Also, no filamentous bacteria were found in the sludge.

### 5.3.1.3 Effect of treatment temperature

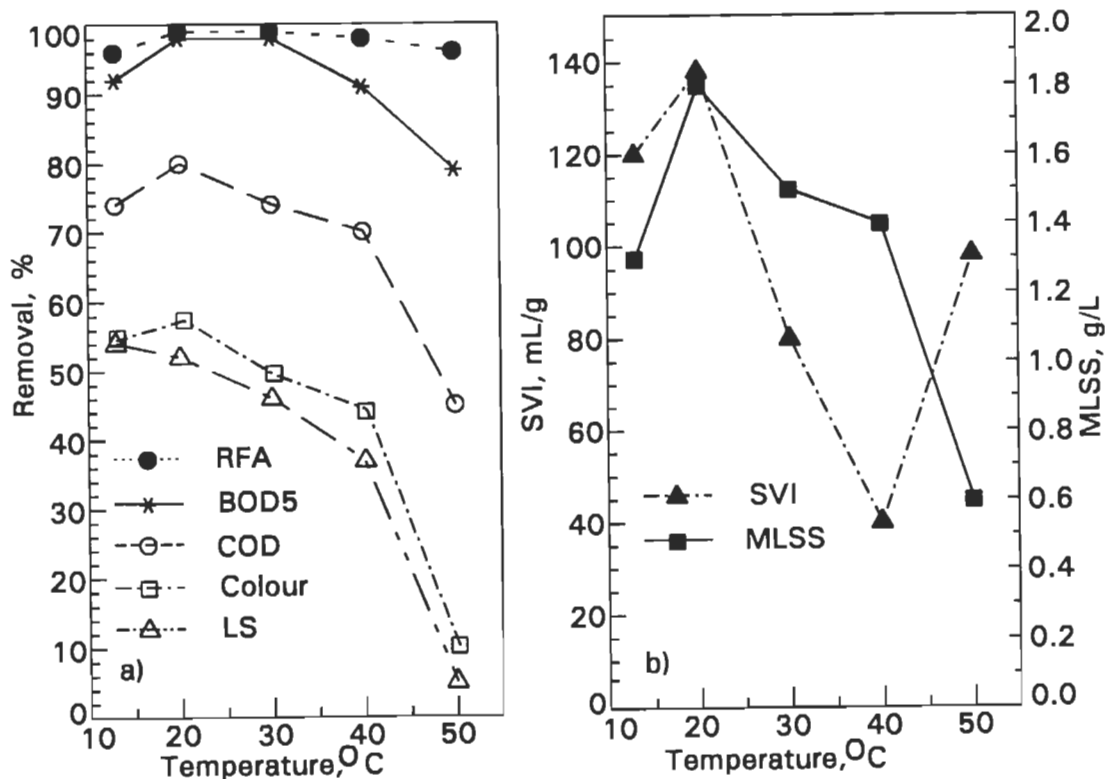


Fig. 5.5 Effect of temperature on aerobic treatment performance

**Removals of pollutants :** The effect of treatment temperature ranging from 10

to 50 °C on removal efficiency was investigated with other fixed conditions (i.e., HRT : 3 days; pH : 7; and DO; 7-8 mg/L), as shown in **Table 5.1**. As observed in Fig. 5.5a, temperature has a very significant influence on the removals of pollutants. Raising temperature from 13 to 20 °C induced positive effects on pollutant removals. A further increase from 20 to 40 °C provoked negative effects on the removals of pollutants. When the temperature was raised a step further from 40 to 50 °C, the % removals of BOD<sub>5</sub> and COD dropped significantly from 91 and 70% to 79 and 46%, respectively. Very similar temperature effect on an activated sludge treatment of bleachery kraft wastes was observed in a recent study [143]. The authors found that temperature above 40 °C, in some cases, even as low as 32 °C, produced adverse effects, as expected, on the treatment performance, such as decreased BOD removal and poor sludge settling.

As shown in Fig. 5.5a, temperature in the range between 10 and 20 °C appears to have no distinct influence on the removal (about 53%) of the LS. However, raising temperature in the range of 20 to 50 °C produces a significant negative effect on the removal of the LS. The removal decreases from 52% (46%) to 46% (37%) as temperature was raised from 20 (30) to 30 (40) °C, and dropped drastically from 37% to about 5% as temperature was raised further from 40 to 50 °C. The corresponding colour reduction was 55, 57, 48, 44 and 20%. A similar linear correlation between the two removals, as in the cases of HRT and pH effects, was also observed.

**RFA removal :** Temperature in the range studied (10 to 50 °C) has no significant effect on RFA removal, as shown in Fig. 5.5a. The reduction of RFA for all the temperature studied were from 96 to 99%. It has been reported [144] that the upper limit temperature for detoxification of a bleached kraft mill effluent is about 50 °C. The above results from temperature effects suggest that the favourable treatment temperature for the effluent is in the range between 20 and 30 °C.

**Sludge characteristics :** As shown in Fig. 5.5b, raising temperature from 40 to

50°C produces a very negative effect, as expected, on MLSS concentration which decreases from 1.4 to 0.6 g/L. Raising temperature from 10 to 40 still produced good settling sludge, as indicated by the SVI values shown in Fig. 5.5b. The increase of SVI from 40 to 98 mL/g, obtained when raising temperature from 40 to 50 °C, was due to the filamentous bacteria developed in the treatment system at 50 °C, observed by microscopic examination of the sludge sample.

When the treatment was carried out in the temperature range of 10 to 40 °C, the microbial populations were observed to consist mainly of bacteria as well as of representative protozoa and metazoa; there were no filamentous bacteria present. When the treatment was conducted at 50 °C, the microbial populations were observed to be composed of bacteria and filamentous organisms only, indicating that a shift had occurred in the composition of the populations as a result of raising temperature from 40 to 50 °C. Traditionally, microorganisms are classified into three groups : psychrophiles, mesophiles and thermophiles. The first group grows in the temperature range from - 2 to 30 °C, while the second and third in the range from 20 to 45 °C and from 45 to 75 °C, respectively. The disappearance of protozoa and metazoa from the system, when operated at 50 °C, was due to the occurrence of a shift in microbial population, i.e., a shift from mesophiles to thermophiles. The decrease in microbial species, a much lower MLSS concentration, and probably the poorer oxygen transfer rate at higher temperature could be the reasons to account for the significant drop in the removals obtained at 50 °C.

#### 5.3.1.4 Effect of dissolved oxygen (DO) level

**Removals of pollutants :** Fig. 5.6 shows the effect of DO on the treatment efficiency. The DO level studied covered a very wide range from about 2 mg/L to more than 8 mg/L as presented in **Table 5.1**. As shown in Fig. 5.6a, in the range studied, DO has no significant effects on the removals of both BOD<sub>5</sub> and RFA; about 94 to 98% of BOD<sub>5</sub> and almost 98% of RFA can be removed from the effluent by the



treatment. An increase in DO level above 2 mg/L has been also found to have no effect on the treatment performance, *in terms of  $BOD_5$  removal*, of an activated sludge process [145]. These results suggest that, from the economic point of view, it would be better to carry out the CTMP effluent treatment at a low DO level (e.g. 1 to 2 mg/L).

However, DO has a significant influence on the COD removal, as seen in Fig. 5.6a. The removal of COD increases from 70 to 80% as DO level increases from 2.5 to 8.2 mg/L. According to the results reported by Chapman *et al* [146] and Williamson *et al* [147-148], a higher DO level would increase the sludge activity due to more penetration of oxygen into the sludge flocs. Thus, more COD removal should be achieved at higher DO level.

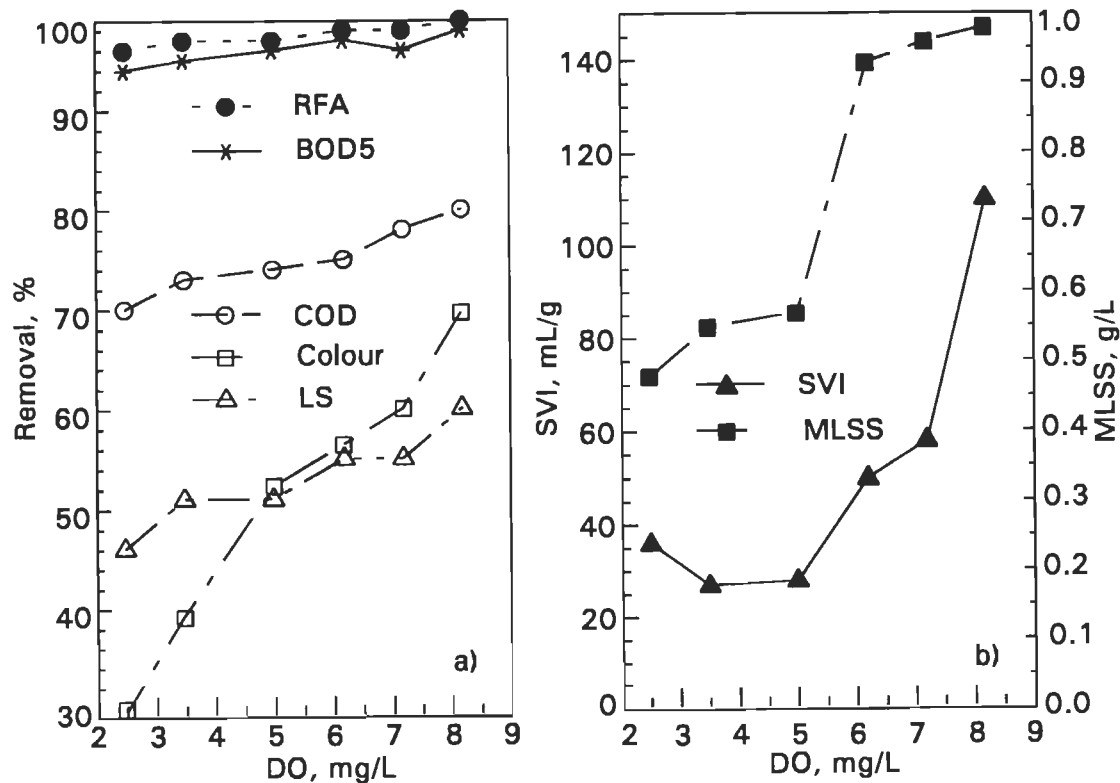


Fig. 5.6 Effect of DO level on aerobic treatment performance

Fig. 5.6a shows that more DO favours the removal of LS, which increases from about 46 to 60% as DO is raised to 2.5 to 8.2 mg/L. As illustrated, DO has a more significant effect on colour removal than on LS removal (Fig. 5.6a). The above results suggest that there might be other reasons, in addition to the reduction caused by ~~due to~~ the removal of LS, for the more colour reduction. It is well known that oxygen has been employed as an effective bleaching agent in pulp bleaching to remove the colour groups in pulp. Therefore, an increase in DO level should improve also the colour removal through bleaching mechanisms. Thus, the large increase in colour removal is not only due to the increase in the LS removal but might be due to the bleaching of the effluent by oxygen as well.

**Sludge characteristics :** As shown in Fig. 5.6b, an increase in DO in the sub-range from 5 to 6.2 mg/L has a very significant effect on the growth of microorganisms, as indicated by the MLSS concentration which increases from 570 to 930 mg/L. The positive effect of DO outside that sub-range is marginal, as indicated by the slight increase in MLSS concentration. An increase in DO level did not generate an adverse effect on sludge settling, even if there was a big increase of SVI from 58 to 110 mL/g when DO was raised from 7.2 to 8.2 mg/L. Good sludge settling has been observed for all the DO levels studied.

As in the case of HRT or pH effect, no difference in microbial population was observed microscopically, when DO increased from 2.5 to 8.2 mg/L. At DO of 3.5 mg/L, the mixed liquor generated a bad odour and was dark in colour. More odour was produced and the mixed liquor became darker in colour when DO was reduced to 2.5 mg/L. The odour might be due to the hydrogen sulphide formed from the reduction of sulphate present in the mixed liquor when DO was low. In view of effluent COD and colour removals, treatment of the CTMP effluent should be conducted at DO level of at least 2.5 mg/L or higher .

### 5.3.1.5 Treatment-system stability

For biological treatment, system or process stability is very important in practice. Good stability or stable operation of a treatment system is always expected. Good stability is indicated by both no up-set operation and little change in treatment efficiency under stable operating conditions.

The stability of the aerobic treatment system was monitored. No up-set operation was observed for all the treatment conditions studied. Fig. 5.7 presents, as an example, the variations of inlet and outlet COD concentrations as well as % COD removal with operating time. The results in Fig 5.7 were obtained under the conditions of HRT : 2 days; pH : 7; temperature: 20 °C; and DO : 7-8 mg/L. The shapes of the curves in this figure are the stable state operation characteristics of biological treatment systems.

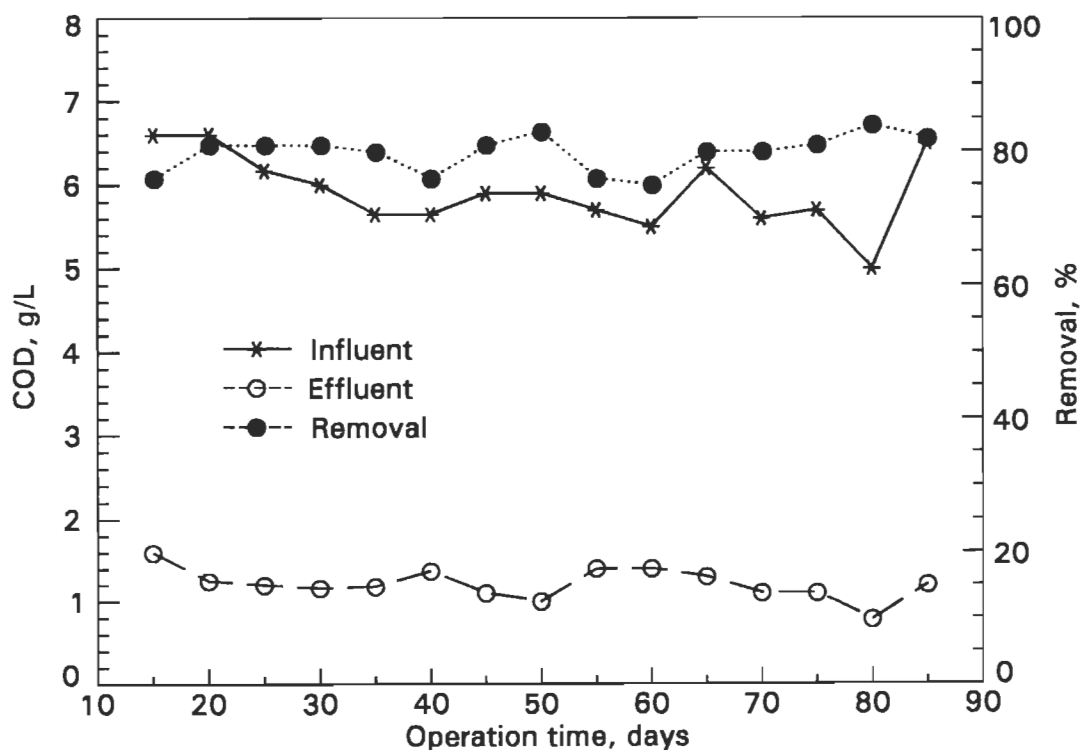


Fig. 5.7 Concentration and % removal of COD versus operation time for aerobic treatment

### 5.3.2 Anaerobic treatment

#### 5.3.2.1 Treatment performance

Fig. 5.8 presents the removals of pollutants by the anaerobic treatment under the conditions studied. The HRT studied ranged from 0.5 to 4 days and the MLSS in the reactor was around 5000 mg/L.

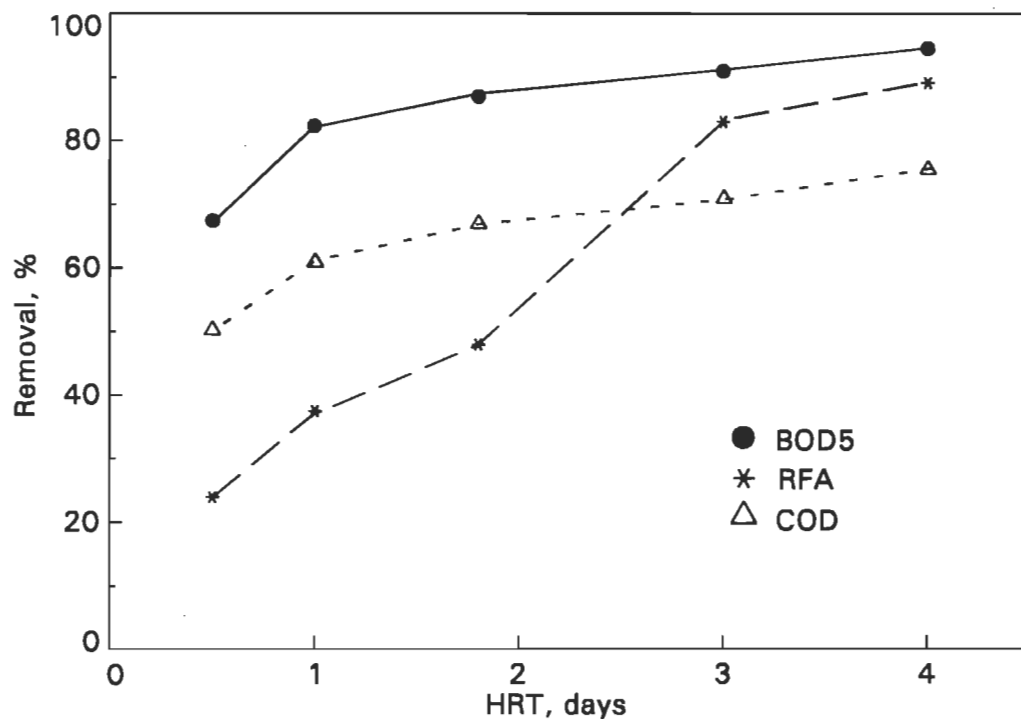


Fig. 5.8 Performance of anaerobic treatment of the CTMP effluent

**Removals of pollutants :** As seen, both BOD<sub>5</sub> and COD removals improve significantly as HRT increases from 0.5 to 2 days; a further increase in HRT does not induce a distinct effect on the two removals. Under the conditions studied, about 70 to 83% of the BOD<sub>5</sub> and 52 to 63 % of the COD in the effluent can be removed with 0.5 to 1 day HRT. The HRT that is usually used in full scale high-rate anaerobic

treatments of pulp and paper mill effluents ranges from 4 to 24 hours (see Table 4 in ref. 15 and Table 8.1 in ref 21], achieving the removals of 60 to 70% of COD and 75 to 85 of  $BOD_5$  [15, 19, 21]. Therefore, the  $BOD_5$  and COD removals obtained with the HRT in the 0.5-1 day range studied are comparable to those reported for full-scale anaerobic treatment of pulp and paper mill including CTMP effluents. As shown previously, aerobic treatment can remove about 88% of the  $BOD_5$  from the CTMP effluent with 0.5 day HRT, for which the MLSS concentration was only about 1200 mg/L. Therefore, compared with aerobic treatment, anaerobic treatment is much less effective for  $BOD_5$  removal.

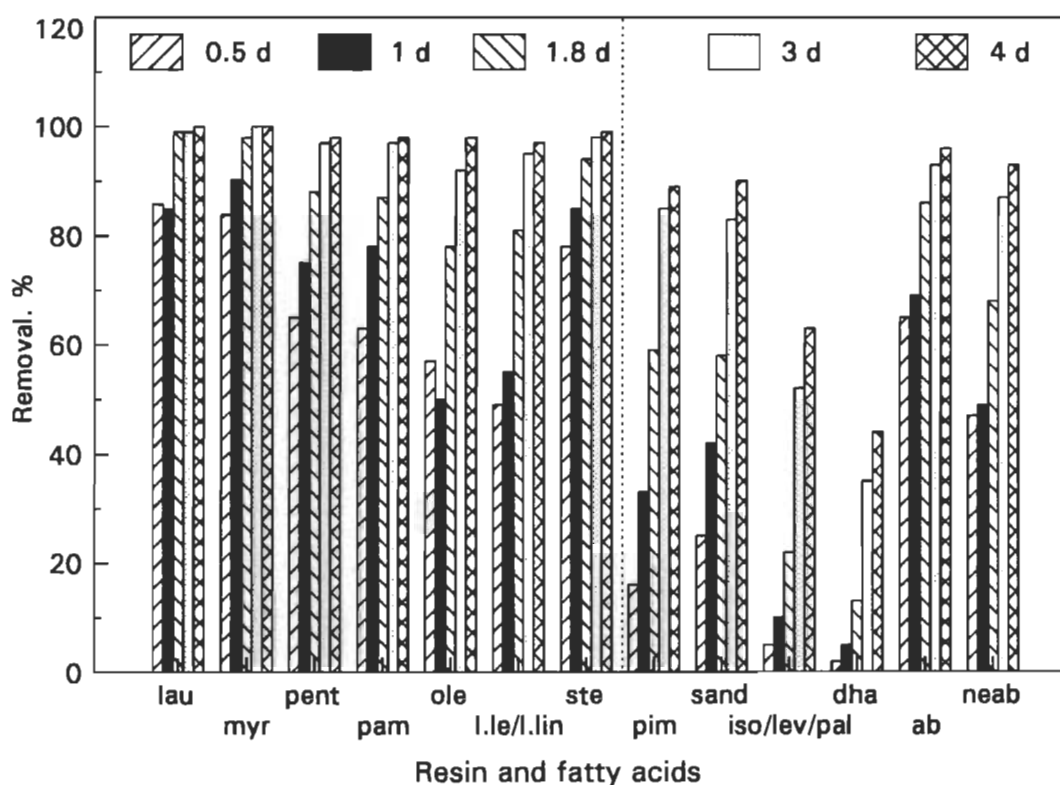


Fig. 5.9 Removals of individual RFA by anaerobic treatment at several HRT's

**RFA removal :** Unlike aerobic treatment, anaerobic treatment was ineffective for RFA removal, as shown in Fig. 5.8. RFA removal (23 to less than 80%) was very poor when HRT is shorter than 3 days which is probably the major reason for insufficient detoxification of CTMP effluents by anaerobic treatment with a normal HRT of 1 or 2 days. To achieve 90% of RFA removal from the CTMP effluent, HRT longer than 4 days would be required for the anaerobic treatment. Poor removals (40 to 80%) of RFA from pulp and paper mill effluents by anaerobic treatment have been reported in the literature [59, 104].

Fig. 5.9 presents the removals of individual RFA by anaerobic treatment of the effluent. As seen, anaerobic treatment seems to be more effective for the removals of fatty acids (left side of the dotted line in Fig. 5.9) than for resin acids (right side of the dotted line right). Most of the fatty acids were removed at all the HRT's studied. Among the resin acids, the removal of abietic acid was relatively high, ranging from about 60 to over 95%. The removals of both pimaric and sandaracopimaric acids were HRT dependant, while the abatements of dehydroabietic, isopimaric, levopimaric and palustric acids were not significant. The removal of dehydroabietic acid was extremely low, this acid has been reported to be recalcitrant to anaerobic biodegradation [104, 108].

#### 5.3.2.2 Biogas production

One of the major advantages of anaerobic treatment is the generation of biogas from the treatment. Throughout the treatment operation, biogas yield and its methane content were occasionally measured for each HRT studied. Fig. 5.10 shows the yields and the contents obtained with the HRT's studied. As seen, biogas yield increases very slightly as HRT increases -- equivalent to the decrease in organic loading. The yield varied in the range of 0.23 to 0.33 m<sup>3</sup>/kg of COD removed, which matches well the values obtained from most of the anaerobic treatments of pulp and paper mill effluents [15, 19, 21]. On an average, the yield was about 0.26 m<sup>3</sup>/kg of COD

removed which is quite below the theoretical value of 0.35. One important reason for this relatively low biogas production was due to the leaking of the methane gas from the ordinary tygon tubing used as gas line. Various types of rubber and plastic tubings were tested for methane leaking. There is no methane leaking only from teflon tubing.

The methane content in the biogas produced ranged from about 70 to 80%, as shown in Fig. 5.10. These results fall in the typical ranges reported for most of the anaerobic treatments of pulp and paper mill effluents [15, 19, 21]. The composition of the biogas, however, was not analyzed.

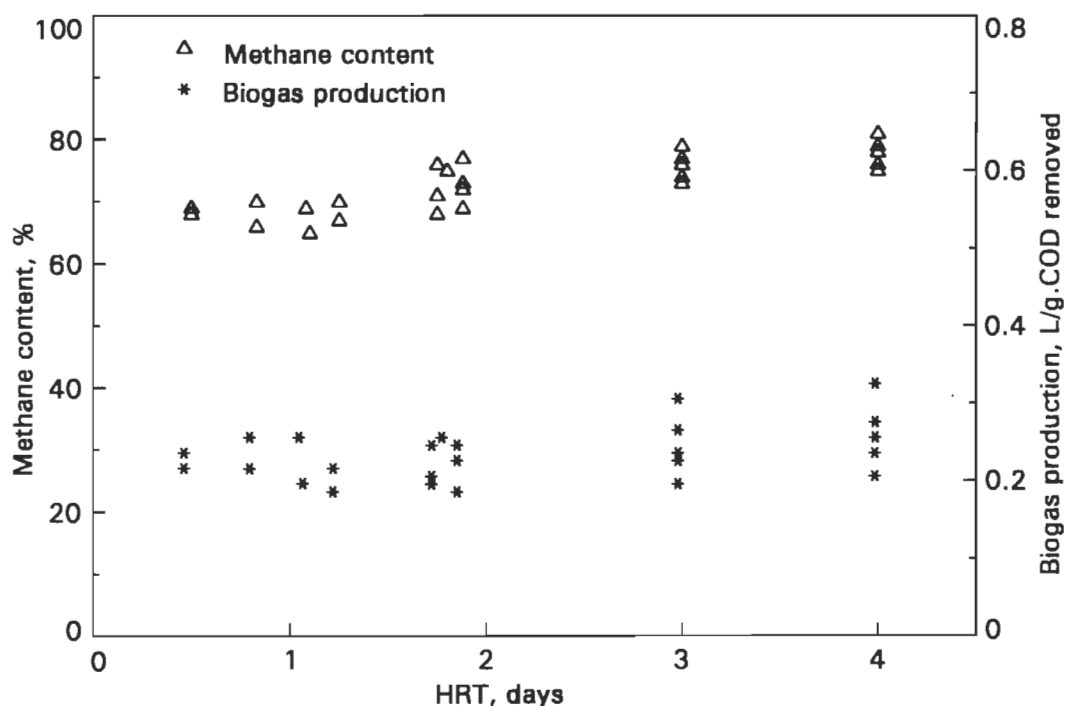


Fig. 5.10 Biogas production and methane content versus HRT

### 5.3.2.3 pH, VFA and alkalinity

pH, VFA and alkalinity are the three important parameters for monitoring and controlling anaerobic treatment. Throughout the whole treatment operation of about 120 days, these three parameters in the reactor were monitored almost each day. Fig. 5.11 shows the variations of these parameters with operation time.

As illustrated in Fig. 5.11a, the pH in the reactor stabilized well around 7 to 7.5 -- the optimum pH range for methanogenic bacteria growth. As shown in Fig. 5.11b, during approximately the first 40 days of operation, the VFA in the reactor stabilized at about 2.5 meq/L (150 mg/L). The concentration of this parameter increased with the progress of the operation during the period in-between 40 and 80 days. The concentration then stabilized again and varied around 10 meq/L (600 mg/L) from day 80 to the end of the operation, as a result of using short HRT (1 to 0.5 day). At such VFA content, however, the treatment system still operated well since the increased content was neutralized by the corresponding increase in alkalinity (Fig. 5.11c), resulting in optimum pH condition for methanogenic bacteria growth.

The alkalinity in the reactor followed about the same profile as the VFA concentration and varied around 26 meq/L for the first 40 days of operation, as illustrated in Fig. 5.11c. From day 80 to the end of the operation, it stabilized and varied between 40 and 49 meq/L with an average of 45 (recommended range : 10 to 50 meq/L).

## 5.4 Conclusions

### 5.4.1 Aerobic Treatment

- 1) An hydraulic retention time longer than two days exerts no influence on the removals of pollutants. A decrease of hydraulic retention time in the range of



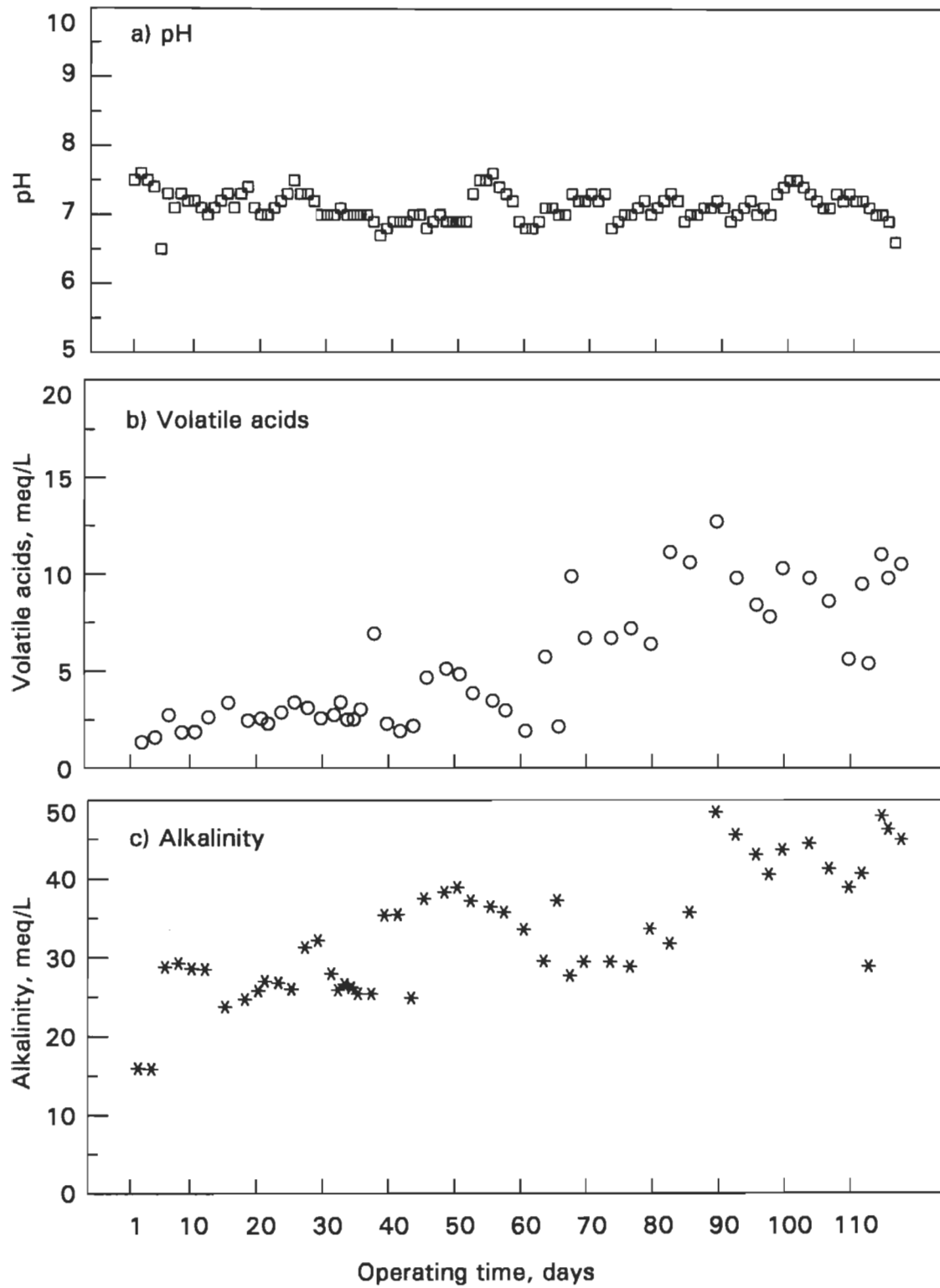


Fig. 5.11 Variations of pH, volatile acids and alkalinity in the anaerobic reactor versus operation time

0.5 to 2 days results in a significant drop in the removal of pollutants, except that for RFA. About 88% of  $BOD_5$  and 95% of RFA can be removed from the CTMP effluent using a short hydraulic retention time of 0.5 day.

pH in the range of 5 to 8 has no negative effect on the removals of  $BOD_5$  and RFA. However, increasing pH from 5 to 7 generally improves the abatements of COD, lignosulphonates and effluent colour.

In the range of 10 and 50 °C, temperature has no influence on RFA removal, however, it exerts distinct effects on the removals of other pollutants, as expected. From 40 to 50°C, the removals of pollutants except that for RFA decrease drastically and filamentous bacteria develop in the system. Therefore, temperature above 40°C is not suitable for aerobic treatment of the CTMP effluent.

The level of dissolved oxygen in the range studied does not have influence on the removals of  $BOD_5$  and RFA. Thus, from economic point of view and in terms of  $BOD_5$  and RFA removals, aerobic treatment of the CTMP effluent can be operated at a low DO level not exceeding 2.5 mg/L. An increase in dissolved oxygen level always, however, induce better removals of COD, lignosulphonates and colour.

- 2) Good sludge settling prevails for all the treatment conditions studied. The sludge volume indices obtained are low and range from 30 to 140 mL/g. Microbial population in the aerobic sludge, except that for 50 °C, consists mainly of bacteria as well as of representative protozoa and metazoa.
- 3) Temperature 20 to 30°C and pH 7 appear to be the favourable environment conditions for aerobic biological treatment of the CTMP effluent. A dissolved oxygen level of about 2.5 mg/L is required for aerobic treatment of the effluent.

Under these favourable conditions, almost 98% of BOD<sub>5</sub> and RFA as well as about 80% of COD can be removed from the CTMP effluent through aerobic treatment.

#### 5.4.2 Anaerobic Treatment

- 1) About 70 to 85 % of the BOD<sub>5</sub> and 52 to 63 % of the COD in the CTMP effluent can be removed by the anaerobic treatment with a normal HRT of 0.5 to 1 or 2 days under the conditions studied. These levels of removals are comparable to those reported by full scale anaerobic treatments of pulp and paper mill effluents.
- 2) Anaerobic treatment is ineffective for RFA removal. With an HRT of 0.5 to 3 days, RFA removal by the treatment ranges from about 20 to 80%.
- 3) Biogas yield from the treatment ranges from 0.23 to 0.33 m<sup>3</sup>/kg of COD removed, with an average of around 0.26. The biogas produced contains 70 to 80% of methane.

## CHAPTER - 6

### KINETICS OF AEROBIC AND ANAEROBIC TREATMENTS OF A CTMP EFFLUENT

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In this chapter, the kinetics of substrate removal and design parameters (sludge yield coefficients, oxygen utilization constants (for aerobic treatment) and temperature coefficient) for a CTMP effluent were evaluated under the favourable conditions found in Chapter 5 for aerobic and anaerobic treatments.

#### 6.1 Introduction

As mentioned previously in Chapter 2, treatment kinetics and design parameters play central roles in the design, optimization and operation of a biological process. For constructing an optimum full scale biological treatment system, the design parameters for any effluent to be treated are needed and usually established in small-scale study. A given set of parameters (and also treatment conditions) established for one effluent is not necessary applicable to other effluents, due to the fact that effluents are quite different in characteristics from mill to mill. Moreover, the kinetics for both anaerobic and aerobic treatments of the CTMP effluent are essential for optimizing the design and operation of the two-stage system for the CTMP effluent.

To date and to our knowledge, no study on either kinetics or design parameters has been reported for either aerobic or anaerobic biological treatment of CTMP effluents. Thus, experiments were carried out to evaluate the removal kinetics and the design parameters for both the aerobic and anaerobic treatments of the CTMP effluent studied.

## 6.2 Kinetic models and design equations

### 6.2.1 Kinetic models

The first order reaction model (equ. (2.8)) and the Monod model (equ. (2.9)) presented in Chapter 2 were used to study the removal kinetics. If there is non-biodegradable matter in the wastewater, equs. (2.8) and (2.9) are modified to equs. (6.1) and (6.2), respectively :

$$(S_o - S)/(Xt) = k(S - S_n) \quad (6.1)$$

$$(S_o - S)/Xt = K(S - S_n)/[K_s + (S - S_n)] \quad (6.2)$$

To determine the parameters K and  $K_s$  using Lineweaver-Burk plot, equs. (2.9) and (6.2) are rearranged to give :

$$Xt/(S_o - S) = (K_s/K)(1/S) + 1/K \quad (6.3)$$

$$Xt/(S_o - S) = (K_s/K)[1/(S - S_n)] + 1/K \quad (6.4)$$

At low substrate concentration, neglecting S in the denominators of equs. (6.2) and (6.4) as compared to  $K_s$  yields :

$$(S_o - S)/Xt = (K/K_s)S = k^*S \quad (6.5)$$

$$(S_o - S)/Xt = (K/K_s)(S - S_n) = k(S - S_n) \quad (6.6)$$

which are first order reaction equations.

### 6.2.2 Design equations

Equations (2.10) and (2.11) presented in Chapter 2 were used to determine the sludge yields in both anaerobic and aerobic treatments, and oxygen requirement parameters for aerobic treatment, respectively.

The experimental set-up and the procedures used have been described in Chapter 3. Experimental conditions and results for each kinetics study are presented, respectively, in **Tables 6.1** and **6.2**. The method of least squares was employed in all the linear regression analyses to establish the kinetic and design parametric values.

### 6.3 Results and discussion

#### 6.3.1 Kinetics and design parameters for aerobic treatment

**Table 6.1.** Experimental results from aerobic treatment of the CTMP effluent for the evaluation of kinetics and design parameters .

Exper. conditions <sup>(1)</sup>		Experimental results -- Kinetics data						
HRT ( $t_s$ )	MLSS	BOD <sub>5</sub>		COD		RFA		SOUR*
days	mg/L	S <sub>o</sub> , mg/L	S', mg/L	S <sub>o</sub> , mg/L	S, mg/L	S <sub>o</sub> , mg/L	S, mg/L	mg.O <sub>2</sub> /mg. MLSS.day
5	1600	3400	38	5590	1230	41.4	0.34	0.42
5	1600	3150	53	5700	1120	23.8	0.25	0.39
3	1730	3400	50	5590	1140	41.4	0.37	0.64
3	1570	2980	62	5820	1210	23.8	0.24	0.62
2	1760	3400	67	5590	1330	41.5	0.61	0.95
2	1870	3550	67	5150	1150	44.5	0.54	0.93
1	1420	3300	166	5590	1730	41.6	0.87	2.21
1	1710	3060	176	5140	1790	44.5	0.55	1.68
0.5	1310	3150	373	5010	1870	41.5	1.39	4.24
0.5	--	--	--	--	--	--	--	4.30

(1) -- Other conditions : 1) pH = 7; 2) temperature = 20 °C and 3) DO = 6-8 mg/L

\* -- Specific Oxygen Uptake Rate

**Table 6.1** presents the experimental results from aerobic treatment of the CTMP

effluent studied for the evaluation of kinetic and design parameters. Based on these experimental data, the substrate removal kinetics and design parameters for the treatment were evaluated, using the kinetic and design equations presented in Section 6.2.

### 6.3.1.1 Kinetics of substrate removal

The correlations obtained by the method of linear regression are presented, respectively, in Fig. 6.1 for first order reaction kinetics (equ. (6.1)) and in Figs. 6.2 and 6.3 for kinetics following Monod model (equ. (6.2)) for BOD<sub>5</sub>, COD and RFA.

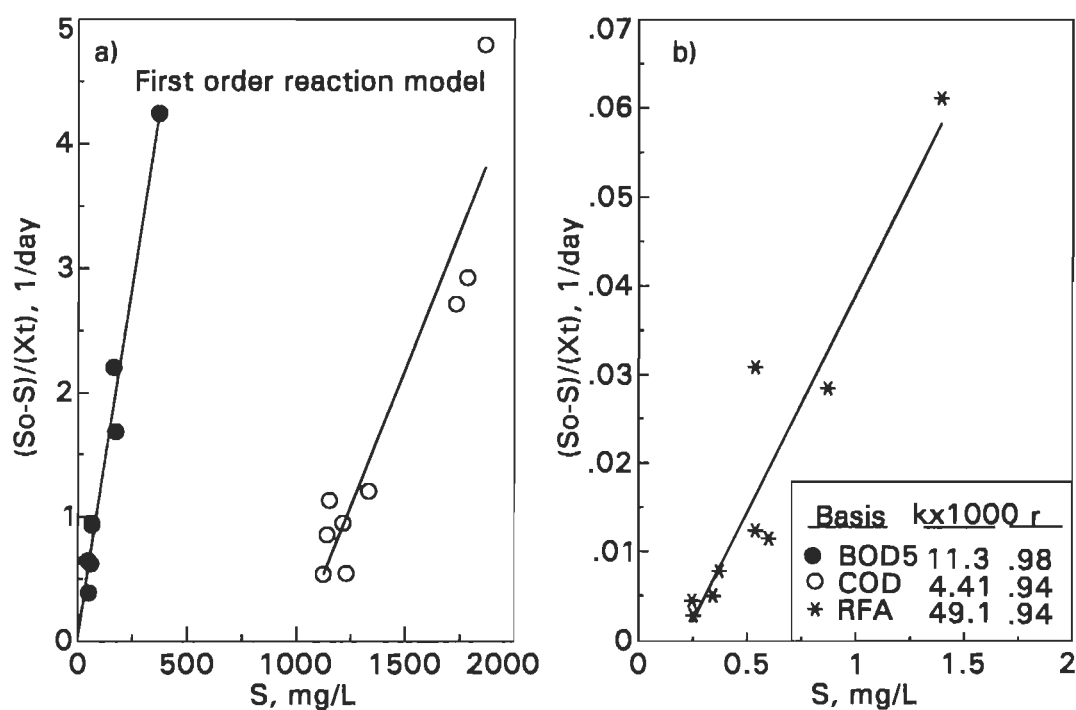


Fig. 6.1 Determination of substrate removal rate constant  $k$  for aerobic treatment

**First order reaction kinetics :** Fig. 6.1 clearly shows that biodegradation of the effluent studied follows very well a first order reaction, as indicated by the correlation coefficients ranging from 0.94 to 0.98. The value of substrate removal rate constant

$k$  of  $11.3 \times 10^{-3} \text{ (mg MLSS/L)}^{-1} \text{ (day)}^{-1}$  obtained in this study for  $\text{BOD}_5$  is almost identical to those reported for two TMP mill effluents [149]. It is in the same order of magnitude as those ( $17\text{--}30 \times 10^{-3}$ ) reported for some wastewaters [131]; but considerably much higher than those ( $5.5\text{--}10 \times 10^{-4}$ ) for bisulphite spent liquor [150].

The non-biodegradable substance concentrations  $S_n$ 's in terms of  $\text{BOD}_5$ , COD and RFA in the effluent studied were found, by linear regression, to be 1.9, 1000 and 0.2 mg/L, respectively. The initial concentrations  $S_0$ 's of those substrates were 3000, 6200 and 45 mg/L. Based on these  $S_0$ 's and  $S_n$ 's, therefore, the maximum removals that could be achieved should be 99.9, 83.8 and 99.6%, respectively, for  $\text{BOD}_5$ , COD and RFA. As presented previously in Chapter 5, the experimental removals of  $\text{BOD}_5$ , COD and RFA by the single stage aerobic treatment under some sets of treatment conditions were as high as 98, 80 and 99%, respectively, which are quite near the calculated maximum % removals. Theoretically, the maximum % removal of  $\text{BOD}_5$  that can be achieved is 100. There should be no non-biodegradable substance present in the substrate measured as  $\text{BOD}_5$ ; therefore, the  $S_n$  found should equal zero. The  $S_n$  of 1.9 mg/L found for  $\text{BOD}_5$  is the result of curve fitting by the method of linear regression. The high  $S_n$ 's obtained for COD were thought to come from the non-biodegradable lignosulfonates and other non-biodegradable organic matters, which have contributions to COD, but not to the  $\text{BOD}_5$ , in the effluent studied. The very low  $S_n$  for RFA might indicate that RFA in the effluent could be completely removed by aerobic treatment.

**Monod kinetics :** As shown in Fig. 6.2,  $\text{BOD}_5$  and RFA removals can also be well described by the Monod kinetic model with a correlation coefficient of 0.92 for  $\text{BOD}_5$  and 0.88 for RFA. When the linear regression analysis was re-made without including the data from HRT of 5 days in the analysis, all the substrate removals can be described well by the Monod model with  $r$ 's ranging from 0.90 to 0.97, as shown in Fig. 6.3. It is speculated that, when the effluent being treated at HRT longer than 3 days, the mechanisms of substrate biodegradation shifts to first order kinetics,



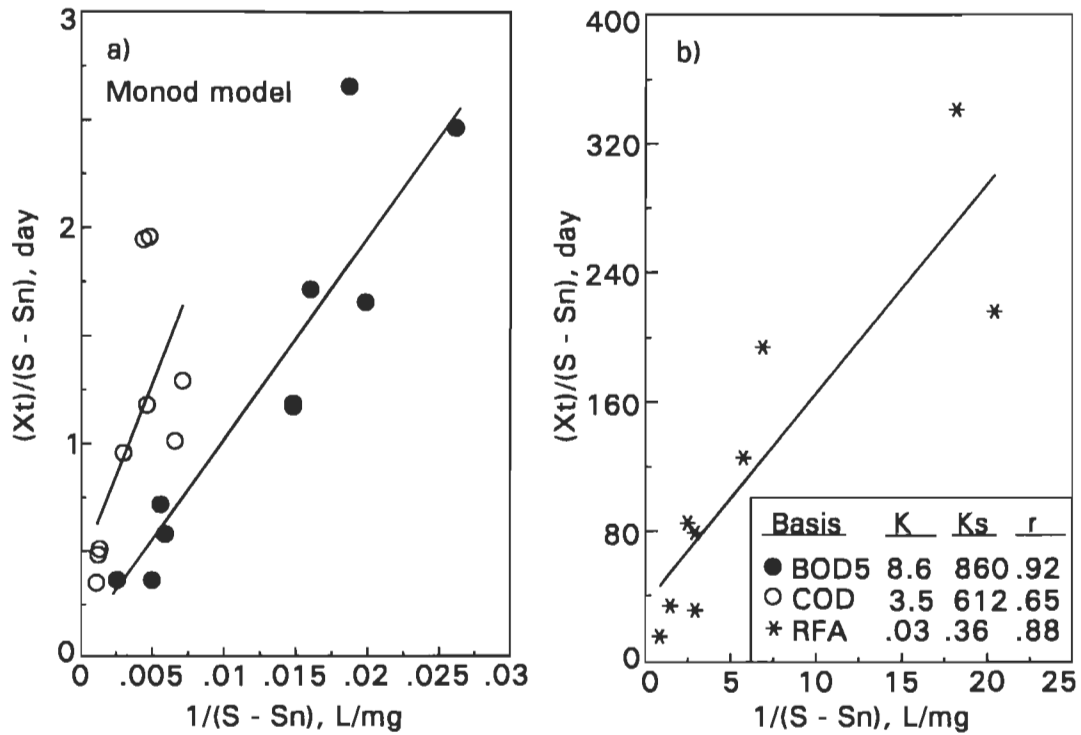


Fig. 6.2 Determination of kinetic parameters K and Ks in Monod model for aerobic treatment

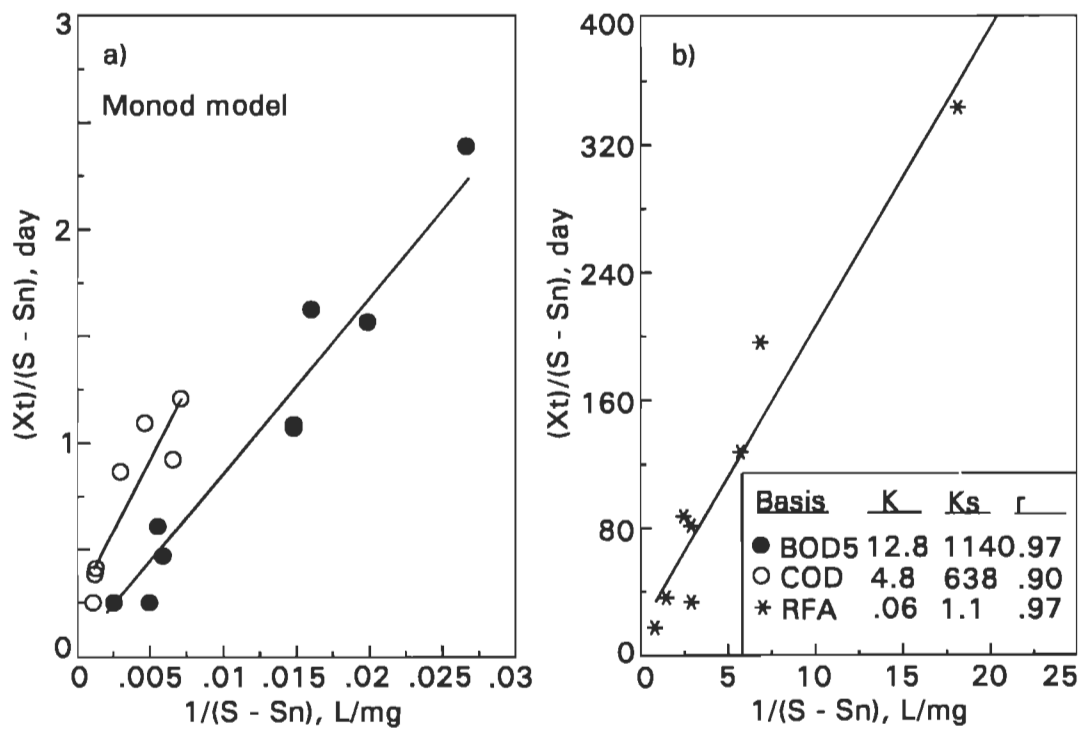


Fig. 6.3 Determination of kinetic parameters K and Ks in Monod model for aerobic treatment, excluding the results from HRT = 5 days

suggested by the results presented in Fig. 6.3. The value (8.65) obtained for the maximum specific substrate removal rate  $K$  based on  $BOD_5$  is much higher than the typical value (5) reported for domestic wastewater [134]. This implies that aerobic biological treatment would be much more efficient when applied to the removal of  $BOD_5$  from CTMP effluents. In fact, as shown in Fig. 5.1a, about 94% of  $BOD_5$  can be removed from the effluent studied with one-day HRT.

The  $K_s$  obtained for  $BOD_5$  was 860 mg/L (Fig. 6.2). This  $K_s$  is very large as compared to the  $S$  of  $BOD_5$  in the reactor. Therefore, based on  $BOD_5$ , the Monod model is essentially in the same form as the first order reaction kinetic model :

$$(S_o - S)/Xt = K*S/K_s = 0.01S \quad (6.7)$$

The value of  $K/K_s$  (0.01) in the above equ. (6.7) is very close to that of  $k$  (0.0113, Fig. 6.1) obtained based on first order reaction kinetics. Therefore, for the effluent studied, the biodegradation of  $BOD_5$  can be described very well by both first order kinetics and Monod model.

#### 6.3.1.2 Growth of microorganisms

The linear regression plots displayed in Fig. 6.4 indicate clearly that the specific growth rate of microorganisms in terms of different substrates are well represented by equ. (2.10), since  $r$ 's are higher than 0.98.  $Y$  and  $K_d$  are the two important parameters required for the design of an optimum industrial biological treatment system including sludge handling. The value of  $Y$  (0.54) based on  $BOD_5$  for the CTMP effluent studied is greater than those reported for two TMP mill effluents [149], but matches very well the value (0.5) reported for kraft mill wastewater [131]. This value falls in the range (0.3-0.8) reported for other wastewaters [131, 134].

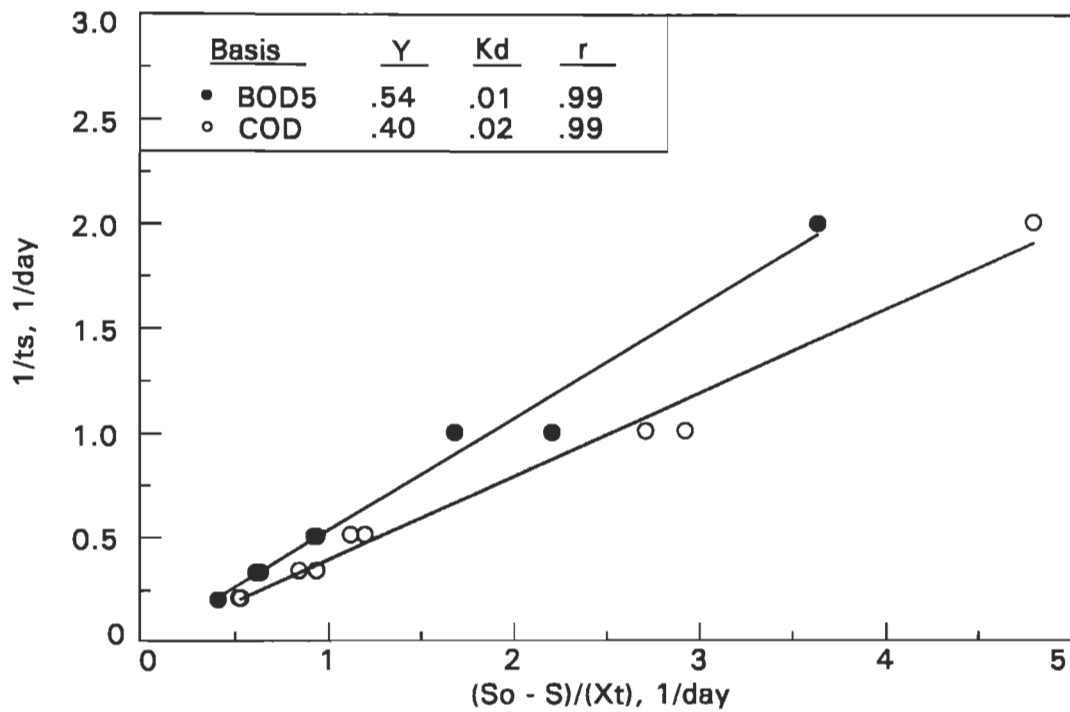


Fig. 6.4 Determination of sludge yield parameters  $Y$  and  $K_d$  for aerobic treatment

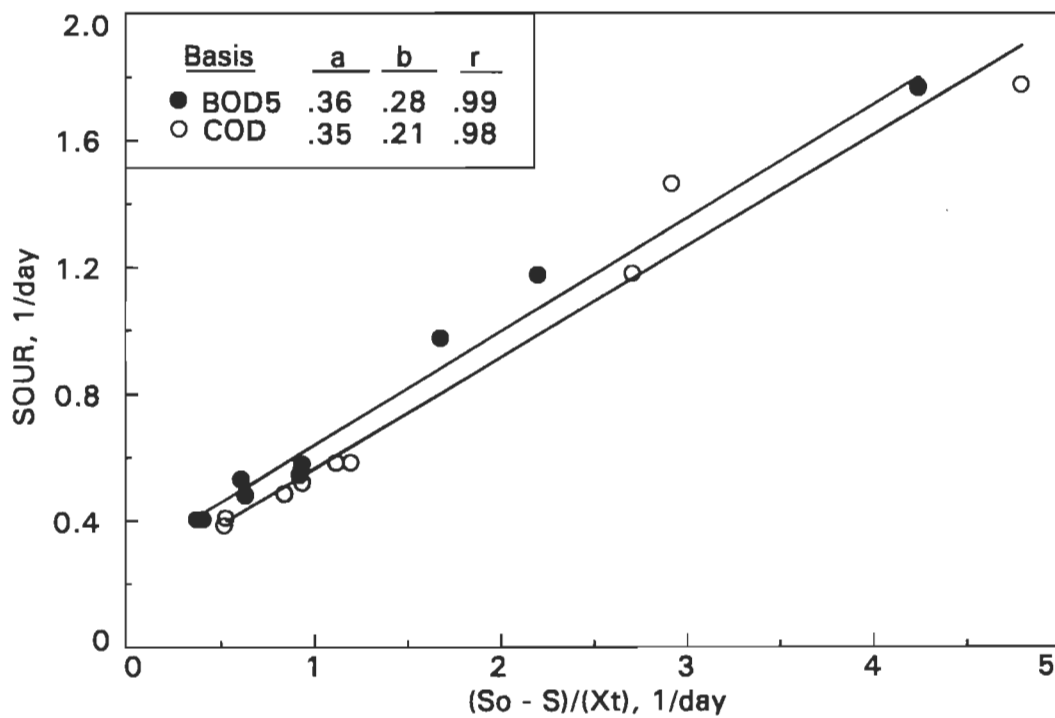


Fig. 6.5 Determination of oxygen utilization parameters  $a$  and  $b$  involved in aerobic treatment

### 6.3.1.3 Oxygen utilization

For the design of a full scale aerobic biological treatment process, it is necessary to evaluate the oxygen requirement for the selection and sizing of aeration equipment. The two related parameters,  $a$  (coefficient for oxygen required to oxidize substrate) and  $b$  (coefficient for oxygen rate required for endogenous respiration), were evaluated for the fixed conditions studied, using Equ. (2.11). The results obtained by the regression method for the different substrates are presented in Fig. 6.5. The value of  $a$  found for  $BOD_5$  was  $0.36 \text{ mg O}_2/\text{mg BOD}_5$  removed which is almost identical to those reported for two TMP mill effluents [149]; however it is much lower than those reported for kraft pulping and bleaching wastewater (0.65 to 0.8) [131] and that (0.54) for bisulphite spent liquor [150]. Therefore, the design of aerobic treatment of the CTMP effluent can not be based on the design parameters for other types of pulp and paper mill effluents.

### 6.3.1.4 Temperature effect on overall oxygen transfer coefficient $K_La$

The overall oxygen transfer coefficient for the effluent to be treated is an important parameter in the design of an aerobic treatment system. To investigate the effect of temperature on this transfer coefficient for the CTMP effluent, the  $K_La$  at different temperatures was determined according to the unsteady-state aeration method recommended by Ramalho [131], and calculated by the following equation (6.8).

$$\text{Log}(C_{st} - C_t) = -K_Lat + \text{constant} \quad (6.8)$$

Where :  $C_{st}$  : Saturated oxygen concentration in the CTMP effluent;  
 $C_t$  : Oxygen concentration at the time  $t$ .

Fig. 6.6 shows temperature effect on the overall oxygen transfer coefficient of the CTMP effluent. As seen, the  $K_La$  increases with temperature, i.e., elevated

temperature improves the oxygen transfer between the gas phase and the mixed liquor in the reactor. However, this advantage may be offset by the low solubility of oxygen in the liquor at high temperature. The basic relationship between  $(K_La)_T$  and temperature was found to be:

$$(K_La)_T = (K_La)_{20^\circ\text{C}} \times 1.028^{T-20} \quad (6.9)$$

For the conditions investigated, the temperature coefficient of 1.028 found for the effluent is almost equal to that of 1.024 that has been commonly used for design purpose [131].

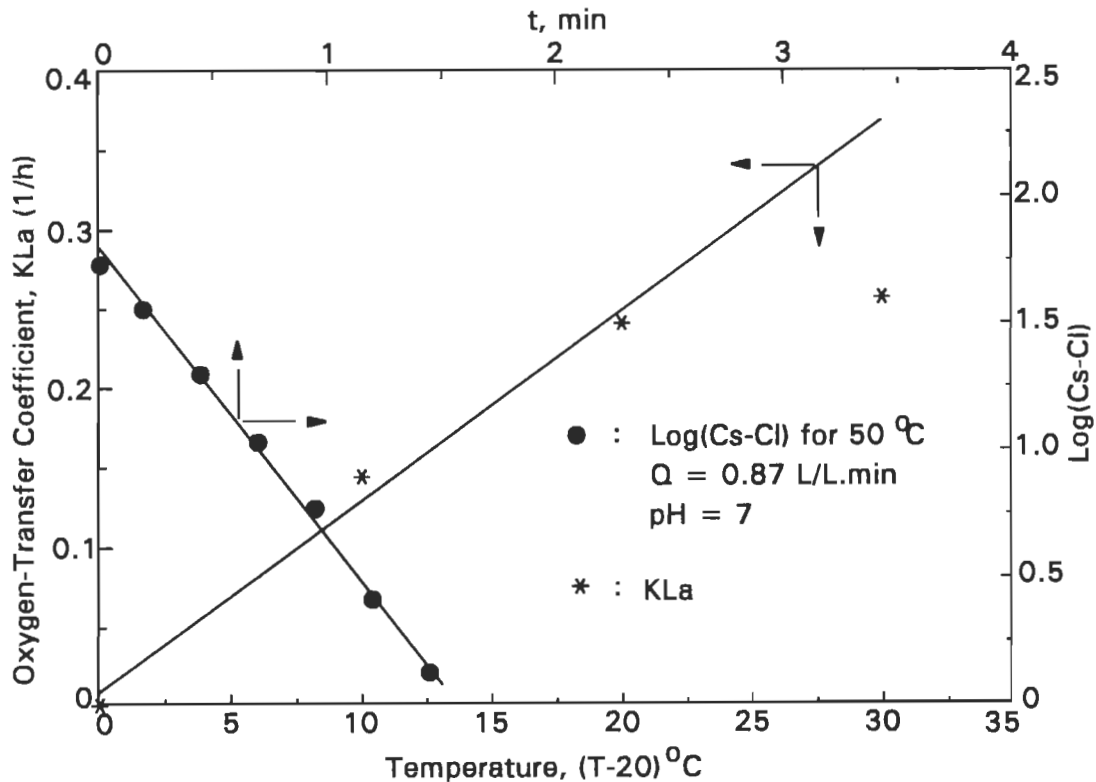


Fig. 6.6 Effect of temperature on overall oxygen transfer coefficient  $K_La$  and determination of temperature coefficient

### 6.3.2 Kinetics and design parameters for anaerobic treatment

**Table 6.2** presents the experimental results from anaerobic treatment of the CTMP effluent studied for the evaluation of kinetics and design parameters.

**Table 6.2.** Experimental results from anaerobic treatment of the CTMP effluent for the evaluation of kinetics and design parameters .

Exper. conditions <sup>(1)</sup>		Experimental results				
HRT ( $t_s$ )	MLSS	BOD <sub>5</sub>		RFA		▲X
days	mg/L	S <sub>o</sub> , mg/L	S, mg/L	S <sub>o</sub> , mg/L	S, mg/L	mg/day
4	4950	3030	146	40.8	4.01	--
3	5500	3090	255	38.6	5.65	830
1.8	4600	3010	410	42.3	21.32	1000
1	5130	2980	510	41.0	25.21	1900
0.5	3850	3050	950	39.3	29.6	4500

(1) -- Other conditions : 1) pH = 7; 2) temperature = 35 °C

#### 6.3.2.1 Kinetics of substrate removal

The first order reaction kinetics (equ. (6.1)) and the Monod model (equ. (6.2)) are used to fit the experimental data from anaerobic treatment. The regressions obtained are presented, respectively, in Fig. 6.7 for first order reaction model and in Fig. 6.8 for Monod model for BOD<sub>5</sub> and RFA.

**First order reaction kinetics :** Fig. 6.7a shows that, as in the case of aerobic treatment, the removal rate of BOD<sub>5</sub> follows well a first order reaction model, as indicated by the correlation coefficient of 0.97. The rate constant  $k$  of  $1.3 \times 10^{-3}$  (mg MLSS/L)<sup>-1</sup> (day)<sup>-1</sup> obtained, however, is much lower than that ( $11.3 \times 10^{-3}$ ) found for aerobic treatment, implying that the removal rate of BOD<sub>5</sub> in the effluent studied is

much slower for anaerobic treatment than for aerobic treatment. There are no reported  $k$  data on anaerobic treatments of CTMP effluents as well as of other pulp and paper mill effluents. Therefore, comparison of the value of  $k$  obtained with other data is impossible to be made.

Unlike the case of aerobic treatment, the removal of RFA in the CTMP effluent by anaerobic treatment can not be expressed very well by a first order reaction kinetics, as seen in Fig. 6.7b ( $r = 0.84$ ).

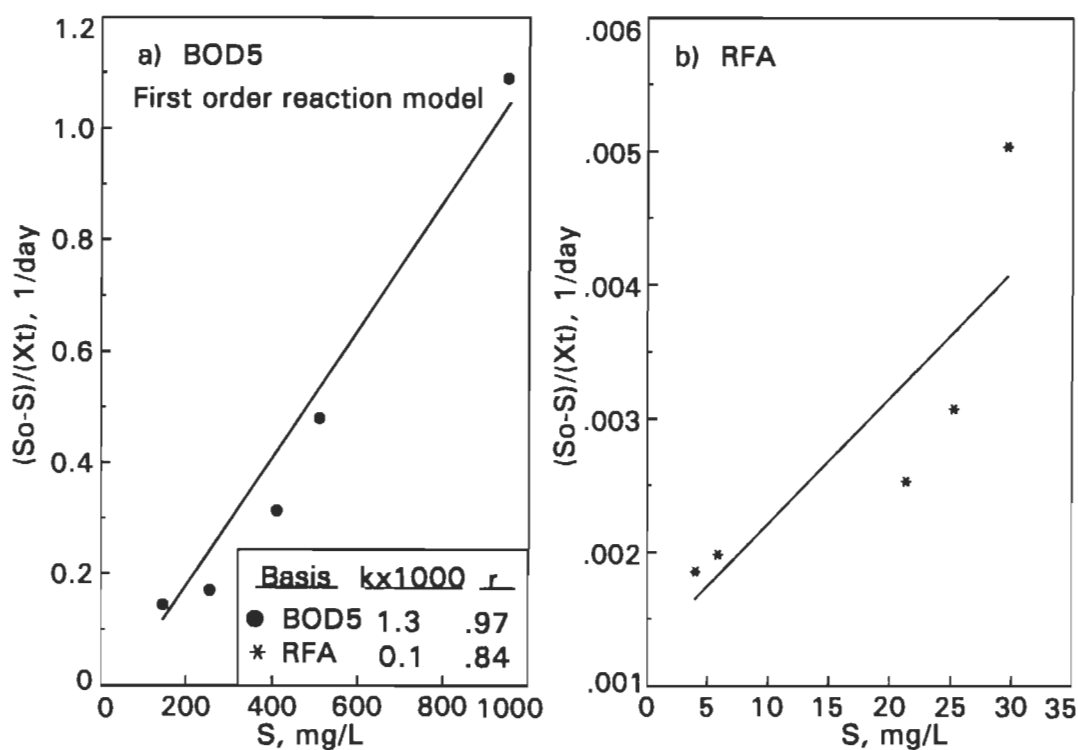


Fig. 6.7 Determination of substrate removal rate constant  $k$  for anaerobic treatment

**Monod model :** As shown in Fig. 6.8a,  $BOD_5$  removal by anaerobic treatment can be also described by the Monod model with a correlation coefficient of 0.95. Zhou [151] also found in a batchwise anaerobic treatment of a cotton kraft black liquor that Monod model can approximately represent COD removal kinetics. The

value of the maximum specific BOD<sub>5</sub> removal rate  $K$  found for anaerobic treatment of the CTMP effluent was about  $2.6 \text{ day}^{-1}$  which is much lower than that (8.65) found for aerobic treatment. Reported studies on anaerobic treatment kinetics for other pulp and paper mill effluents are quite limited; Lee *et al* [19] reported the  $K$  values of 2 to  $5 \text{ day}^{-1}$  on the basis of BOD<sub>5</sub> for groundwood and coated paper wastewaters, while Zhou [151] found that the  $k$  value for a cotton kraft black liquor was  $0.85 \text{ day}^{-1}$  in terms of COD. Therefore, the  $K$  value found for the CTMP effluent is comparable to that found for groundwood and coated paper wastewater.

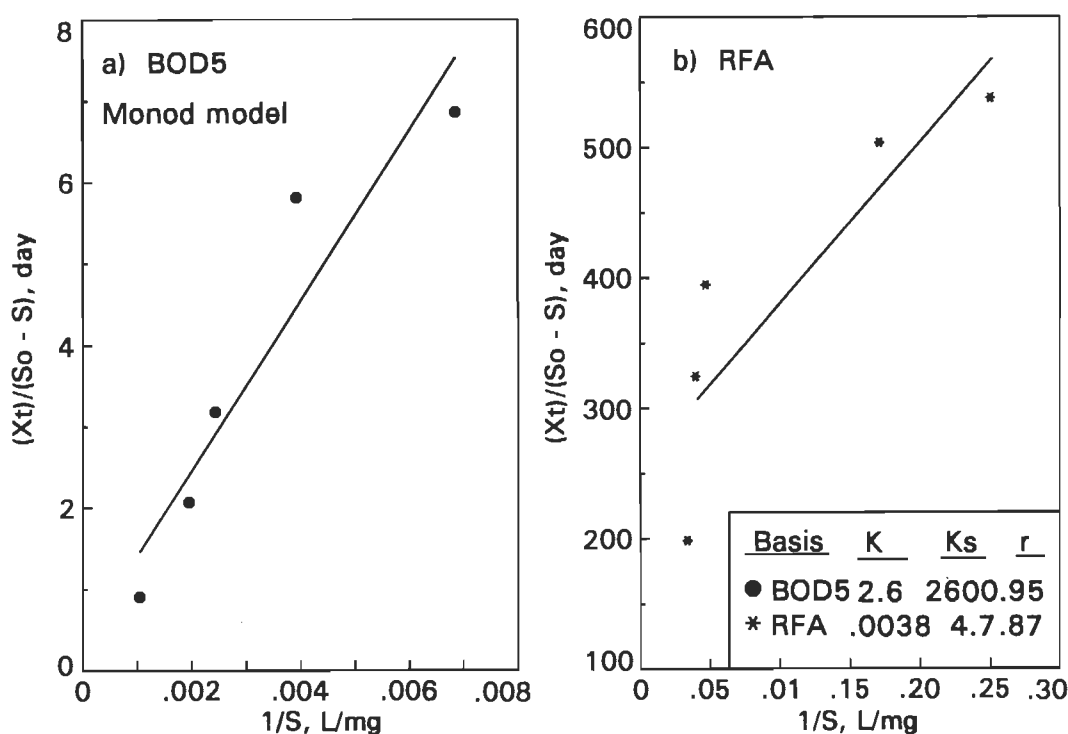


Fig. 6.8 Determination of kinetic parameters  $K$  and  $K_s$  in Monod model for anaerobic treatment

As shown in Fig. 6.8b, the RFA removal by anaerobic treatment can be also only approximately described by the Monod model, with a  $r$  value of 0.87. Therefore, quantitative description of RFA removal by anaerobic treatment seems to be difficult and can be only approximate. The  $K$  value of  $0.0038 \text{ day}^{-1}$  found is, however, very



much lower than that (0.06) found for aerobic treatment. Since the K value is very low, anaerobic treatment with a normal HRT of 0.5 to 1 or 2 days has, therefore, generally produced a poor RFA removal from pulp and paper mill effluents [35, 59, 104, 108].

### 6.3.2.2 Sludge production

Since biomass growth in anaerobic treatment is generally very slow, there was actually no wastage of the sludge from the anaerobic treatment of the CTMP effluent at HRT of 4 days. The amount of sludge wasted at this HRT was difficult to estimate exactly. Therefore, the sludge yield was estimated using the data presented in **Table 6.2**, excluding those from HRT = 4 days.

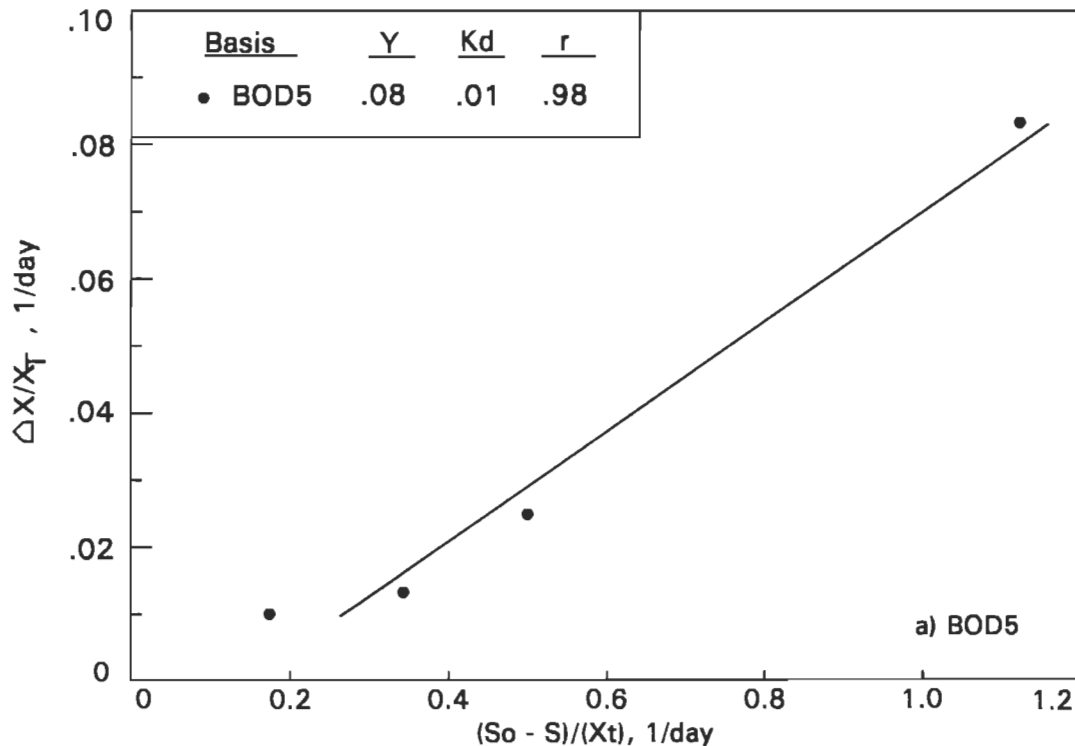


Fig. 6.9 Determination of sludge yield parameters Y and Kd for anaerobic treatment

The regression results presented in Fig. 6.9 show that the biomass growth in the anaerobic treatment of the CTMP effluent can be expressed by equ. (2.10), with a  $r$  of 0.98. The  $Y$  value found for  $BOD_5$  was about 0.08 mg MLSS/mg  $BOD_5$  removed, which falls in the range of 0.04 to 0.1 reported for anaerobic treatment of other pulp and paper mill effluents [19, 21]. This  $Y$  value is much lower than that (0.54) found for aerobic treatment of the effluent.

## 6.4 Conclusions

### 6.4.1 Kinetics and design parameters for aerobic treatment

- 1) Removals of both  $BOD_5$  and RFA by aerobic treatment can be described better by a first order reaction kinetics than by the Monod model.
- 2) For  $BOD_5$ , the values of the two design parameters  $Y$  and  $K_d$ , related to sludge yield, found for the conditions investigated were 0.54 g MLSS/g  $BOD_5$  removed and  $0.01\text{ d}^{-1}$ , respectively.
- 3) The values of the other two design parameters  $a$  and  $b$ , involved in the evaluation of oxygen requirement, were  $0.36\text{ g O}_2/\text{g } BOD_5$  removed and  $0.28\text{ g O}_2/\text{g MLSS oxidized/day}$ , respectively.
- 4) For the effluent studied, the value of 1.028 obtained for the temperature coefficient  $\Theta$  in  $(K_L a)_T = (K_L a)_{20^\circ\text{C}} \times \Theta^{T-20}$  is almost equal to that of 1.024, which has been commonly used for the design of full-scale biological treatment systems.

### 6.4.2 Kinetics and design parameters for anaerobic treatment

- 1) Removal of  $BOD_5$  by anaerobic treatment can be well represented by a first order reaction kinetics, while that of RFA follows only approximately the Monod model.
- 2) The parameters  $Y$  and  $K_d$ , related to the sludge yield for the treatment of the

CTMP effluent, were found to be about 0.08 g MLSS/g BOD<sub>5</sub> removed and 0.01 d<sup>-1</sup>, respectively, which agree well with the reported values for anaerobic treatments of other pulp and paper mill effluents.

## CHAPTER 7

### EFFECTS OF OPERATING CONDITIONS ON THE BEHAVIOUR AND OPTIMIZATION OF THE TWO-STAGE SYSTEM FOR TREATMENT OF A CTMP EFFLUENT

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In this chapter, the effects of the main operating conditions on the behaviour of the two-stage system for the CTMP effluent treatment were first simulated, using the corresponding basic equations presented in Chapter 2 and the kinetic parametric values obtained in Chapter 6 for anaerobic and aerobic treatments of the effluent studied. Optimization of the two-stage treatment system was then followed using the corresponding optimization methods developed in Chapter 2 and the same kinetic parameters as used in the system behaviour simulation. *The major purpose of this chapter is to demonstrate how to study the treatment behaviour of the two-stage system and how to optimize the design and operation of this system.*

#### 7.1 Introduction

It has been reported in Chapter 6 that the removals of  $BOD_5$  in the CTMP effluent by both anaerobic and aerobic treatments follow well the kinetics of a first order reaction kinetics. The rate of RFA removal through aerobic treatment can be approximately described by the kinetics of a first order reaction while that through anaerobic treatment follows approximately the Monod model. Theoretically, the corresponding models should apply also to the  $BOD_5$  and RFA removal rates in each stage, when the two treatment processes are combined together to form a two-stage system as was shown in Fig. 3.1c. On that basis, the models can be used to study the behaviour and optimization of the two-stage system. As an example, the first order reaction kinetics was used to simulate the removals of the  $BOD_5$  in both stages

and the removal of the RFA in the aerobic stage. The Monod model was employed to express the RFA removal rate in the anaerobic stage.

## 7.2 Effects of operating conditions on system behaviour

Using the corresponding basic equations established in Chapter 2, the effects of the main operating conditions (initial substrate concentration  $S_0$ , HRT, mean cell age, and MLSS concentration) on the effluent concentrations,  $S_1$  and  $S_2$ , of  $BOD_5$  and RFA and their corresponding removals were simulated. The situation which could lead to unstable operation of the anaerobic stage was examined with the help of analysis of sensitivity.

The corresponding kinetic parametric values (**Table 7.1**) obtained in Chapter 6 for both anaerobic and aerobic treatments were used in the simulation study.

**Table 7.1.** Kinetic parametric values used in the simulations.

Kinetic parameters	Anaerobic stage		Aerobic stage	
	$BOD_5$	RFA	$BOD_5$	RFA
Kinetics followed	First order	Monod	First order	First order
$k$ , (mg MLSS/L) <sup>-1</sup> d <sup>-1</sup>	0.0013, 35°C	--	0.0113, 20°C	0.049, 20 °C
$K$ , d <sup>-1</sup>	--	0.0038, 35°C	--	--
$K_s$ , mg/L	--	4.7	--	
$Y$ , mg/mg	0.08		0.54	
$K_d$ , d <sup>-1</sup>	0.01		0.01	

### 7.2.1 Effects of operating conditions on effluent quality

**Effect of initial effluent  $S_0$  :** The effects of the initial effluent concentration  $S_0$  on  $S_1$  and  $S_2$  as well as on the corresponding removals were studied using equs.

(2.16) , (2.26) for  $BOD_5$  in both stages and RFA in the aerobic stage, respectively, and equ. (2.32) for RFA in the anaerobic stage.

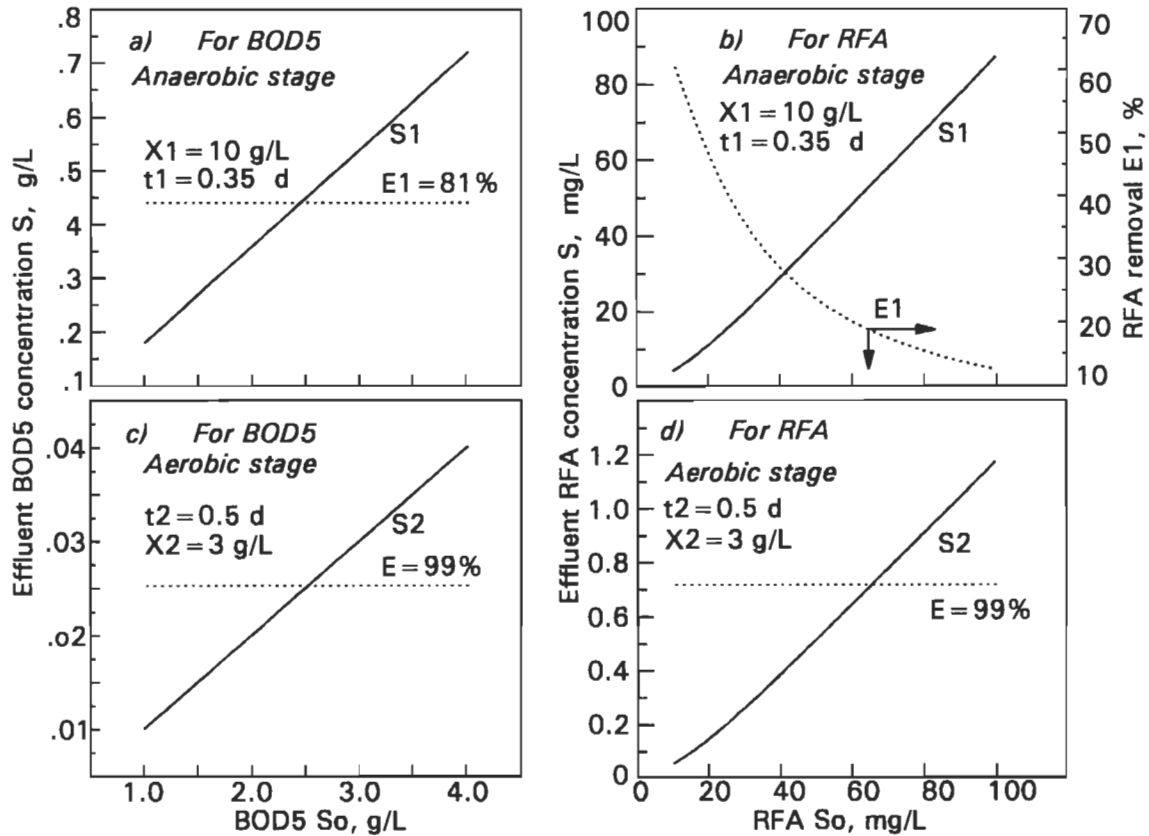


Fig. 7.1 Simulated effect of initial substrate concentration  $S_o$  on  $S_1$  and  $S_2$

Fig. 7.1 presents the results of the effects. As seen, in all the cases, both  $S_1$  and  $S_2$  increase proportionally with the increase of  $S_o$  in the range studied, which can be observed from Eqs. (2.16) and (2.27). When other conditions are fixed,  $S_o$  does not induce any effects on the % removals  $E_1$  and  $E$  of  $BOD_5$  in both stages as well as on that of RFA in the aerobic stage, since the removals of these pollutants follow a first order reaction kinetics. From eqs. (2.16) and (2.17) or (2.26) and (2.27), the expression for the % removal of  $BOD_5$  or RFA can be established as follows :

$$E = \frac{kXt}{kXt + 1} \quad (7.1)$$

Equ. (7.1) shows that % removal  $E$  has no relation to  $S_0$  if the first order reaction kinetics is applicable.

The influence of  $S_0$  on the removal of RFA in the anaerobic stage is, however, very significant as shown in Fig. 7.1b because Monod model has been used to simulate the removal of RFA in this stage. As shown in Fig 7.1b, the lower the RFA concentration is, the higher is the removal, which might be one of the reasons for the very inconsistent results reported on RFA removals by anaerobic treatments.

**Effects of hydraulic retention time :** The effects of the hydraulic retention times  $t_1$  and  $t_2$  on the effluent concentrations in both stages were investigated using equs. (2.16) and (2.26). Fig. 7.2 shows the influences of  $t_1$  on the effluent concentrations  $S_1$  and  $S_2$  of both  $BOD_5$  and RFA for different levels of  $X_1$ . When other conditions are fixed, both  $S_1$  and  $S_2$  are generally decreased with the increase of  $t_1$  in the anaerobic stage.

To discuss the effect on  $S_1$ , the  $t_1$  range has been approximately divided into two sub-ranges. The extents of these two sub-ranges are different for each level of  $X_1$  and also different for  $BOD_5$  and RFA, as shown in Figs. 7.2a and 7.2b. The first sub-range for  $BOD_5$  is much smaller than that for RFA. For example, at  $X_1 = 10$  g/L, the value of  $t_1$  in the first sub-range for  $BOD_5$  is from 0 to about 0.4 day and that in the second sub-range is longer than 0.4 day. At  $X_1 = 10$  g/L, the  $t_1$  value in the first sub-range for RFA is from 0 to about 2 days and that in the second sub-range is longer than 2 days. As shown, the effluent concentration  $S_1$  drops rapidly as  $t_1$  is increased in the first sub-range. Most of the  $BOD_5$  can be removed within this range.

In the second sub-range, the reduction of  $S_1$  is extremely low as  $t_1$  is further

increased, indicating that there is no advantage in terms of  $\text{BOD}_5$  removal to conduct the anaerobic treatment with a  $t_1$  in this sub-range. For example, at  $X_1 = 10 \text{ g/L}$ , it takes more than 2.5 days by the anaerobic treatment alone to achieve a final effluent with  $\text{BOD}_5$  concentration of  $50 \text{ mg/L}$ . While it only requires a total HRT of less than one day to obtain the same final  $S_2$ , first by anaerobic treatment then followed by aerobic treatment of the effluent (for example, an HRT 0.5 to 0.75 day anaerobic treatment followed by an HRT 0.2 day aerobic treatment), as shown in Fig. 7.2c.

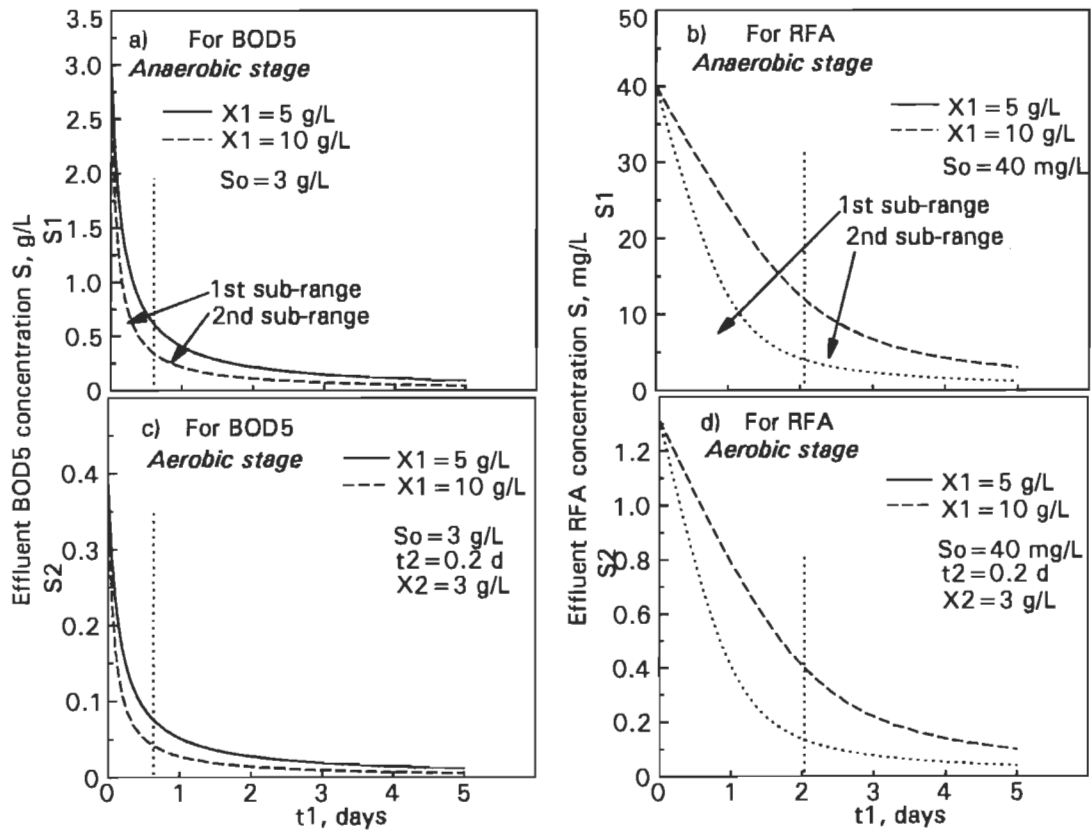


Fig. 7.2 Simulated effects of HRT  $t_1$  and MLSS conc.  $X_1$  on  $S_1$  and  $S_2$

From the economic point of view, the anaerobic stage should not be operated in the second sub-range with a  $t_1$  far from the boundary dividing the first and second



sub-ranges, since most of the  $BOD_5$  can be removed by the treatment with a  $t_1$  in the first sub-range. The reactor volume would be over-sized, leading to low production rate of methane gas per unit of reactor volume, if an excessive  $t_1$  in the second sub-range is used for a given feed flowrate. The effects of  $t_1$  on  $S_1$  and  $S_2$  indicate that there would be an optimum  $t_1$  at which the total HRT,  $t$ , required for obtaining a fixed overall treatment efficiency  $E$  is minimal, which initiated the idea to optimize the design of the two-stage treatment system, which will be presented later in this chapter.

As shown in Fig. 7.2b, it would not be expected to achieve a low effluent RFA concentration by the anaerobic treatment with a short  $t_1$ , for example,  $t_1 < 1$  day. This could be one of the reasons why the removal of RFA by anaerobic treatment is usually very low because the designed  $t_1$  has been normally based on the removal of  $BOD_5$  as well as why anaerobic treatment alone is insufficient to detoxify CTMP effluents. To obtain an acceptable effluent RFA concentration, a post aerobic treatment is needed. For the conditions listed, it would take more than 5 days by the anaerobic treatment alone to achieve a final effluent RFA concentration of lower than 0.5 mg/L. While only a total HRT of less than one day is required to achieve the same final  $S_2$  by the use of two-stage anaerobic-aerobic treatment at  $X_1 = 10$  g/L and  $X_2 = 3$  g/L, as exhibited in Figs. 7.2b and 2d.

Fig. 7.3 presents the effects of  $t_2$  in the aerobic stage on the final effluent concentrations of both  $BOD_5$  and RFA at different levels of  $X_2$ . As shown, the final effluent  $S_2$  decreases as  $t_2$  increases. For the conditions listed, a 0.3 day HRT post aerobic treatment can produce a very low  $S_2$  for both  $BOD_5$  ( $< 30$  mg/L, Fig. 7.3a) and RFA ( $< 1$  mg/L, Fig. 7.3b). Similar to the effect of  $t_1$ , the  $t_2$  range may be also divided into two sub-ranges; however, the first  $t_2$  sub-ranges, particularly for RFA, are usually much smaller than those of  $t_1$ , as shown in Figs. 7.2a and 7.2b as well as in Figs. 7.3a and 7.3b.

Based on the above results from the effects of hydraulic retention times  $t_1$  and  $t_2$ , it is, therefore, suggested that the selection of  $t_1$  for the anaerobic stage be based on the expected overall  $BOD_5$  removal. The acceptable RFA removal is then achieved by the post aerobic treatment since the RFA removal rate in the aerobic stage is very much higher than that in the anaerobic stage. However, on the other hand, the effluent concentration  $S_1$  might be very sensitive to the change of  $t_1$  when  $t_1$  is in the first sub-range, since  $S_1$  is decreased very rapidly as  $t_1$  is increased in this range as mentioned previously.

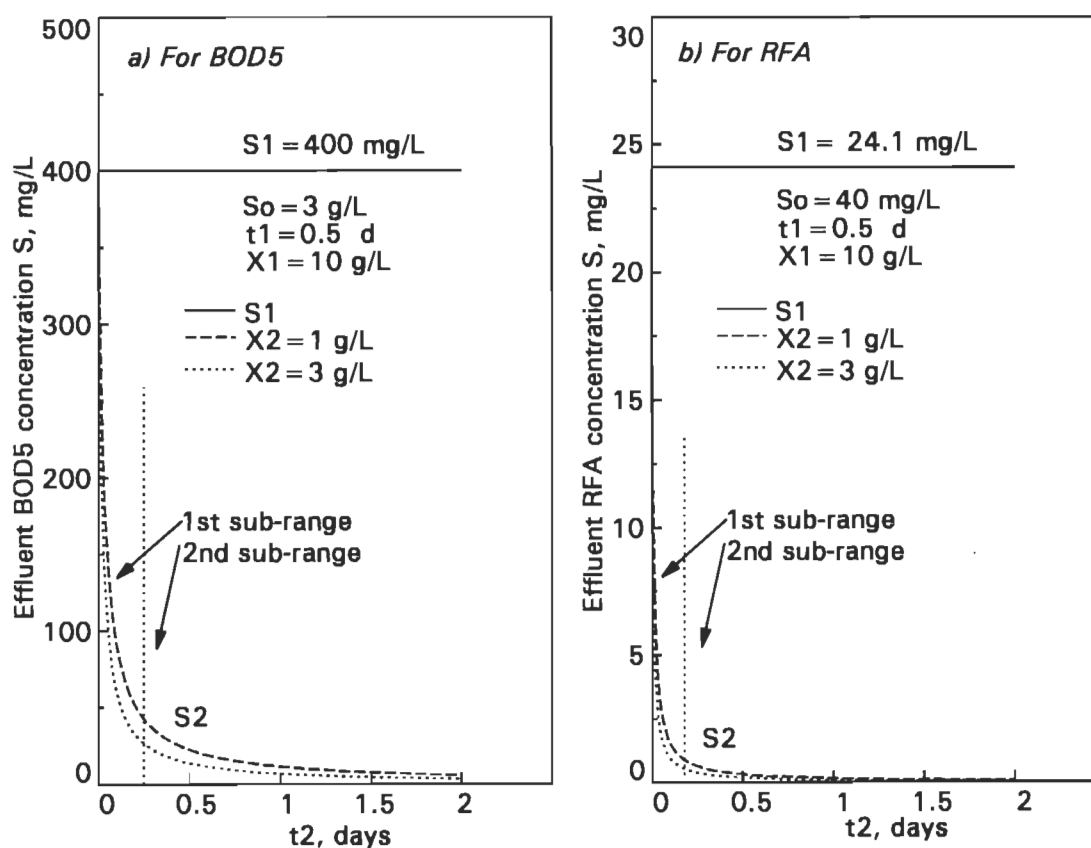


Fig. 7.3 Simulated effects of HRT  $t_2$  and MLSS conc.  $X_2$  on  $S_2$

To see how sensitive is the response of  $S_1$  to the change in  $t_1$ , the rate of the change of  $S_1$  with  $t_1$  is evaluated by the following equation:

$$\frac{\partial S_1}{\partial t_1} = -\frac{k_1 X_1 S_o}{(k_1 X_1 t_1 + 1)^2} \quad (7.2)$$

$$\frac{\partial S_1}{\partial t_1} = -\frac{1}{2} K_1 \left[ 1 + \frac{S_o - K_{s1} - K_1 X_1 t_1}{\sqrt{(S_o - K_{s1} - K_1 X_1 t_1)^2 + 4 K_{s1} S_o}} \right] \quad (7.3)$$

which has been derived by differentiating equs. (2.16) and (2.32) respectively with respect to  $t_1$ . The results calculated for  $X_1 = 10$  g/L with equ. (7.2) for BOD<sub>5</sub> and equ. (7.3) for RFA are presented in Fig. 7.4.

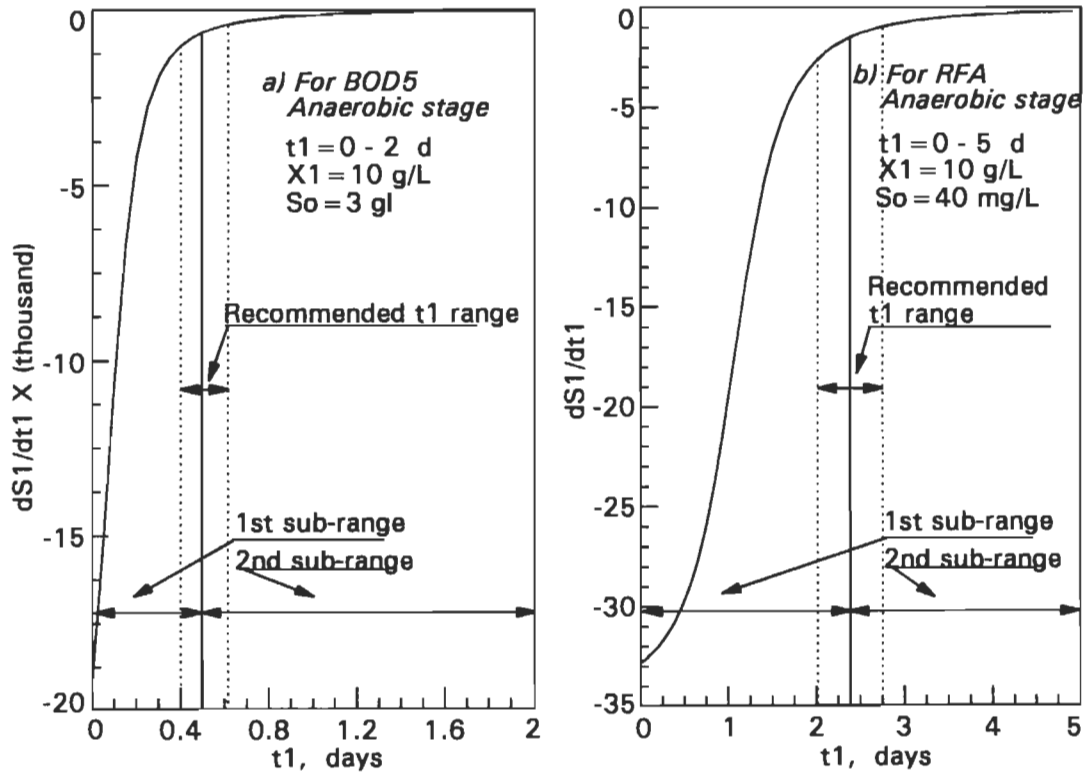


Fig. 7.4 Rate of the change of  $S_1$  with  $t_1$

This figure shows that, in the first sub-range, the rate of the change of  $S_1$  with respect to  $t_1$  for both  $BOD_5$  and RFA is very high, as illustrated by the very sharp slope of the curve, indicating that the effluent concentration  $S_1$  is very sensitive to the change in  $t_1$  in this sub-range. In full scale system, unstable operation could be encountered due to the change in  $t_1$ , caused by the change in feed flowrate, if the anaerobic treatment is conducted in this sub-range. On the contrary, the rate of the change of  $S_1$  with  $t_1$  for  $BOD_5$  in the second sub-range is quite low, indicating that the effluent  $BOD_5$  concentration is not sensitive to the change in  $t_1$ , implying that the operation of the anaerobic stage with a  $t_1$  in this range should be stable. Therefore, for a stable operation, the anaerobic stage has to be operated with a  $t_1$  in the second sub-range. Thus, for the selection of a  $t_1$  for the anaerobic stage one should consider concurrently two aspects : the economic aspect and the operation aspect. The sensitivity analysis of variations in operating conditions which will be presented later may be useful for the consideration of the  $t_1$  selection.

Fig. 7.4a also suggests that there would be no advantage to increase  $t_1$  in the second sub-range since the change rate of  $S_1$  is quite marginal, and that the anaerobic reactor would be over-sized. This result also initiated the idea for optimizing the design of the two-stage system.

**Effects of the concentrations of microorganisms  $X_1$  and  $X_2$  on  $S_1$  and  $S_2$  :** Presented in Figs. 7.2 and 7.3 are also the effects of  $X_1$  and  $X_2$  on the effluent concentrations  $S_1$  and  $S_2$  of both  $BOD_5$  and RFA. Generally, when other operating conditions are fixed, an increase in  $X_1$  reduces the  $S_1$  in the anaerobic stage and also the  $S_2$  in the aerobic stage. To achieve a fixed  $S_2$ , the higher the level of  $X_1$  is, the shorter HRT is required, as shown in Fig. 7.2. This is also true for the effect of  $X_2$  on  $S_2$ , as illustrated in Fig. 7.3.

In practical operation, in order to maintain constant levels of the MLSS concentrations  $X_1$  and  $X_2$  in both stages, the required sludge recycle ratios  $R_1$  and  $R_2$

for the anaerobic and the aerobic stages must be calculated by the following two equations:

$$R_1 = \frac{Q_{r1}}{Q_o} = \frac{(t_{s1} - t_1) X_1}{(X_{r1} - X_1) t_{s1}} \quad (7.4)$$

$$R_2 = \frac{Q_{r2}}{Q_o - Q_{w1}} = \frac{(t_{s2} - t_2) X_2}{(X_{r2} - X_2) t_{s2}} \quad (7.5)$$

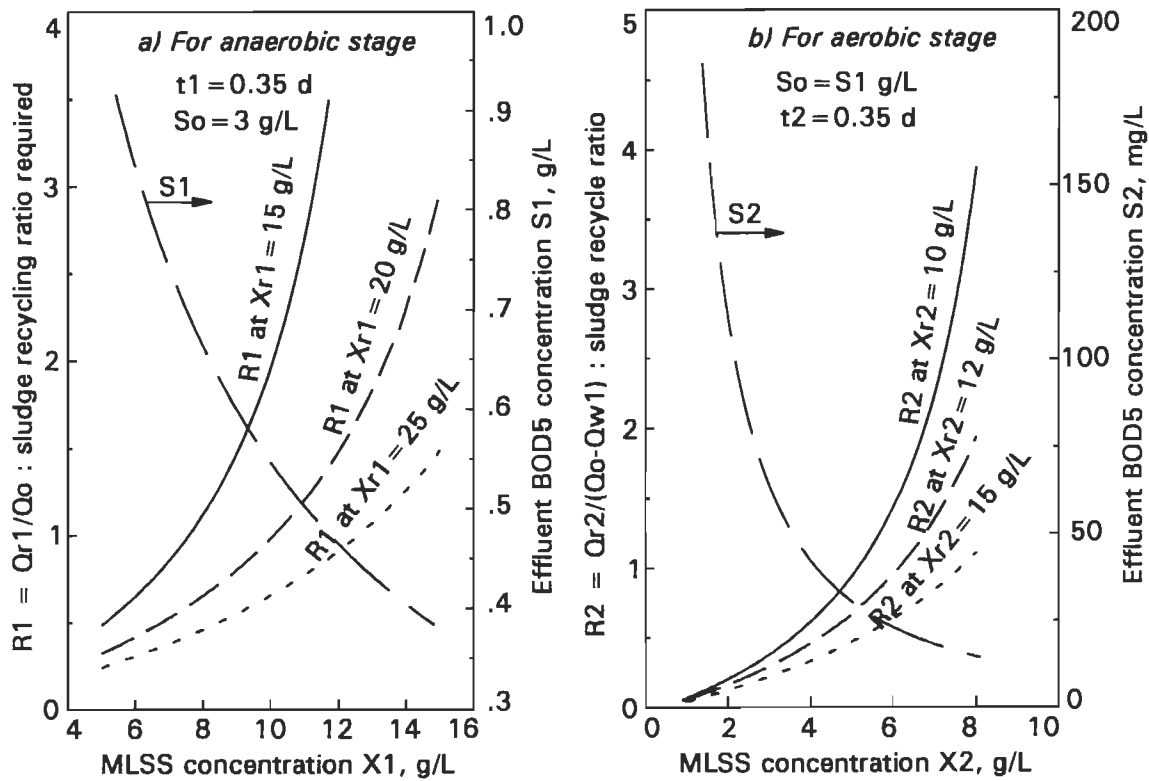


Fig. 7.5 Relationship between sludge recycle ratio  $R$  and MLSS conc.  $X$

These two equations are obtained by making a biomass balance around the reactor in each stage, followed by simplification with the use of eqs. (2.15), (2.23), (2.25) and (2.29). Presented in Fig. 7.5 are the results calculated with eqs. (7.4) and (7.5) in

in conjunction with equs. (2.16), (2.24), (2.26) and (2.30). As illustrated, for a fixed return-sludge microorganism concentration  $X_{r1}$  or  $X_{r2}$ , the required recycle ratio  $R_1$  or  $R_2$  must be raised as  $X_1$  or  $X_2$  is increased. For a fixed  $X_1$  or  $X_2$ , the required recycle ratio  $R_1$  or  $R_2$  is reduced with the increase of the return-sludge concentration  $X_{r1}$  or  $X_{r2}$ . The maximum concentration  $X_1$  or  $X_2$  can not exceed the corresponding return sludge concentration  $X_{r1}$  or  $X_{r2}$ .

**Effect of mean cell age :** The effects of mean cell age  $t_{s1}$  in the anaerobic stage and  $t_{s2}$  in the aerobic stage on BOD<sub>5</sub> concentrations  $S_1$  and  $S_2$  in both stages were studied using equs. (2.24) and (2.30). Presented in Figs. 7.6a to 7.6b are the effects. Similar to the effects of  $t_1$  and  $t_2$ , the  $t_{s1}$  and  $t_{s2}$  ranges may be divided into three sub-ranges, as illustrated in the figure.

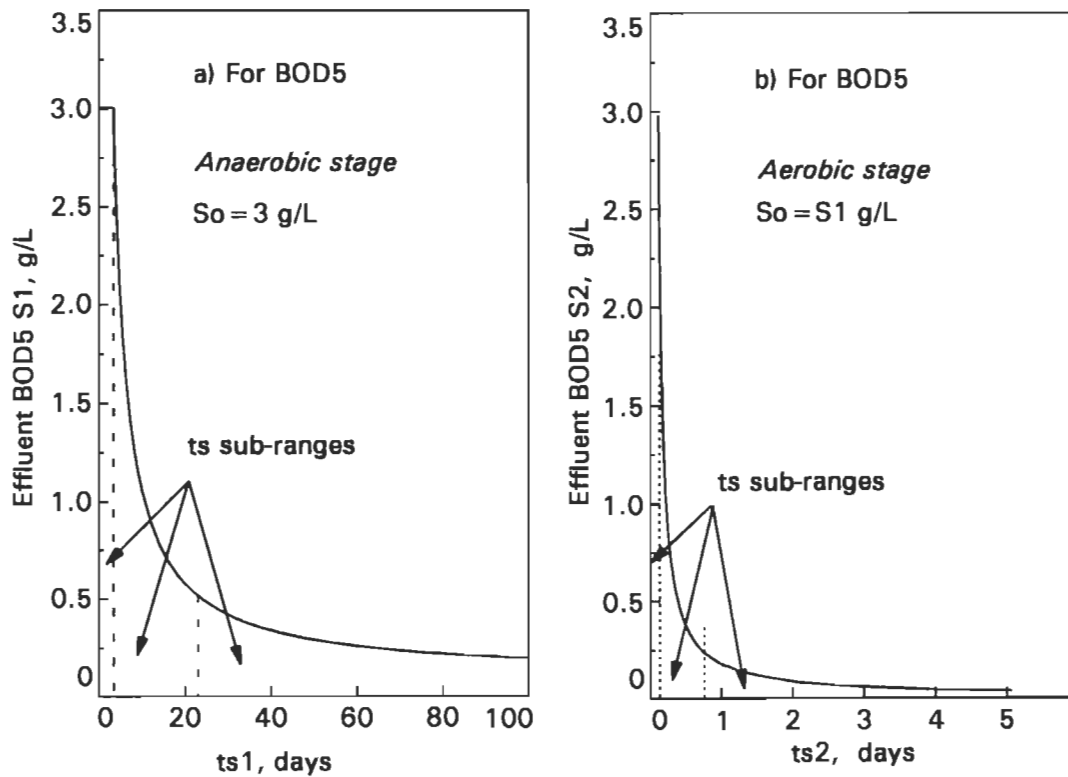


Fig. 7.6 Simulated effects of mean cell age  $t_s$  on  $S_1$  and  $S_2$

As seen, in the first sub-range the effluent concentration  $S_1$  or  $S_2$  of  $BOD_5$  does not change and equals  $S_o$ , indicating that the treatment must not be carried out in this range. In the second sub-range,  $S_1$  or  $S_2$  is reduced/increased very rapidly as  $t_{s1}$  or  $t_{s2}$  is increased/decreased; therefore, both  $S_1$  and  $S_2$  are sensitive to the change in  $t_{s1}$  or  $t_{s2}$ . In the last sub-range,  $S_1$  or  $S_2$  decreases/increases slowly with increasing/decreasing  $t_{s1}$  or  $t_{s2}$ ; consequently, either  $S_1$  or  $S_2$  is not sensitive to the change in  $t_{s1}$  or  $t_{s2}$ . Based on the above results, the treatment should be run in the last sub-range for having a stable operation.

The upper limit of the first sub-range is called the minimum mean cell age  $t_s^m$ , below which biodegradation of wastewater does not occur (washout). The value of  $t_s^m$  is affected by the initial effluent  $S_o$  as well as by the kinetic parametric values. As seen in Figs. 7.6a to 7.6b, the values of these  $t_s^m$ 's for  $BOD_5$  for the anaerobic and aerobic stages are different. The value of  $t_s^m$  for the anaerobic and aerobic stages can be calculated using eqs. (2.22) and (2.28), respectively, by substituting  $S$  in the equations with  $S_o$ . For the CTMP effluent studied, the  $t_s^m$ 's for  $BOD_5$  ( $S_o = 3$  g/L) are equal to around 3.3 and 0.1 days, respectively, for the anaerobic and aerobic stages.

**Relationship involving  $X$ ,  $S_o$ ,  $S$ ,  $t$  and  $t_s$  :** The relationship involving  $X$ ,  $S_o$ ,  $S$ ,  $t$  and  $t_s$  for the anaerobic stage is given by equ. (2.23) and that for the aerobic stage by equ. (2.29). For a given substrate concentration in feed and a fixed  $X$ , the effluent  $BOD_5$  concentration  $S$  is dependant on the HRT  $t$ , as governed by equ. (2.16) or equ. (2.26). If  $t$  is also fixed, therefore, the mean cell age  $t_s$  can be determined with eqs. (2.23) and (2.29) for the first and second stages, respectively. For both stages, the relationships for some parametric values are illustrated in Fig. 7.7.

As shown in the figure, for a fixed  $X_1$  or  $X_2$ ,  $t_{s1}$  or  $t_{s2}$  increases rapidly with the increase of  $t_1$  or  $t_2$ . The rate of the increase of  $t_{s1}$  or  $t_{s2}$  is increased with the increase of  $X_1$  or  $X_2$  -- meaning that to obtain a higher microorganism concentration in either stage, the required mean cell age increases considerably. The design and operation

of an anaerobic-aerobic treatment system should be based on this relationship.

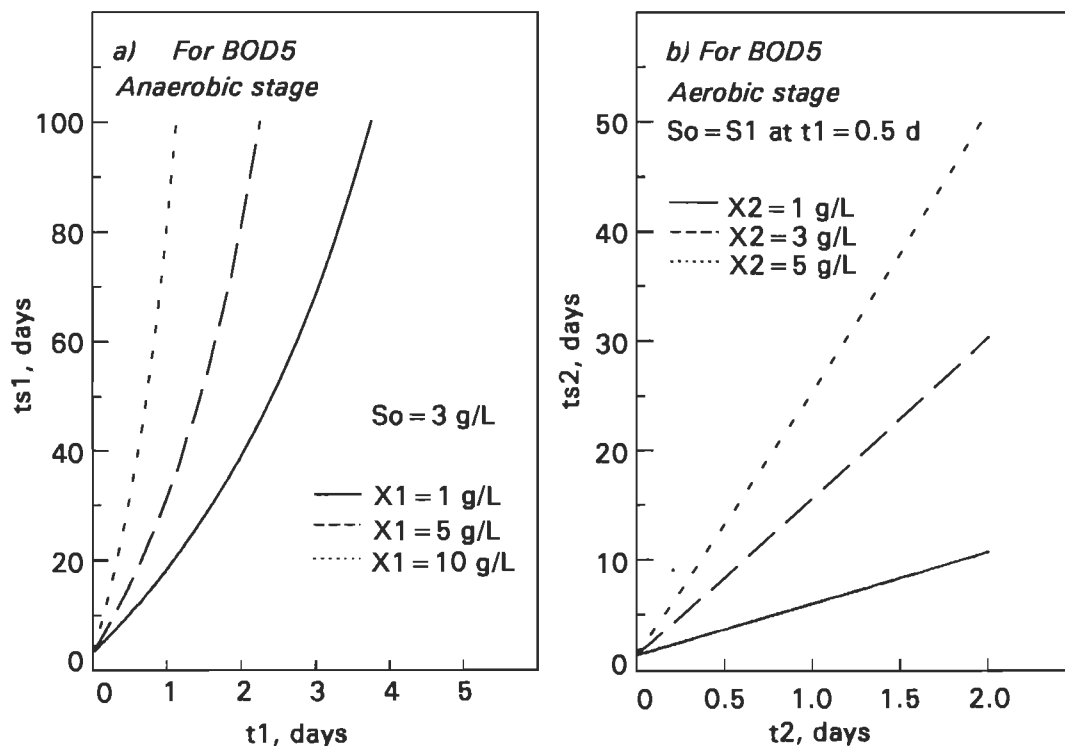


Fig. 7.7 Relationships of mean cell age  $t_s$ , HRT  $t$  and MLSS conc.  $X$

### 7.2.2 Analysis of sensitivity to variation in operating conditions

It has been reported that unstable operation problems are often encountered during the anaerobic treatments of pulp and paper mill effluents. The reasons for these are still not quite clear. It has been generally thought that they may be caused by the toxic materials (such as wood extractive, sulphur compounds, hydrogen peroxide, etc., as described in Chapter 2) in the effluents. However, the problems also might be due to an unreasonable design of the treatment system. For example, the



operating  $t_1$  has been selected to situate in the first sub-range or the mean cell age  $t_{s1}$  to locate in the second sub-range, as illustrated by the effects of  $t_1$  (Fig. 7.2) and  $t_{s1}$  (Fig. 7.6) on  $S_1$ . To examine if the variations in operating conditions are among the reasons to cause the unstable operation problems, a sensitivity analysis of the variations was thus undertaken. The sensitivity of a substrate concentration  $S_p$  in the effluent to a change in an operating condition  $P$  has been defined as [152] :

$$S_P = \frac{\Delta E_1 / E_{1o}}{\Delta P / P_o} \quad (7.6)$$

Where :

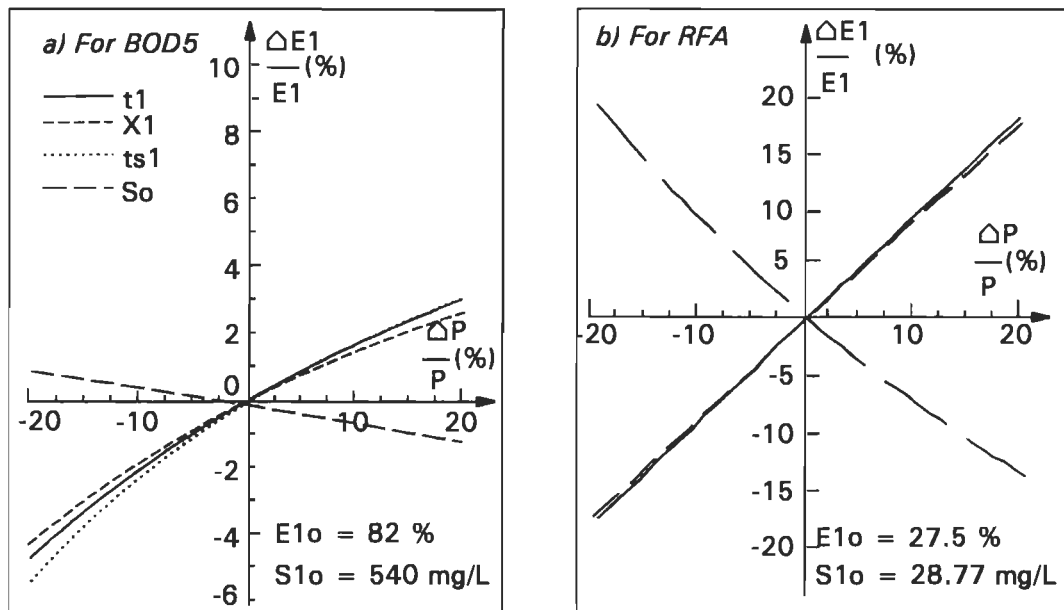
- $P$  =  $t_1$ ,  $t_{s1}$ ,  $X_1$  and  $S_o$
- $P_o$  = value of  $P$  at reference point
- $E_{1o}$  = treatment efficiency at  $P_o$ , %
- $\Delta E_{1o}$  = the change of  $E_1$ , %
- $\Delta P_o$  = the change from  $P_o$

To examine the sensitivity to variations in operating conditions in the sub-ranges, an analysis was made for both the first and second  $t_1$  sub-ranges with the corresponding  $t_{s1}$  in the second and third sub-ranges. Based on the curve presented for  $BOD_5$  in Fig. 7.4, the reference point chosen for the first  $t_1$  sub-range was :  $t_1 = 0.35$  days,  $t_{s1} = 23$  days,  $X_1 = 10$  g/L, at which the  $E_1$  equals 82% for  $BOD_5$  and 27.5% for RFA. The reference point for the second  $t_1$  sub-range was: 1 day, 78 days, 10g/L, the  $E_1$  at this point is 93% for  $BOD_5$  and 69% for RFA. The calculated results from equ. (7.6) together with equs. (2.16), (2.17) and (2.24) for  $BOD_5$  and equs. (2.32), (2.17) for RFA are presented in Fig.7.8.

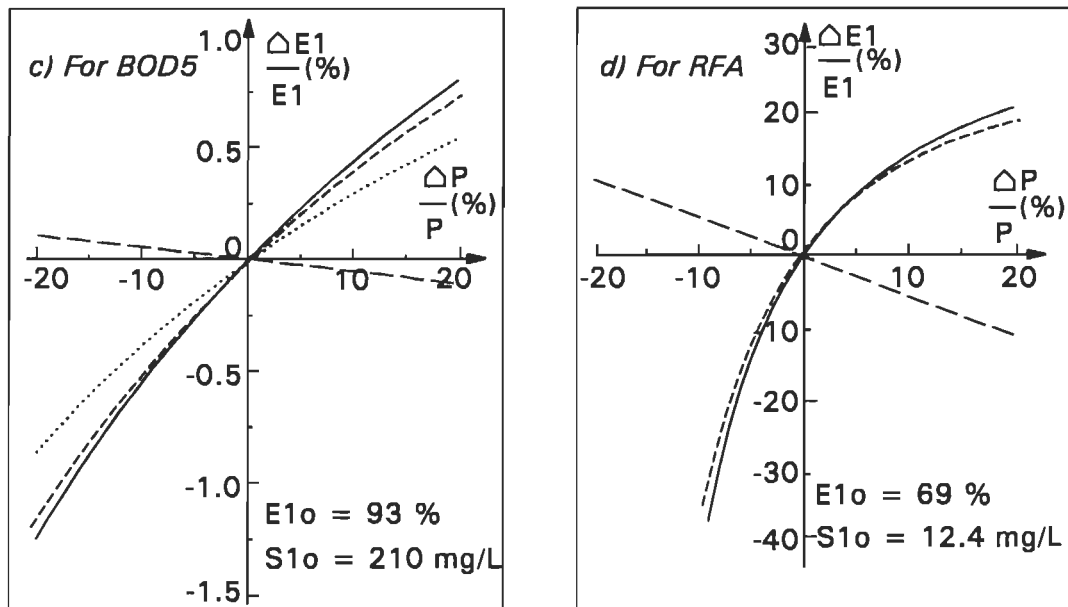
As seen, the sensitivities for  $BOD_5$  to the changes in operating conditions in the first  $t_1$  sub-range (Fig. 7.8a) are much higher than those in the second (Fig. 7.8c), implying that the treatment operation, in terms of  $BOD_5$  removal, in the first  $t_1$  sub-range is more sensitive to the changes in operating conditions than in the second sub-range. This result suggests that it is better not to conduct the treatment in the first

$t_1$  sub-range; otherwise, unstable operation problems could be encountered due to the variations in operating conditions which often happen in a mill effluent treatment. The HRT's used in the present high rate anaerobic treatment systems for pulp and paper mill effluents generally vary from 4 to 24 hours [15, 21]; most of which are in the range of 6 to 8 hours [15, 21]. Therefore, some of these high-rate anaerobic systems might be carried out with an HRT in the first  $t_1$  sub-range. This reason would become more obvious and more important when there exists inhibitory effects. Of course, if the control systems in an effluent treatment plant are highly reliable, from the economic point of view, it is to recommend to run the treatment with a  $t_1$  in a region marked between the two dotted lines as shown in Fig. 7.4a for  $BOD_5$ . The sensitivities for RFA in both the first and second  $t_1$  sub-ranges are equally very high (Figs. 7.8b and 7.8d), meaning that the RFA removal in the anaerobic stage in both the sub-ranges is very sensitive to the variations in all the operating conditions studied.

Fig. 7.8 also provides the information on which is the most important operating condition to control for a stable operation of the anaerobic treatment. As shown, if the treatment is conducted in the first  $t_1$  sub-range,  $t_1$ ,  $t_{s1}$  and  $X_1$  are all the important conditions to control for  $BOD_5$  since their sensitivities are almost the same (Fig. 7.8a). If the treatment is performed in the second  $t_1$  sub-range, the sensitivities for  $BOD_5$  to the changes in the operating conditions are very low, even if with a change of 20% in the conditions (Fig. 7.8c). In both the two  $t_1$  sub-ranges, the sensitivity for  $BOD_5$  to the variation in  $S_0$  is seen to be low (Figs. 7.8a and 7.8c). While for RFA, in both the sub-ranges all the conditions studied are important and must be well controlled for a stable operation since the sensitivities to the changes in these conditions are very high (Figs. 7.8b and 7.8d).



a and b) : Sensitivity to the changes of operating conditions in the first  $t1$  sub-range at the point :  $(t1, ts1, X1, So) = (.35 \text{ d}, 21 \text{ d}, 10 \text{ g/L}, 3 \text{ g/L})$



c and d) : Sensitivity to the changes of operating conditions in the second  $t1$  sub-range at the point :  $(t1, ts1, X1, So) = (1 \text{ d}, 78 \text{ d}, 10 \text{ g/L}, 3 \text{ g/L})$

Fig. 7.8 Sensitivity to variations in operating conditions in the first and second  $t1$  sub-ranges

### 7.3 Optimization of the two-stage anaerobic-aerobic system for the CTMP effluent studied

Optimization of the two-stage anaerobic-aerobic system for the CTMP effluent treatment was made using the method established on the basis of the first order reaction kinetics and presented in Chapter 2. Before to optimize the two-stage system, equs. (2.42) and (2.52) were, respectively, plotted first in Fig. 7.9a for  $BOD_5$  and in Fig. 7.9b for RFA to show the variation of  $t_o$  with  $E_1$  for  $E = 95\%$  for both  $BOD_5$  and RFA, at different values of  $S_o$  with  $X_1 = 10$  g/L and  $X_2 = 1$  g/L. The selection of 95% for  $E$  is based on the usual requirement in actual treatment that to arrive at an acceptable final effluent concentration of  $BOD_5$  or RFA, the required overall removal efficiency is normally at least equal to 95%. For the variation of time  $t_o$  versus %  $BOD_5$  removal  $E_1$  using  $S_o$  as parameter, only one curve has been generated, as shown in Fig. 7.9a, instead of a family of curves as in Fig. 7.9b. It should be the case, since  $t_o$  is not a function of  $S_o$ , when  $S_o = BOD_5$ , due to the use of first order reaction kinetics. Fig. 7.9a shows that there is a minimum point on the curve of  $t_o$  versus  $E_1$ , implying that  $t_o$  can be minimized with respect to the  $E_1$  of or the  $t_1$  in the anaerobic stage. The value of  $E_1$  corresponding to the minimum point is situated in the region around 75%. There are no minimum points on the family of curves plotted in Fig. 7.9b for RFA, indicating that  $t_o$  can not be minimized with respect to % RFA removal  $E_1$ . The reason why there are no minimum points on the curves in Fig. 7.9b can be explained by using equs. (2.47) and (2.51) -- the necessary condition for  $E_{1opt}$  to have a real value for  $BOD_5$  and RFA, respectively.

For the curves presented in Fig. 7.9, we have assumed  $E = 95\%$  for both  $BOD_5$  and RFA, using  $S_o = 1000 - 4000$  and  $40 - 100$  mg/L for  $BOD_5$  and RFA, respectively. The calculated value of the term on the right side of equ. (2.47) is  $0.42 - 0.71$  for  $BOD_5$ , while that on the right side of equ. (2.51) is  $28.8 - 67.5$  for RFA. The ratio of  $X_1/X_2$  used to plot the curves was equal to 10 which is much larger than  $0.42 - 0.71$  but much less than  $28.8 - 67.6$ . This is why there are no minimal points occurring on

the curves in Fig. 7.9b for an overall RFA removal of 95%. In fact, due to the big difference between  $K_2$  and  $K_1$  in the case of RFA, the inequality expressed by equ. (2.51) is very difficult to meet or even can not be met with any fixed  $E$ . Therefore, the required  $t_0$  can be minimized only on the basis of the overall  $BOD_5$  removal  $E$  for the two-stage anaerobic-aerobic treatment of the CTMP effluent. *Thus, the following discussions will be based on  $BOD_5$  removal.*

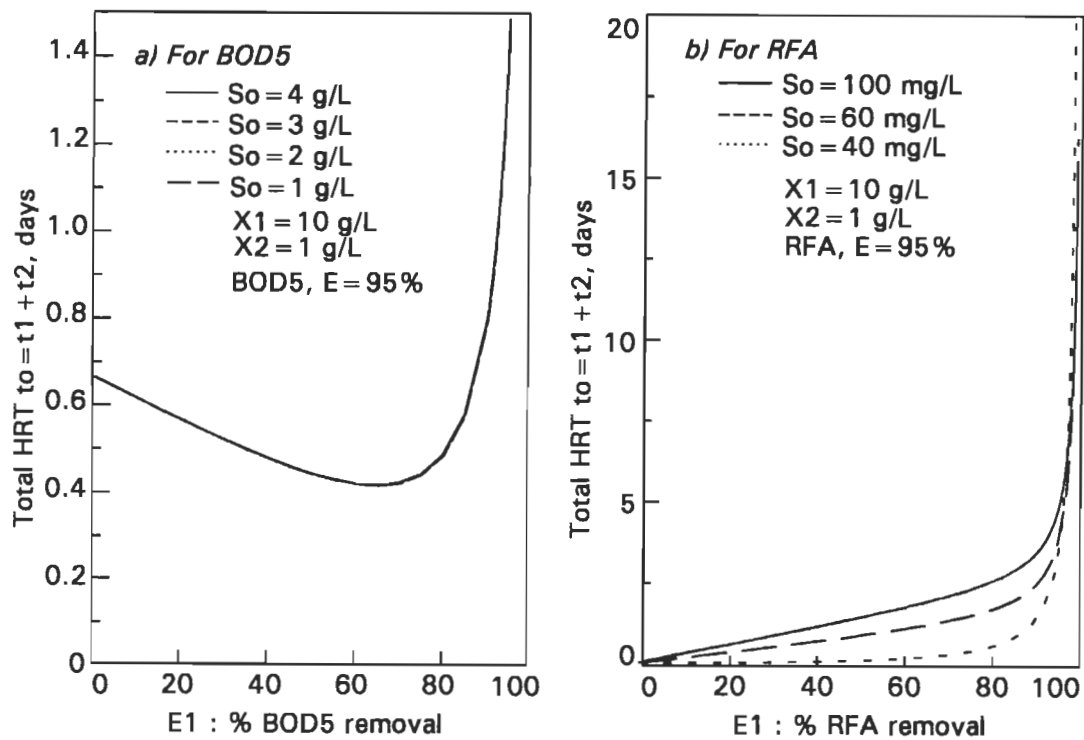


Fig. 7.9 Variation of the total HRT  $t_0$  versus the removal  $E_1$  for a fixed overall removal  $E$

### 7.3.1 Minimization of total HRT $t_0$ for a fixed overall $BOD_5$ removal $E$

Presented in Fig. 7.10a are the plots of the optimal  $E_{1opt}$ , expressed by equ. (2.45), and the corresponding  $t_1$  and  $t_2$  versus the  $E$  for  $BOD_5$ , with  $S_o = 3$  g/L and the same values of  $X_1$  and  $X_2$  used in Fig. 7.9. As illustrated,  $E_{1opt}$ ,  $t_1$ , and the required

minimum total HRT,  $t_m = (t_1 + t_2)$ , all increase with the increase of  $E$ . The corresponding  $E_1$  and  $E$  for RFA were calculated with the  $t_1$  and  $t_2$  determined on the basis of the fixed  $E$  for  $BOD_5$ , using equs. (2.16), (2.17), (2.26) and (2.27). The  $E_1$  and  $E$  for RFA thus calculated were then plotted versus the corresponding  $E$  for  $BOD_5$  in Fig. 7.10b. By this way, one can determine easily the corresponding RFA removal  $E$  from a fixed  $BOD_5$  removal  $E$ . For example, if one would expect to achieve an overall  $BOD_5$  removal of 98% under the conditions listed, the  $E_{1opt}$  for the anaerobic stage was found to be 81.4% from Fig 7.10a, the corresponding  $t_1$  and  $t_2$  were 0.67 day and 0.74 day, respectively. With these  $t_1$  and  $t_2$ , the  $E_1$  and the  $E$  for RFA were found, respectively, to be 28% and 98% from Fig. 7.10b.

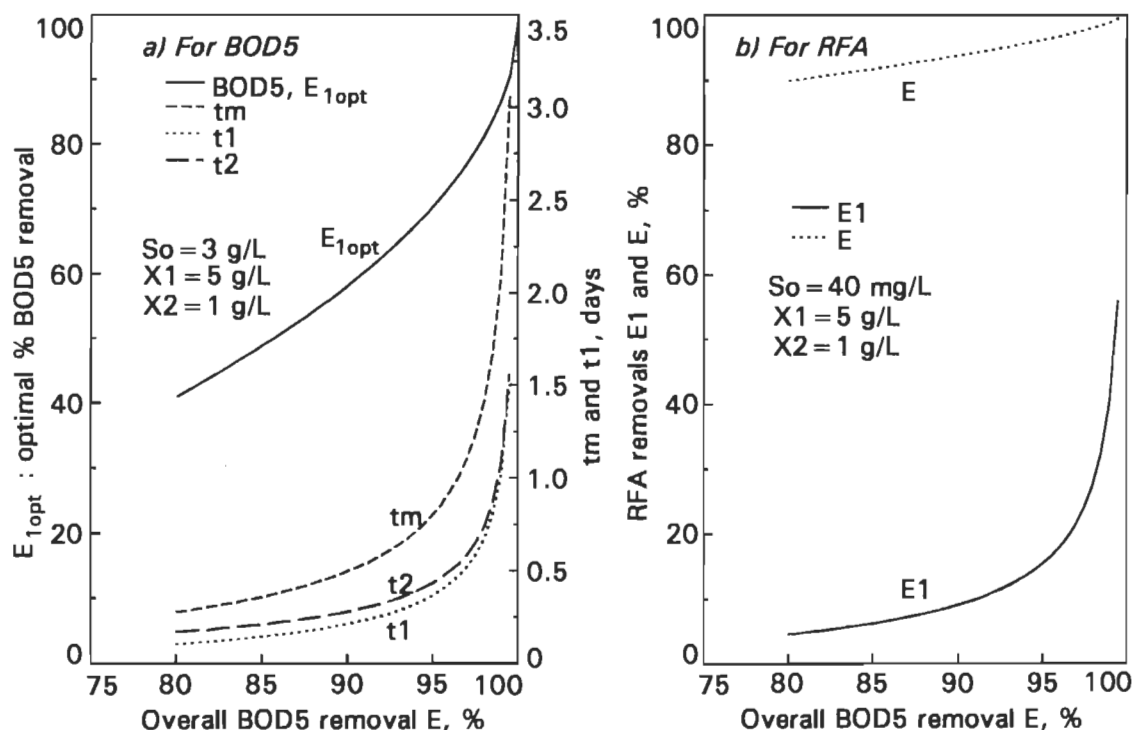


Fig. 7.10 Variations of removals and HRTs versus the overall  $BOD_5$  removal  $E$

As seen in Fig. 7.10b, the overall RFA removal  $E$  is very near to or higher than that of  $BOD_5$ . However, even if with the same overall removal as that of  $BOD_5$ , the

overall RFA removal may not be sufficient to result in a non-toxic effluent. Therefore, an acceptable removal  $E$  of RFA may not be achieved with the minimized total time  $t_m$ , determined on the basis of the  $BOD_5$  removal  $E$ . If the RFA removal  $E$  determined is not acceptable, the total treatment time  $t_o$  should be adjusted to be longer than  $t_m$  and be long enough to achieve an acceptable  $E$  for RFA. Normally, the  $E$  for  $BOD_5$  is set to be greater than 95% at which the  $E$  for RFA is very close to that of  $BOD_5$ , as shown in Fig. 7.10b. A little increase in  $t_o$  may be sufficient to achieve the acceptable overall RFA removal. Adjustment of  $t_o$  can be made by increasing either  $t_1$  or  $t_2$ . It is preferable to increase  $t_2$  since aerobic treatment is much more effective than anaerobic treatment for the removal of RFA. However, as demonstrated previously, if  $t_1$  is too short (in the first sub-range), unstable operation of the anaerobic stage could be encountered due to the variation in operating conditions. Therefore, if  $t_1$  is in the first sub-range and far from the boundary, adjustment of  $t_o$  is better made by increasing  $t_1$  for stable operation of the anaerobic stage.

In summary, to optimize the performance for anaerobic-aerobic treatment, the steps to follow are listed below :

- 1) Determine the optimal  $E_{1opt}$  by equ. (2.45) for a fixed overall  $BOD_5$  removal  $E$  (normally,  $E > 95\%$ );
- 2) Calculate the  $t_1$  and  $t_2$  ( $t_m = t_1 + t_2$ ) corresponding to the  $E_{1opt}$  determined, using equs. (2.17) and (2.15) as well as equs. (2.27) and (2.25);
- 3) Calculate the corresponding overall RFA removal  $E$  with the  $t_1$  and  $t_2$  obtained, using equs. (2.32), (2.26) and (2.27);
- 4) Verify the overall RFA removal  $E$  to see if it is acceptable;
- 5) If the calculated RFA removal  $E$  is not acceptable, prolonging  $t_o$  to be long enough to achieve an acceptable  $E$  for RFA, by increasing either  $t_1$  or  $t_2$ .

### 7.3.2 Effects of operating conditions on $E_{1opt}$ as well as on $t_m$ and $t_1$ required for a fixed overall BOD<sub>5</sub> removal $E$

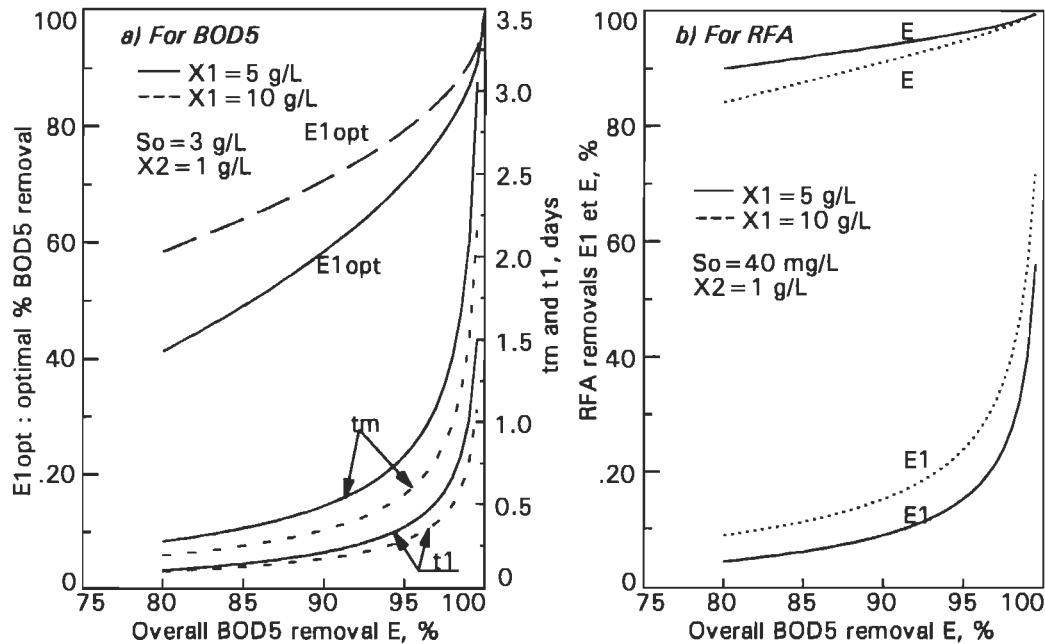


Fig. 7.11 Simulated effects of  $X_1$  on  $E_{1opt}$  as well as on the  $t_m$  and  $t_1$  required for a fixed overall BOD<sub>5</sub> removal  $E$

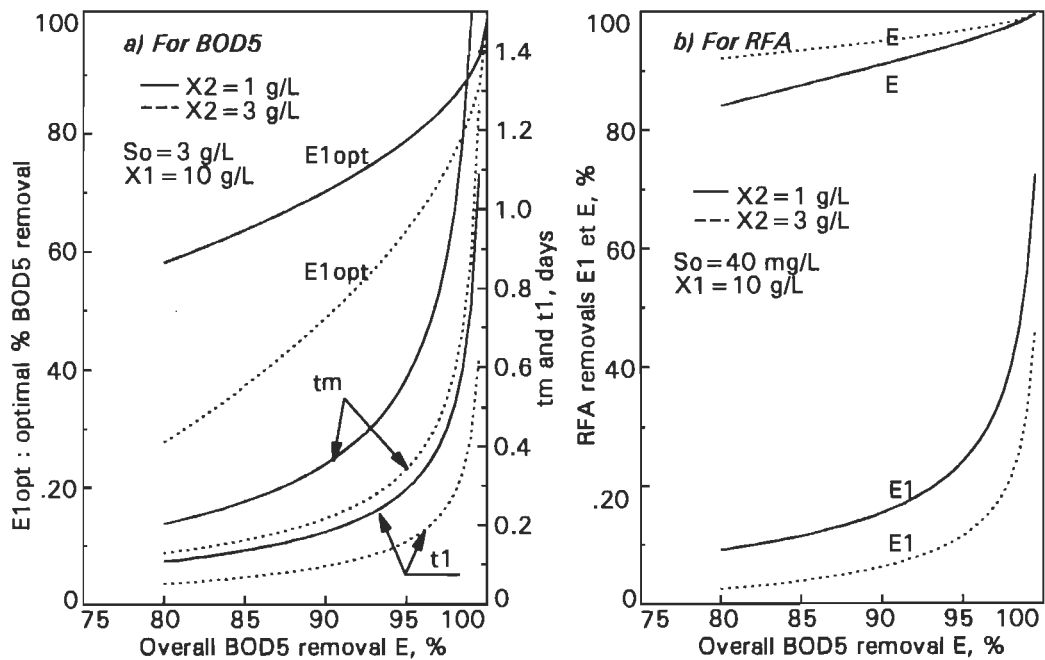


Fig. 7.12 Simulated effects of  $X_2$  on  $E_{1opt}$  as well as on the  $t_m$  and  $t_1$  required for a fixed overall BOD<sub>5</sub> removal  $E$



**Effects of  $X_1$  and  $X_2$  on  $E_{1opt}$ ,  $t_1$  and  $t_m$  :** As shown by equ. (2.45), the value of  $E_{1opt}$  is affected by  $X_1$  and  $X_2$ . Fig. 7.11 presents the effect of  $X_1$  on the  $E_{1opt}$  for  $BOD_5$ . As illustrated in Fig. 7.11a, for a fixed  $BOD_5$  removal  $E$ , the higher the  $X_1$  is the higher the  $E_{1opt}$  will be, consequently, the shorter the required  $t_m$  and  $t_1$ . On the contrary, the higher the  $X_1$  is the lower the RFA removal  $E$  will be obtained, as shown in Fig. 7.11b.

Fig. 7.12a shows, for a fixed  $BOD_5$  removal  $E$ , the influence of  $X_2$  in the aerobic stage on the optimal  $BOD_5$  removal  $E_{1opt}$ . In contrast with the effect of  $X_1$ , the higher the  $X_2$  is the lower the  $E_{1opt}$  will be, consequently, the shorter the required  $t_m$  and  $t_1$ . Conversely, the higher  $X_2$  is the higher the RFA removal  $E$  will be, as displayed in Fig. 7.12b.

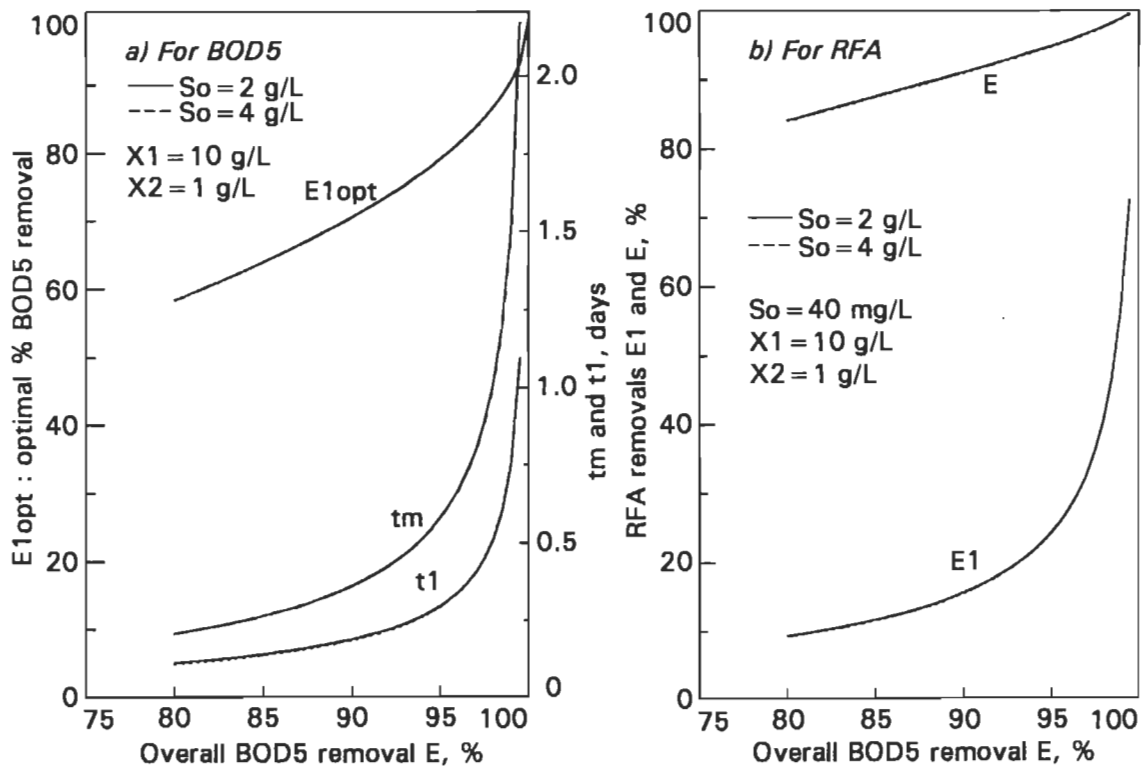


Fig. 7.13 Simulated effects of  $So$  on  $E_{1opt}$  as well as on the  $t_m$  and  $t_1$  required for a fixed overall  $BOD_5$  removal  $E$

**Effect of  $S_o$  on  $E_{1opt}$ ,  $t_1$  and  $t_m$  :** As shown in Fig. 7.13a, the initial effluent concentration  $S_o$  has no effect on  $E_{1opt}$ ,  $t_1$  and  $t_m$  for a fixed overall BOD<sub>5</sub> removal, due to that the removal rates of BOD<sub>5</sub> in both stages follow a first order reaction kinetics. This result (no effect) is very useful for the application of the optimization method to the design of full scale two-stage system. Since  $S_o$  does not affect the  $E_{1opt}$  and  $t_m$ , therefore, it also produce no influence on the removals  $E$  and  $E_1$  of RFA, as shown in Fig. 7.13b.

### 7.3.3 Optimal reactor volume ratio for a fixed overall BOD<sub>5</sub> removal $E$

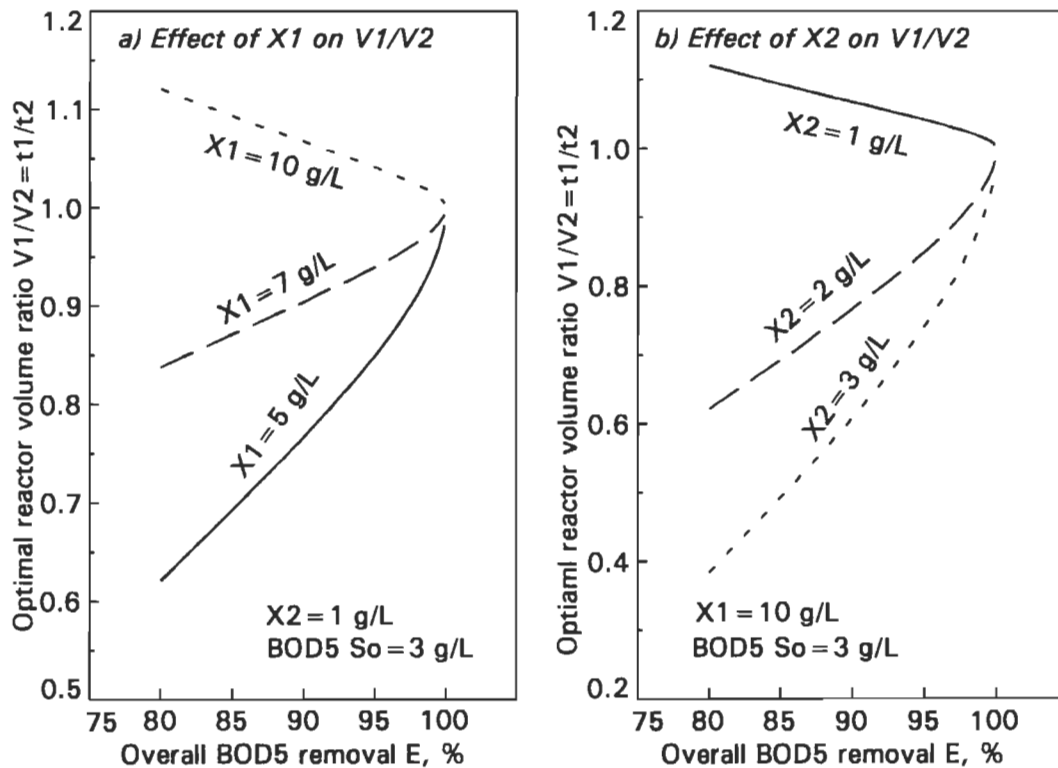


Fig. 7.14 Simulated effects of  $X1$  and  $X2$  on optimal reactor volume ratio  $V1/V2$

As mentioned previously, the reactor volumes used in both stages in existing full scale two-stage treatment systems for CTMP effluents might be over-sized since the designs of the systems have not been optimized. Using equs (2.15), (2.25) and (2.49) established in Chapter 2, the optimal reactor volume ratio can be determined

versus overall BOD<sub>5</sub> removal. Figs. 7.14 and 7.15 show the variation of this ratio overall BOD<sub>5</sub> removal  $E$  and the effects of some operating conditions on this ratio for a given  $E$ .

Fig. 7.14 shows the effects of  $X_1$  and  $X_2$  on this ratio for a given BOD<sub>5</sub> removal  $E$ . As shown, the concentrations of the microorganisms in both stages have significant effects on this ratio. At a fixed  $X_2$ , this ratio increases very rapidly with the increase in  $X_1$  when BOD<sub>5</sub> removal  $E$  is less than 95%, as illustrated in Fig. 7.14a. In contrast with the effect of  $X_1$ , this ratio is reduced considerably as  $X_2$  is increased at a fixed  $X_1$ , also when the BOD<sub>5</sub> removal  $E$  is less than about 95%, as displayed in Fig. 7.14b. The effects of  $X_1$  and  $X_2$  on this ratio diminish very significantly when the BOD<sub>5</sub> removal  $E$  is higher than 95%, as shown in Fig. 7.14, and the volume ratio trends towards 1.

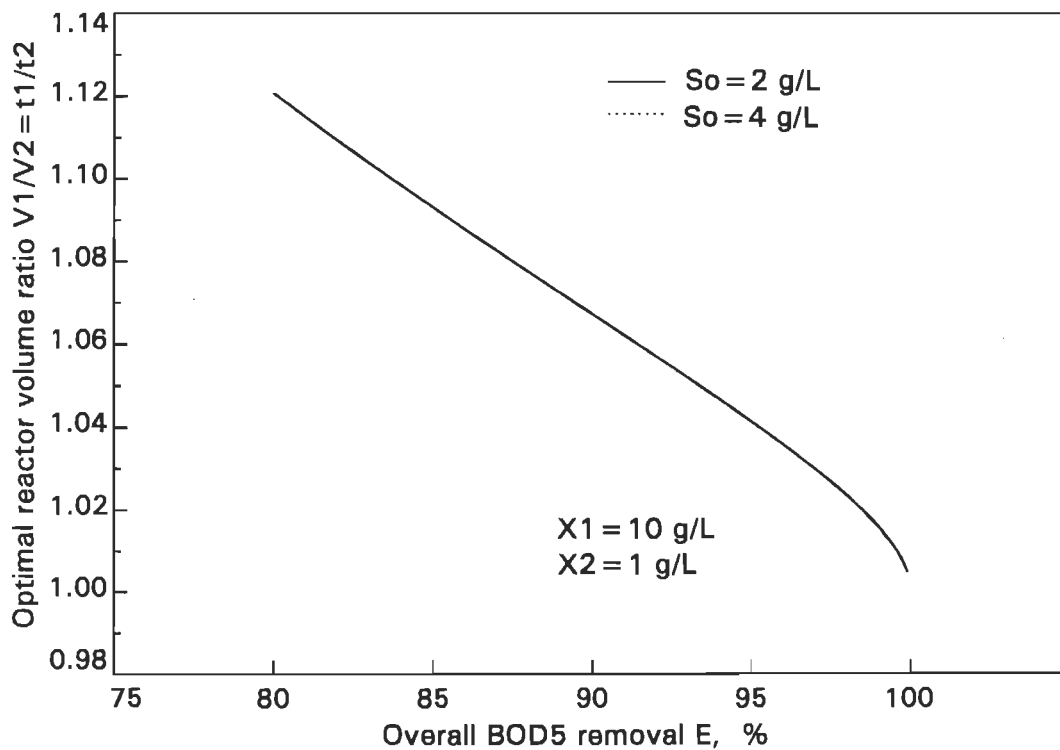


Fig. 7.15 Simulated effect of  $S_o$  on optimal reactor volume ratio  $V1/V2$

The effect of  $S_o$  on this ratio for constant  $X_1$  and  $X_2$  is shown in Fig. 7.15. As seen, at a given overall  $BOD_5$  removal  $E$ ,  $S_o$  has no effect on the ratio because it has no influence on  $E_{1opt}$ ,  $t_m$ , and  $t_1$ , as described for the effect presented in fig.7.13a. The zero influence of  $S_o$  on both  $E_{1opt}$  and the volume ratio  $V_1/V_2$  makes the method of optimization simpler for the design of full scale two-stage treatment systems for CTMP effluents. In addition, the ratio decreases almost linearly with increasing  $E$ , as shown in Fig. 15.

## 7.4 Conclusions

The work presented in this chapter demonstrates how to study the behaviour of a two-stage anaerobic-aerobic treatment system, through the coupling of the kinetic models for both stages; and, in particular, how to optimize the design of such two-stage system, using the method developed on the basis of the kinetic models for both stages.

The specific conclusions are :

- 1) From the effects of operating conditions on the behaviour of the treatment system, it would not be expected to obtain a high RFA removal from the CTMP effluent with a normal HRT of one or two days in the anaerobic stage.
- 2) In general, unstable operation of an anaerobic process could be due to the treatment carried out in an HRT range in which the operation is very sensitive to the variation in HRT caused by the change in feed flowrate.
- 3) The total HRT required for the CTMP effluent treatment can be minimized only on the basis of a fixed overall  $BOD_5$  removal  $E$ . The  $BOD_5$  removal  $E_1$  of the anaerobic stage is the only key parameter involved in the minimization of the total HRT when other operating conditions are fixed.

- 4) Although the methods presented for both simulation of system behaviour and optimization of system design and operation were established for the two-stage treatment system studied, they should be also applicable to other types of two-stage anaerobic-aerobic treatment systems, provided that substrate removal rate in each stage follows either the kinetics of first order reaction or the Monod model.
- 5) If the above kinetic models are applicable, the simulation and optimization methods developed in this study can also be applied to the two-stage treatment of other types of pulp and paper mill effluents as well. In general sense, the CTMP wastewater used in the study was only as an example of a pulp and paper effluent. So was the two-stage process.

Presented in the following Chapter 8 will be the experimental verifications of 1) the effects of some operating parameters on the system behaviour, and 2) the validity of the optimization method developed for the two-stage system.

## CHAPTER 8

### VALIDITY VERIFICATIONS OF THE BEHAVIOUR AND OPTIMIZATION OF THE TWO-STAGE ANAEROBIC-AEROBIC SYSTEM FOR CTMP EFFLUENT TREATMENT

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#### 8.1 Introduction

In Chapter 7, both the effects of operating conditions on the behaviour and the optimization of the two-stage system for the treatment of a CTMP effluent were studied theoretically, using the methods established in Chapter 2 in conjunction with the kinetic parameters reported in Chapter 6. This chapter reports the comparisons of experimental and theoretical profiles, for the purpose of verifying the validity of the methods developed for behaviour simulation and system optimization.

#### 8.2 Experimental

##### 8.2.1 Effluent to be studied

As mentioned in Section 3.1, since the  $BOD_5$  concentration in the first CTMP effluent after pulping operation modification (**Table 3.1**) was too low for anaerobic treatment, a new concentrated CTMP effluent was collected and used in the two-stage treatment. **Table 3.1** presents the average characteristics of this new effluent. As observed from **Table 3.1**, the ratio of  $BOD_5$  and COD in the new effluent is about 0.4 and lower than that (0.5) in the first CTMP effluent, implying that the new effluent would be relatively more difficult to treat biologically than the first effluent. RFA concentration in the new effluent was also higher than that in the first CTMP

effluent. The change of effluent to be studied, however, should not affect the outcomes of the study, since the objective of the work is just to verify experimentally the validity of what have been established theoretically in Chapter 2 for the two-stage system.

### 8.2.2 Treatment system and experimental conditions

The two-stage system described in Section 3.3.3 was used to carry out the experiments. Conditions for each experiment, together with the corresponding experimental results, are presented in the section "Results and discussion" for each experiment.

## 8.3 Results and discussion

### 8.3.1 Kinetics of substrate removal rates

Since the characteristics of the new CTMP effluent were different from those of the first effluent studied, the substrate removal rate kinetics and the kinetic parameters for the treatments of both effluents might be different. The substrate removal rate kinetics for the new effluent in both anaerobic and aerobic stage treatments, therefore, must be evaluated prior to the verification work. The feed for the anaerobic stage was the raw new CTMP effluent; the  $BOD_5/COD$  ratio was about 0.4. The feed for the aerobic stage was the treated effluent from the anaerobic stage, with HRT's in the range of 0.5 to 2 days which have been usually used in full-scale anaerobic treatment of pulp and paper mill effluents; the  $BOD_5/COD$  was about 0.25 and RFA concentration (about 50 mg/L) was still very high. The experimental data for the kinetics study are presented in **Table 8.1**. The first order reaction kinetics, equ. (2.8), and the Monod model, equ. (2.9), were also used to study the kinetics for both  $BOD_5$  and RFA removals, using the data presented in **Table 8.1**. The kinetic results obtained are presented in **Table 8.2**.

**Kinetics for anaerobic treatment :** As seen in **Table 8.2** (row 1), the removal rate of the  $BOD_5$  in the new effluent can be expressed by both a first order reaction kinetics and the Monod model, as indicated by the  $r$ 's of 0.96 to 0.94, respectively. The rate expressed by the first order reaction kinetics, however, appears to be better than by the Monod model. The value of the rate constant  $k$  and that of the maximum specific removal rate  $K$  found for the new effluent were  $0.00062 \text{ (mg MLSS/L)}^{-1} \text{ day}^{-1}$  and  $1.37 \text{ day}^{-1}$ , respectively, which are much smaller than the corresponding values (0.0013 and 2.6) found for the first CTMP effluent studied, indicating that, as predicted from the effluent characteristics, the new effluent is more difficult to treat anaerobically than the first effluent.

The removal rate of the RFA in the new effluent followed approximately the Monod model, with a  $r$  of 0.82, while a first order reaction kinetics was unable to represent the rate (**Table 8.2** row 2). This result is consistent with that obtained for the first effluent studied. The value of the maximum specific removal rate  $K$  found for RFA was  $0.003 \text{ day}^{-1}$  which is quite close to that (0.0038) found for the first effluent.

**Kinetics for aerobic treatment :** Regression results presented in **Table 8.2** (rows 3 and 4) indicate that the removal rates of both  $BOD_5$  and RFA in the effluent for the second stage aerobic treatment follow well the kinetics of a first order reaction, as indicated by the  $r$ 's of 0.97 to 0.98, respectively. This result agrees well with that obtained for the aerobic treatment of the first effluent studied. The values of the rate constant  $k$  found for both  $BOD_5$  and RFA in the new CTMP effluent for the aerobic stage were 0.004 and  $0.022 \text{ (mg MLSS/L)}^{-1} \text{ day}^{-1}$ , respectively. These values found for the new effluent are much smaller than those (0.0113 for  $BOD_5$  and 0.049 for RFA) for the first effluent studied, also indicating that the new effluent is relatively more difficult to treat biologically than the first effluent.

The removal rate of the  $BOD_5$  in the new CTMP effluent for the second stage



aerobic treatment may be also represented by the Monod model (row 3 in **Table 8.2**). However, this is not the case for the RFA removal rate (row 4). Correspondingly, the value ( $4.1 \text{ day}^{-1}$ ) of the maximum specific  $\text{BOD}_5$  removal rate  $K$  found for the new CTMP effluent for the second stage aerobic treatment is much smaller than that (8.6) found for the first CTMP effluent for aerobic treatment.

In summary, the  $\text{BOD}_5$  removal rates in both the anaerobic and aerobic stages can be represented by the kinetics of a first order reaction for the treatment of the new effluent. The RFA removal rate in the anaerobic stage follows better the Monod model and that in the aerobic stage can be better described by the kinetics of a first order reaction. Therefore, in the validity verification work, first order reaction kinetics will be used to represent the  $\text{BOD}_5$  removal rates in both the anaerobic and aerobic stages as well as the RFA removal rate in the aerobic stage. Monod model will be used to predict the RFA removal in the anaerobic stage. **Table 8.3** summaries the kinetic models and the corresponding kinetic parametric values used in the work of verifications. The initial concentrations of  $\text{BOD}_5$  and RFA in the new effluent were about 2850 and 65 mg/L, respectively.

**Table 8.1.** Experimental conditions and results for evaluating the kinetics for anaerobic and aerobic treatments of the new CTMP effluent.

Treatments	HRT	MLSS	BOD <sub>in</sub>	BOD <sub>eff</sub>	RFA <sub>in</sub>	RFA <sub>eff</sub>
	days	mg/L	mg/L	mg/L	mg/L	mg/L
Anaerobic treatment <sup>(1)</sup>	6	5490	2890	145	65.4	11.54
	5.18	5200	2820	252	64.3	15.23
	3.95	4950	2830	292	67.7	22.31
	2.98	5100	2920	345	68.2	35.15
	2.05	4810	2790	450	65.3	45.32
	1.25	5300	2910	760	67.2	51.06
	0.51	5590	2860	1010	68.9	59.3
Aerobic stage <sup>(2)</sup>	3	3020	530	14	49.23	0.45
	2	2810	543	29	50.14	0.59
	1.12	3010	508	39	47.56	0.65
	0.76	2950	522	41	46.98	1.11
	0.53	3310	568	85	48.89	1.23
	0.31	2910	550	105	47.3	2.12
	0.25	2860	534	145	46.92	3.13

(1) -- pH : 7-7.5 and temperature : 35 °C.

(2) -- pH : 7; DO : 3-5 mg/L and temperature : room temperature;

**Table 8.2.** Kinetic results for the treatment of the new CTMP effluent

Treatments	First order reaction model					Monod model				Row
	Substrate	$k$ (mg MLSS/L) <sup>-1</sup> d <sup>-1</sup>	$S_n$ mg/L	$r$	Significance	$K$ d <sup>-1</sup>	$K_s$ mg/L	$r$	Significance	
Anaerobic treatment	BOD <sub>5</sub>	$62 \times 10^{-5}$	0	0.96	yes	1.37	2510	0.94	yes	1
	RFA	$2.4 \times 10^{-5}$	-59.3	0.79	no	0.003	9.4	0.82	approx.	2
Aerobic stage	BOD <sub>5</sub>	$3.9 \times 10^{-3}$	0	0.97	yes	4.1	1016	0.98	yes	3
	RFA	$21.6 \times 10^{-3}$	0.1	0.98	yes	0.037	-3.4	0.88	no	4

### 8.3.2 Comparisons of experimental and theoretical profiles for the effects of operating conditions on the behaviour of the two-stage system for the treatment of the new CTMP effluent

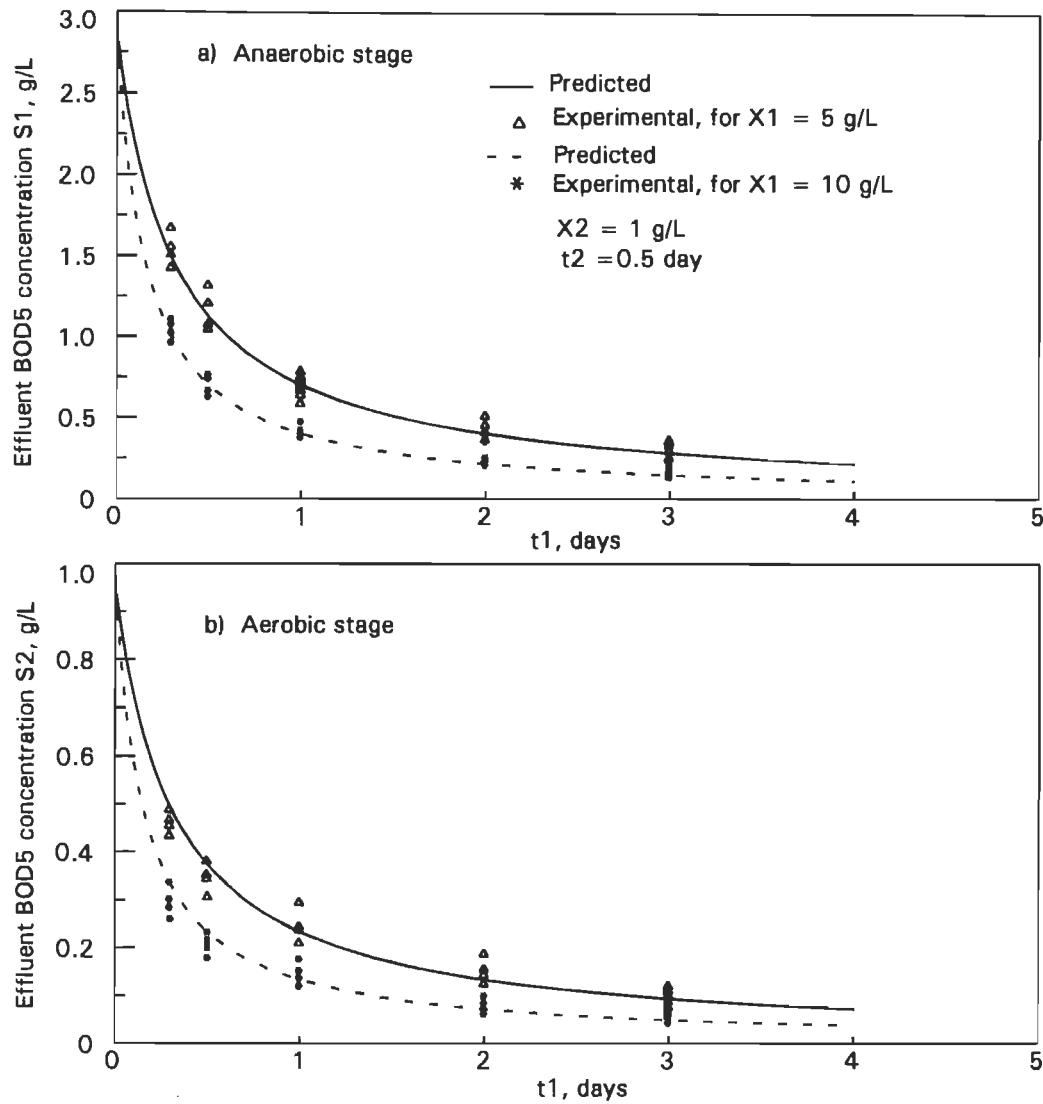
The effects of HRT  $t_1$  and MLSS concentrations  $X_1$  in anaerobic stage as well as  $t_2$  and  $X_2$  in aerobic stage on treatment behaviour were investigated. Based on the simulation results (not reported in the thesis), the levels of  $t_1$ ,  $t_2$ ,  $X_1$  and  $X_2$  presented in **Table 8.4** were chosen to be used in the two-stage treatment of the new effluent. The feed for anaerobic stage was the new CTMP effluent and that for aerobic stage was the treated effluent from the anaerobic stage.

**Table 8.3.** Kinetic models and the parametric values used in the verification work

Stages	Anaerobic stage		Aerobic stage	
Substrate	BOD <sub>5</sub>	RFA	BOD <sub>5</sub>	RFA
Kinetic model	First order	Monod	First order	First order
$k$	0.00062	-	0.004	0.022
$K$	-	0.003	-	-
$K_s$	-	9.4	-	-

**Table 8.4.** Conditions used to generate profiles for the effects of operating conditions

Effect of	Conditions			
	$t_1$ , day	$X_1$ , g/L	$t_2$ , day	$X_2$ , g/L
$t_1$ and $X_1$	0.3 - 3	5 and 10	0.5	1
$t_2$ and $X_2$	1	5	0.3 - 2	1 and 3



**Fig. 8.1 Effects of  $t_1$  and  $X_1$  on effluent BOD5 concentrations  $S_1$  and  $S_2$**   
 - Comparison between experimental results and predicted values

**Effects of  $t_1$  and  $X_1$  :** Fig. 8.1 presents the effects of  $t_1$  and  $X_1$  on the effluent BOD<sub>5</sub> concentrations  $S_1$  and  $S_2$ . The symbols and the curves in Figs. 8.1a and 8.1b represent, respectively, the experimental results and the theoretical profiles generated with equ. (2.16) for the anaerobic stage and equ. (2.24) for the aerobic stage. As shown in Fig. 8.1a, at both levels of  $X_1$ , effluent BOD<sub>5</sub> concentration  $S_1$  from the anaerobic stage can be predicted very well with equ (2.16) for the operating

conditions investigated. As shown in Fig. 8.1b, the effluent  $BOD_5$  concentration  $S_2$  from aerobic stage can be predicted also very well with equ. (2.24) for the operating conditions investigated, except when  $t_1$  was shorter than 0.5 day. When  $t_1$  was shorter than 0.5 day, the experimental results obtained for  $S_2$  at both levels of  $X_1$  were lower than the predicted values. This could be due to the combined effects of high  $BOD_5$  concentration  $S_1$  in the treated effluent from the anaerobic stage (the feed for the aerobic stage) with  $t_1$  shorter than 0.5 and the use of kinetic parametric value obtained from the aerobic stage.

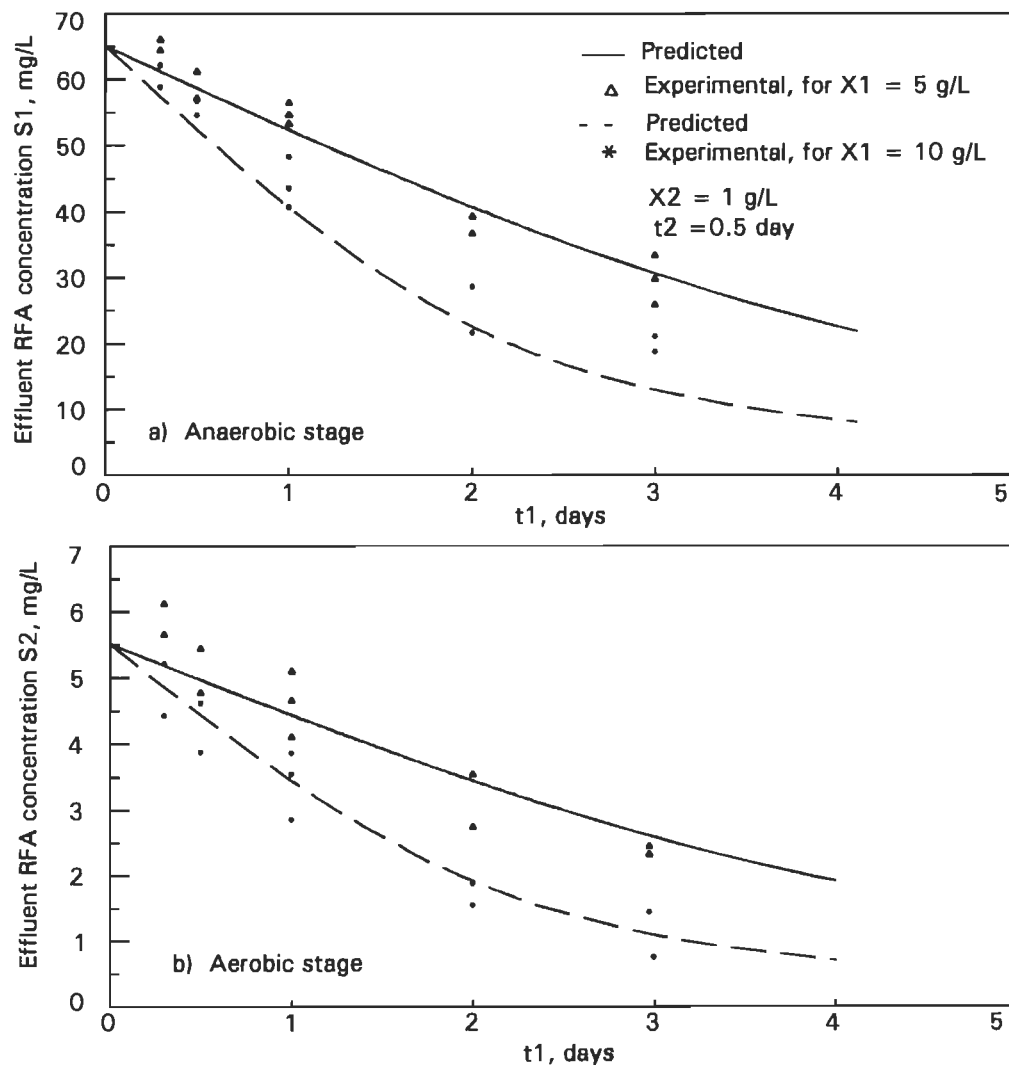


Fig. 8.2 Effects of  $t_1$  and  $X_1$  on effluent RFA concentrations  $S_1$  and  $S_2$   
 - Comparison between experimental results and predicted values

Fig. 8.2 shows the effects of  $t_1$  and  $X_1$  on the effluent RFA concentrations  $S_1$  and  $S_2$ . The theoretical profiles of  $S_1$  in Fig. 8.2a and of  $S_2$  in Fig. 8.2b were generated, respectively, with equs. (2.32) and (2.26). As shown in Fig. 8.2a, for the corresponding values of  $t_1$ , the experimental results of  $S_1$  (symbols) agree not very well with the values read from the theoretical profiles plotted for both levels of  $X_1$ . The deviation between the theoretical and experimental results of  $S_1$  may be due to the use of Monod model, which only approximately represents the RFA removal rate in the anaerobic stage, to generate the theoretical profiles. However, the theoretical profile represents well the tendency of the variation of the experimental  $S_1$  as a function of  $t_1$ , using  $X_1$  as parameter. As an example, both experimental and predicted results indicate that the anaerobic stage with a normal HRT of 0.5 to 1 day produced a poor RFA removal of less than 50% for the effluent studied. Since the agreement between the theoretical values and the experimental results of  $S_1$  is not very well, so is the agreement between the predicted and experimental results of  $S_2$  (Fig. 8.2b).

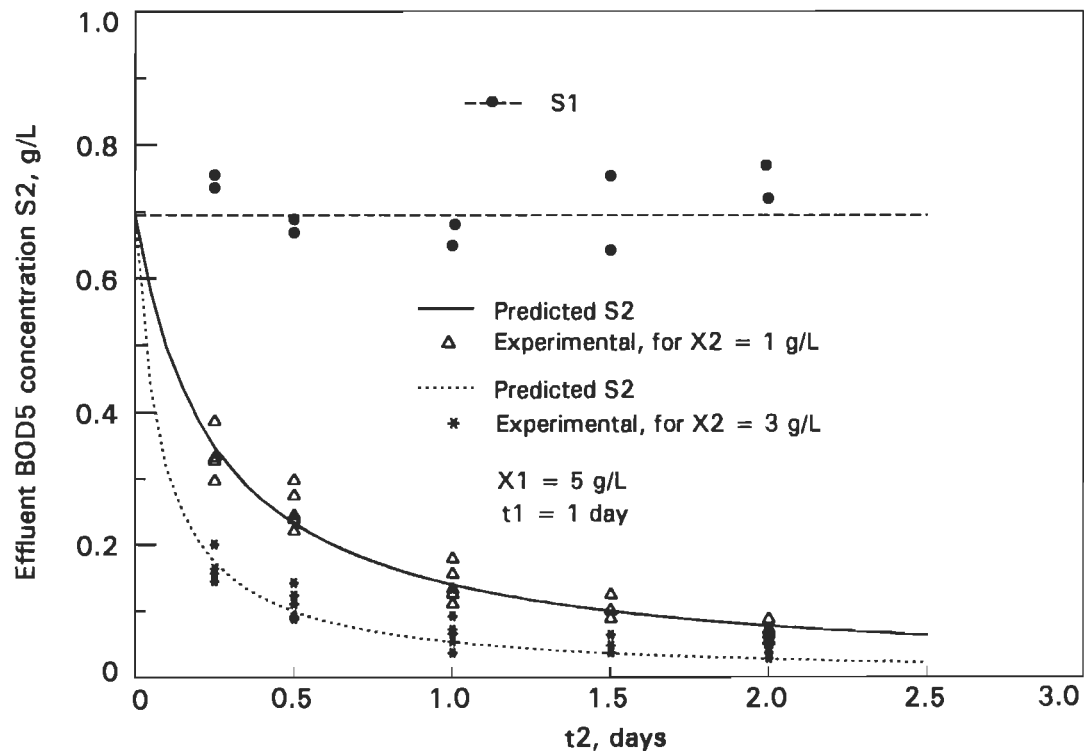
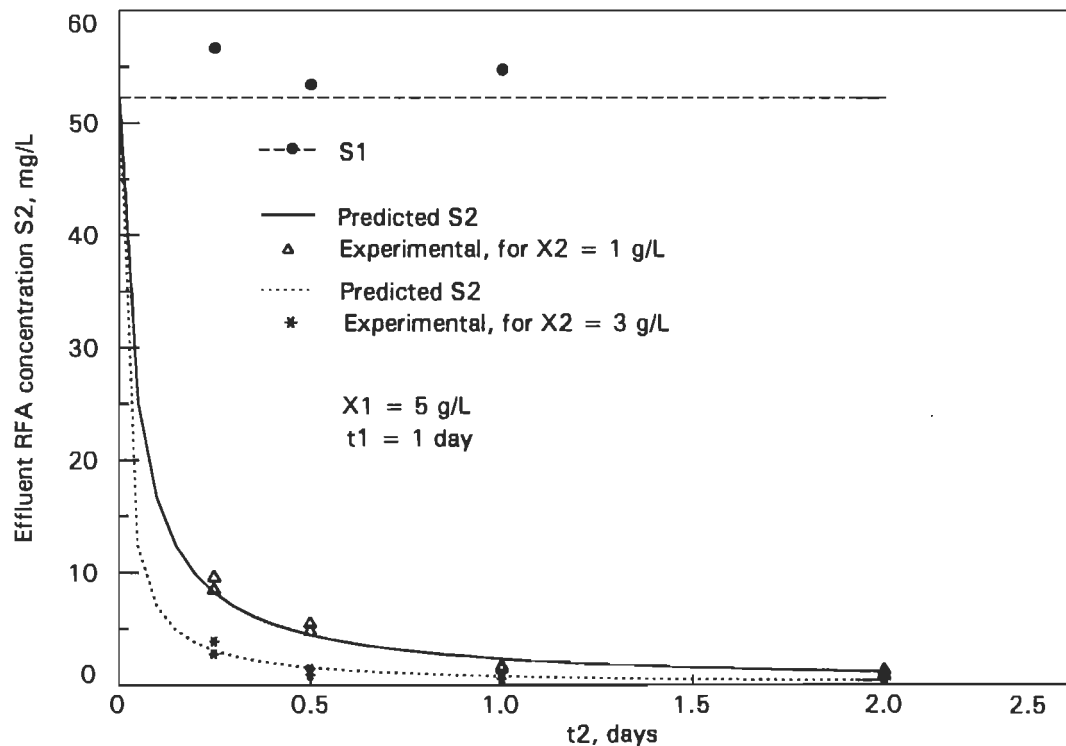


Fig. 8.3 Effects of  $t_2$  and  $X_2$  on effluent BOD5 concentration  $S_2$   
- Comparison between experimental results and predicted values

**Effects of  $t_2$  and  $X_2$  :** Figs. 8.3 and 8.4 show, respectively, the effects of  $t_2$  and  $X_2$  in the aerobic stage on the effluent  $BOD_5$  and RFA concentrations  $S_2$ 's. The feed for aerobic stage was the treated effluent from the anaerobic stage with  $t_1 = 1$  day. The theoretical  $S_2$  curves for both  $BOD_5$  and RFA were plotted with equ. (2.26).

As shown in Fig. 8.3, for the corresponding values of  $t_2$ , the experimental  $S_2$ 's of  $BOD_5$  agree well with the values read from the theoretical curves for both levels of  $X_2$ . The same conclusion applies to the agreement between the experimental results and the predicted values for the concentration  $S_2$  of RFA presented in Fig. 8.4.



**Fig. 8.4 Effects of  $t_2$  and  $X_2$  on effluent RFA concentration  $S_2$**   
 - Comparison between experimental results and predicted values



### 8.3.3 Validity verification of the optimization method for system design

Experimentally, it is impossible to obtain a pre-fixed overall substrate removal for any combination of  $t_1$  and  $t_2$ , in order to arrive at a minimum total hydraulic retention  $t_o = t_m = t_{m1} + t_{2m}$ . However, maximum overall substrate removal can be detected, if any, from the combination of  $t_1 + t_2$  for a pre-fixed  $t_o$ . Therefore, the validity of the method, developed in Chapter 2, for the optimization of the two-stage treatment was verified experimentally with the maximization of the overall BOD<sub>5</sub> removal for a fixed  $t_o$ . In order to use a reasonable fixed  $t_o$ , the theoretical value of the minimum  $t_o = t_m = 1.97$  days, calculated with equs. (2.45) and (2.42) using known values ( $k_1$ ,  $k_2$ ,  $X_1$ ,  $X_2$ ,  $E$  and  $E_{1opt}$ ), for an overall BOD<sub>5</sub> removal  $E = 95\%$  as chosen in the study.

**Table 8.5.** Conditions used in the validity verification of the optimization method for system design

Conditions	Case (1) : $t_1 = t_o$ , $t_2 = 0$	Case (2) : $t_1 > t_{1m}$ , $t_2 < t_{2m}$	Case (3) : $t_1 = t_{1m}$ , $t_2 = t_{2m}$	Case (4) : $t_1 < t_{1m}$ , $t_2 > t_{2m}$	Case (5) : $t_1 = 0$ , $t_2 = t_o$
$X_1$ , g/L	5	5	5	5	--
$X_2$ , g/L	--	1	1	1	Auto-balance (about 1.4)
$t_1$ , d	1.97	1.5	0.95	0.5	0
$t_2$ , d	0	0.47	1.02	1.47	1.97
$t_o$ , d	$t_m = 1.97$	1.97	1.97	1.97	1.97

Verification experiments were carried out with five combinations of  $t_1 + t_2$ , marked as case(1) to case(5) in **Table 8.5**. Case (1),  $t_1 = t_o$  ( $t_m$ ) and  $t_2 = 0$ ; i.e., anaerobic treatment of the CTMP effluent alone without post-treatment through an aerobic stage; Case (2),  $t_1 > t_{1m}$  and  $t_2 < t_{1m}$ ; Case (3),  $t_1 = t_{1m}$  and  $t_2 = t_{2m}$ ; Case

(4),  $t_1 < t_{1m}$  and  $t_2 > t_{2m}$ ; Case (5),  $t_1 = 0$  and  $t_2 = t_o$  ( $t_m$ ), i.e. aerobic treatment of the CTMP effluent alone without pretreatment through an anaerobic stage. The overall removals or the  $S_2$  concentrations of  $BOD_5$  for the five cases were determined and compared.

Since the  $BOD_5$  removal rates in both stages follow very well the kinetics of a first order reaction, the optimal  $BOD_5$  removal  $E_{1opt}$  was determined with equ. (2.45) for a fixed overall  $BOD_5$  removal. The value of  $t_{1m}$  was calculated with equs. (2.17) and (2.15) and that of  $t_{2m}$  with equs. (2.27) and (2.25). In the verification study, the overall  $BOD_5$  removal  $E$  was designed to be 95%. The calculated values of  $E_{1opt}$ ,  $t_{1m}$  and  $t_{2m}$  were, respectively, 71%, 0.95 day and 1.02 days, when  $X_1 = 5$  g/L and  $X_2 = 1$  g/L. The  $t_o = t_m$  is therefore equal to 1.97 days. The conditions used for the study are presented in **Table 8.5**. For the purpose of system control and operation, low levels of the MLSS concentrations  $X_1$  (5 g/L) and  $X_2$  (1 g/L) were used so as to have a longer HRT ( $t_1$  or  $t_2$ ) in each stage.

Presented in Fig. 8.5 are the experimental results obtained and the theoretical curves generated. Eqs. (2.16), (2.26) and (2.27) were used to plot the curves for the kinetics of first order reaction. As illustrated, both experimental and theoretical results have similar profiles of change of  $S_2$  with  $t_1$ , i.e., with the increase of  $t_1$ , both  $BOD_5$  concentrations  $S_2$ 's decrease until minimum values are reached at the same  $t_1$  then increase again. The profile of change of the overall removal  $E$  is exactly the opposite of the  $S_2$  profile. In comparison with the experimental results, the removals predicted with the kinetics of first order reaction seems to be slightly over-predicted.

The experimental  $BOD_5$  removals achieved by both single stage anaerobic (case 1) and aerobic (case 5) treatments were obviously much lower, as seen in Fig. 8.5, than that by the two-stage treatment when  $t_1 = t_{1m} = 0.95$  determined with equ. (2.45) for first order reaction kinetic model. Case 5 was essentially a single stage aerobic treatment without sludge recycling; the MLSS concentration in the reactor

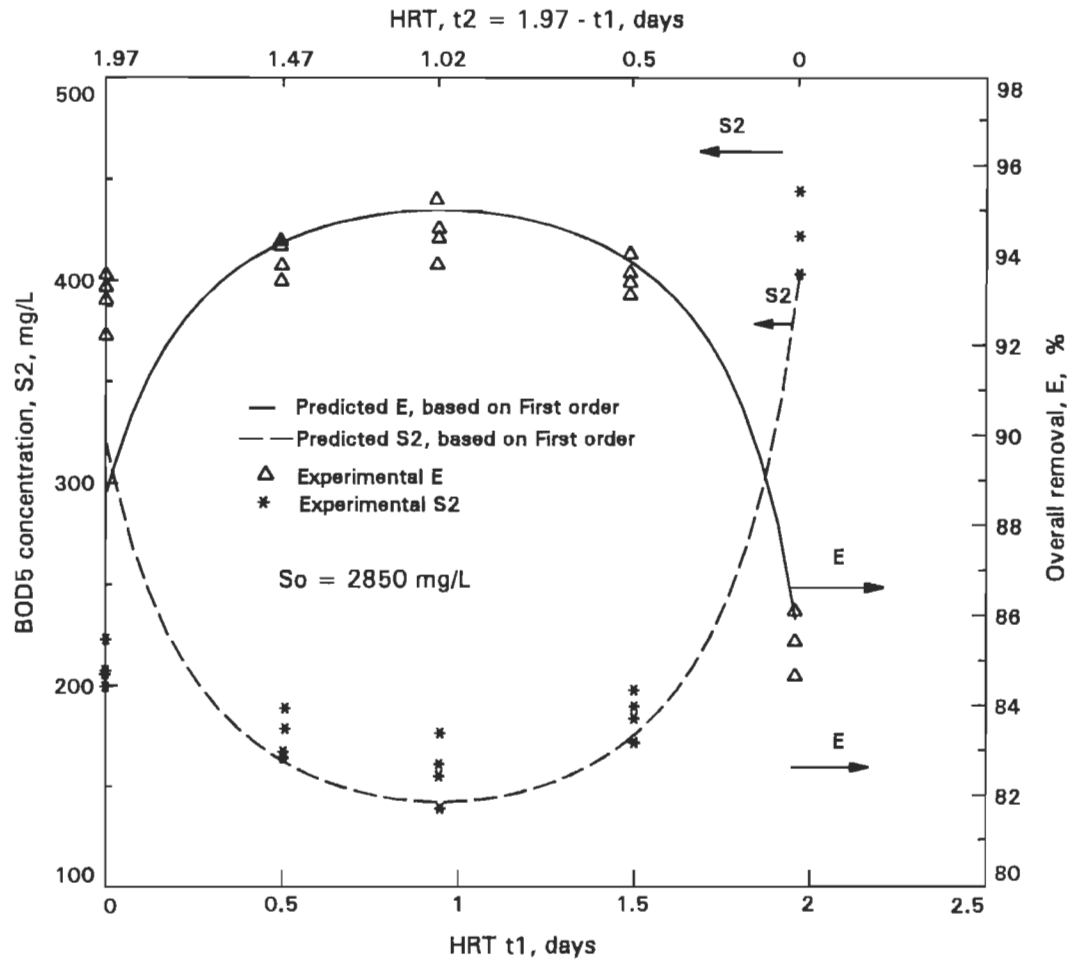


Fig. 8.5 Variations of BOD<sub>5</sub> concentration  $S_2$  and overall removal  $E$  with HRT  $t_1$  or  $t_2$  when  $t_1 + t_2 = t_0 = 1.97$  days

was auto-fixed at about 1400 mg/L (higher than 1000 mg/L). Even with higher MLSS of 1400 mg/L, the resulted BOD<sub>5</sub> removal was, however, still much lower than those produced by the two-stage treatment with the three  $t_1$ 's (0.5, 0.97 and 1.5 days). Although there were some variations in the data, the experimental overall BOD<sub>5</sub>

removal  $E$  achieved at  $t_1 = t_{1m} = 0.95$  day (case 3) is seen to be higher than those obtained at the other two  $t_1$ 's (0.5 and 1.5 days). Indeed, the experimental removal  $E$  obtained at this  $t_1 = t_{1m}$  is the maximum overall  $BOD_5$  removal which can be achieved for a fixed  $t_o = t_1 + t_2 = 1.97$  days, as predicted from the method of optimization based on the kinetics of first order reaction applied to both stages. From the comparison of experimental and theoretical  $E$  profiles and from the obtainment of maximum experimental overall  $BOD_5$  removal at the  $t_1$  exactly predicted from theory, it can be concluded that the validity of the method developed for the optimization of the two-stage treatment have been verified experimentally.

#### 8.4 Conclusions

The removal rate constants of either  $BOD_5$  or RFA found for the anaerobic or the second stage aerobic treatment of the new CTMP effluent are different from those found for the treatment of the first CTMP effluent. The result indicates that different CTMP effluents have their own characteristics and thus their own substrate removal rate constants, therefore, the kinetic parametric values found for one CTMP effluent should not be used in the design of treatment system for other CTMP effluent.

With the new CTMP effluent, the experimental results from the studies of both the effects of operating conditions on the treatment performance and the maximization of the overall  $BOD_5$  removal for a fixed total HRT have verified the validity of the methods developed in Chapter 2, for studying the behaviour and optimization of the two-stage treatment system.

## CHAPTER 9

### **MECHANISMS OF REMOVING RESIN AND FATTY ACIDS IN A CTMP EFFLUENT DURING AEROBIC BIOLOGICAL TREATMENT**

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In this chapter, the mechanisms of removing RFA from the CTMP effluent studied during aerobic biological treatment were studied in batchwise reactor. The effects of treatment conditions on the removals were also investigated. The work was initiated by the results presented in Chapter 5 that the treatment was very effective for RFA removal.

#### **9.1 Introduction**

As mentioned in the Section 1.1 of Chapter 1, acute lethality of effluent to fish (96h LC<sub>50</sub>) has now become a mandatory issue in environment protection regulations. According to the Canadian [23] and Québec [24] Pulp and Paper Effluent Regulations, the final effluents discharged from the pulp and paper mills have to be non toxic to fish by the end of December and of September of 1995, respectively. Consequently, mills will have to remove toxic constituents to fish in their effluents, and any study aiming to explain the mechanisms of removal of effluent toxicity to fish should be useful and of interest to the pulp and paper industry.

As described in the Sub-section 1.2.3.2 of Chapter 1, the RFA released from wood chips during pulping have been identified as the main toxicity-to-fish source in

mechanical pulping effluents [8, 11, 36-39], especially in CTMP effluents due to the very high RFA content frequently observed [3]. Therefore, the removal of RFA from a CTMP effluent before discharge appears to be the key element to remove the effluent toxicity.

It was found from the work presented in Chapter 5 that aerobic treatment is very effective for the removal of RFA in the CTMP effluent studied. Almost 96% of the RFA in the effluent can be removed with 12-hour HRT treatment, as shown in Fig. 5.1a. However, anaerobic treatment produced a poor removal of RFA as compared with aerobic treatment, although the HRT used was much longer and the microbial concentration involved was much higher. Results from earlier studies [11, 13-14, 42, 54] have also shown that aerobic biological treatment is a very effective method for the elimination of RFA from pulping effluents. It has been generally thought that biodegradation alone is responsible for the RFA removal through aerobic biological treatment [3]. However, other removal mechanisms, such as adsorption onto the biosolids and oxidation by air, may exist during the treatment.

The objectives of the work were thus : 1) to determine the removal mechanisms and 2) to investigate the effects of operating conditions on RFA removals by the different mechanisms.

## **9.2 Theoretical considerations**

### **9.2.1 Properties of RFA and possible removal mechanisms**

Eight resin acids and three unsaturated fatty acids (shown in Fig. 9.1) released from wood chips during pulping are usually identified in pulping effluents [11, 13, 56], especially in CTMP wastewaters [7, 39, 50] including the CTMP effluent studied. Among these acids, dehydroabietic acid (DHA) is very frequently the most abundant in quantity.

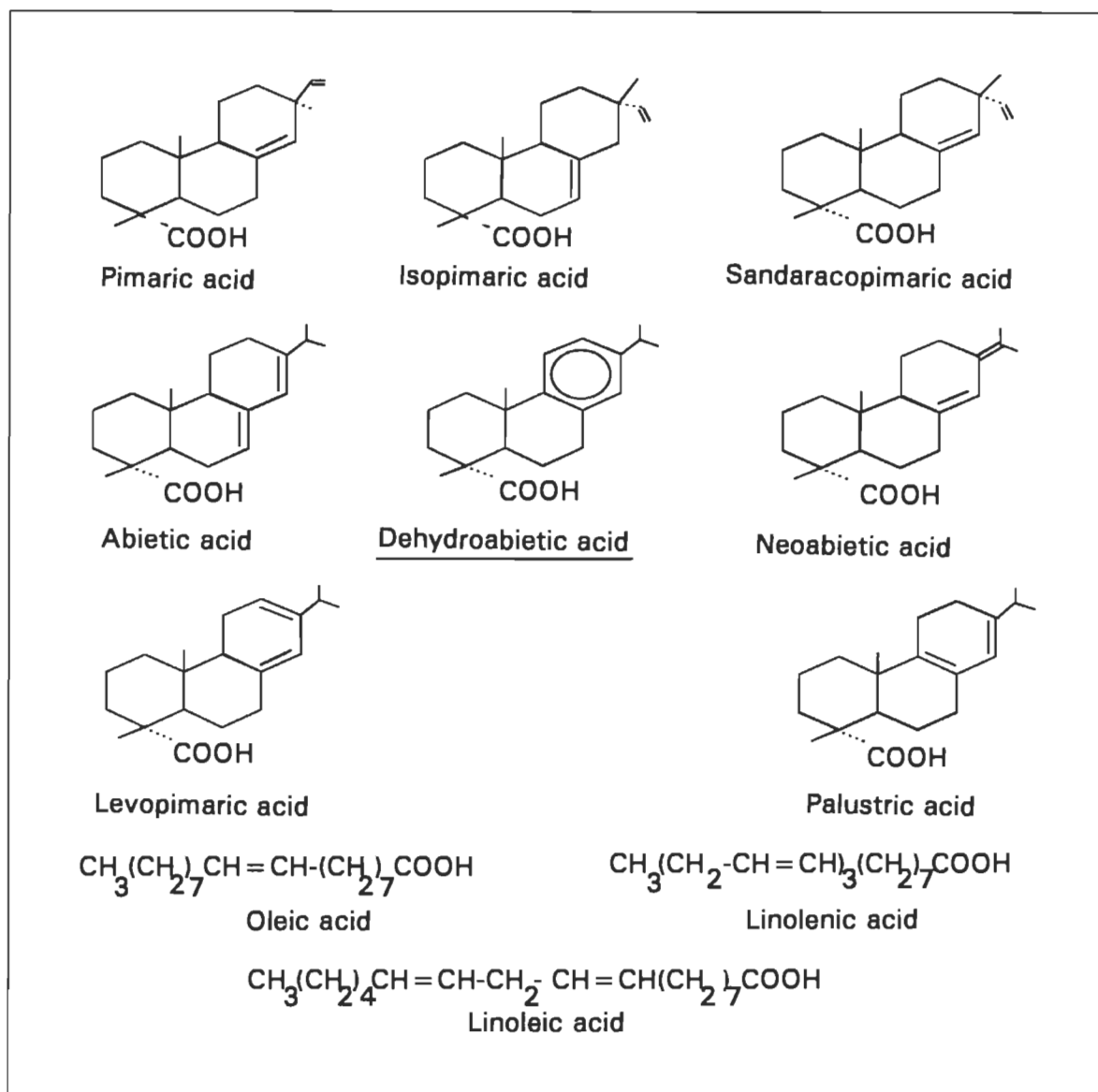


Fig. 9.1 Structural formulae of RFA universally found in CTMP effluents

Theoretically, being natural organic compounds, RFA could be used as food for microorganisms through biodegradation. However, the stable tricyclic ring structures in resin acids, especially in DHA, are "persistent" to biodegradation [140, 153]. In addition, RFA are nearly insoluble in water [140, 154]. Thus, their poor solubilities or high hydrophobicity possibly make them adsorb onto the biosolids during biological treatment [155]. The very small microbial flocs with an average diameter of about 20-50  $\mu\text{m}$  in an aerobic system provide a very large total surface area for RFA adsorption. The fact that RFA, especially DHA, have been found in measurable quantities in the sediments on the bottom of the rivers nearby pulp and paper mills [11, 153, 156-157] supports this adsorption assumption. Due to the presence of unsaturated double bonds in their molecules as shown in Fig. 9.1, these acids may also be oxidized by atmospheric oxygen [158]. Studies have demonstrated that resin acids can be oxidized by photosensitized air oxidation [159-160] and by non-sensitized air oxidation [161-163] in an organic solvent, such as hexane, alcohol, etc. The fact that anaerobic treatment, for which air is totally absent, brings low reduction of RFA from pulping effluent [59, 104, 108] may further support the air oxidation mechanism assumption. Thus, during aerobic biological treatment, RFA may be removed by three mechanisms : biooxidation by microorganisms, adsorption onto the biosolids, and air oxidation.

### 9.2.2 Proposed model for RFA removal by aerobic biological treatment

A model for RFA removals by the three mechanisms assumed above is proposed and presented in Fig. 9.2. It consists of *instantaneous adsorption onto sludge, bio-oxidation and air oxidation*.

In this model, most of the RFA in the feed adsorb (route 1) quickly onto the sludge after contact with the MLSS in the bioreactor. At the same time, the remaining RFA in the feed (bulk phase) are removed by both bio-oxidation (route 2) and air oxidation (route 3). Following the progress of the treatment, a part of the adsorbed



RFA are then gradually degraded by the microorganisms (route 4). The remaining adsorbed RFA are removed together with the excess sludge (route 5), which really represents the quantity removed by the adsorption mechanism. It can be expected that the longer the treatment time, the less important will be the removal of RFA by adsorption, and the removal by bio-oxidation will increase accordingly.

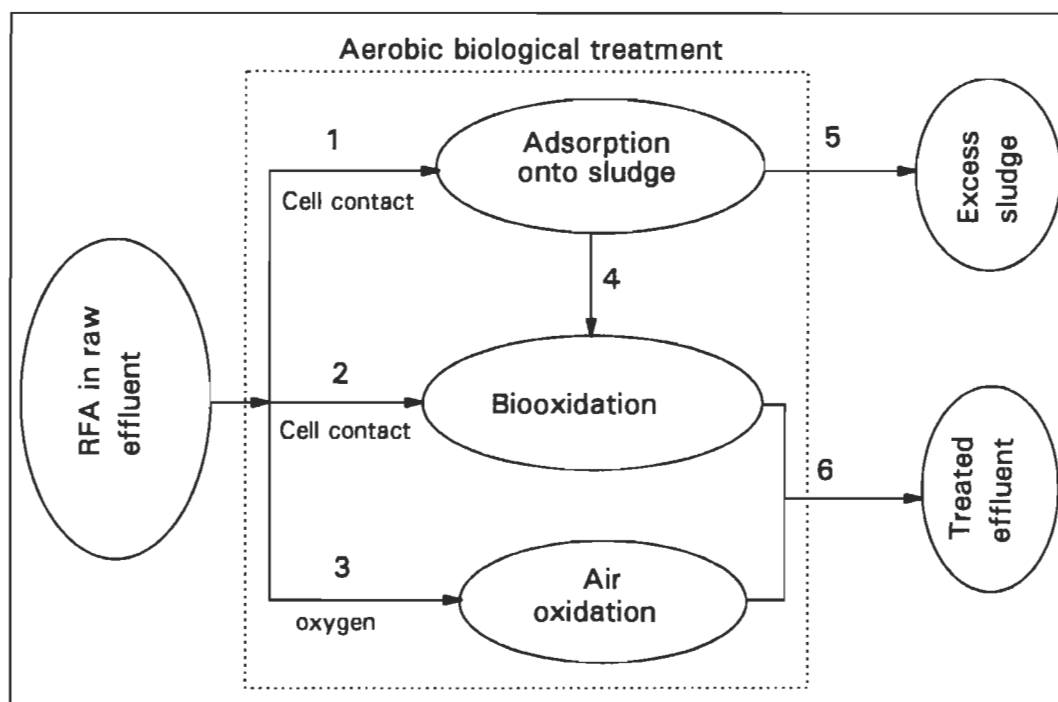


Fig. 9.2 A proposed model for RFA removal during aerobic treatment

### 9.2.3 Adsorption model

It is assumed that the adsorption of RFA onto sludge follows the monomolecule adsorption theory. The Langmuir and Freundlich models [164] are employed to describe this adsorption process.

Langmuir model:  $q = q_m A_o C / (1 + A_o C)$  (9.1)

Freundlich model:  $q = B_o C^{1/n}$  (9.2)

In both models,  $q$  (the amount of adsorption per unit dry mass of sludge) in a batch bioreactor is determined by equation (9.3), using the equilibrium RFA concentration  $C$  in the liquid.

$$q = [(v_o C_o^* + v_s C_{s,i}) - vC] / Xv \quad (9.3)$$

### 9.3 Experimental conditions

Listed in **Table 9.1** are the experimental conditions for evaluating the removal mechanisms and the overall removal kinetics. The selections of the conditions are based on the fact that very short HRT and  $pH \approx 7$  are usually used in a practical high-rate aerobic treatment. In all the experiments carried out in 3-litre beaker, treatment pH and temperature were automatically controlled at values given in **Table 9.1**.

**Table 9.1** Experimental conditions used in the study of RFA removal mechanisms

Mechanisms	pH	Temp. (°C)	MLSS conc. (g/L)	Aeration rate (L/L min)	Aeration time (hour)	Initial conc. of RFA, $C_o$ (mg/L)
Air oxidation	7	25	0	0.224	0-96	45.4
Static adsorption	7	25	3	0	0-7.5	10-33.9
Dynamic adsorption	7	25	3	0.224	0-12	32.5
Bio-oxidation	7	25	3	0.224	0-12	32.5

## 9.4 Results and discussion

### 9.4.1 Mechanisms of removing RFA

Fig. 9.3 presents the chromatograms of RFA where 9.3a is for the untreated CTMP effluent; 9.3b for the treated effluent after 12 hours of aerobic biological treatment; 9.3c for the adsorbed RFA onto the sludge (dynamic adsorption); and 9.3d for the oxidation by air after 12 hours of aeration. As seen, after 12 hours of biotreatment, most of the RFA have been removed from the CTMP effluent, as indicated by the much smaller peaks in the chromatogram of the RFA (Fig. 9.3b) for the treated effluent, as compared to those for the untreated CTMP effluent. All the RFA identified in the CTMP effluent were also found in large quantities in the sludge sample as indicated by the large peaks in the chromatograms (Fig. 9.3c), confirming the adsorption of RFA onto the sludge.

As noted in Fig. 9.3d, after 12 hours of static air aeration, the peaks of the fatty acids (1, 2, 3) disappeared from the chromatograph as compared to those for untreated effluent (Fig 9.3a), implying that air oxidation of fatty acids would take place. Results from the static air oxidation experiments showed that about 10% reduction of the RFA was achieved after 12 hours of aeration at 0.224 L (air)/L (reactor) min. In principle, this RFA removal could be due to air or bio-oxidation or both oxidations as well as to the adsorption onto the suspended solids present in the un-aerated effluent. The adsorption of RFA onto the suspended solids should have reached an equilibrium long before starting the experiment since the untreated effluent had been stored for about one week prior to the experiment. Thus, the presence of suspended solids should not have a net effect on this removal since the sample preparations of both un-aerated and aerated effluents for RFA analysis were identical (without filtration) as mentioned previously. Since there were no microorganisms (seeds) in the beaker at the beginning of aeration and also no nutrients available, the possibility of bacterial growth, if any, in the beaker should be quite small. Thus,

biooxidation of the RFA would not take place, or, if any, would be negligible in the test. Furthermore, no significant changes in both COD and TSS concentrations were observed in the test, also indicating no significant bacterial growth; otherwise, the treated effluent COD would have a measurable reduction as the carbohydrates and low molecular weight organic acids present in the untreated effluent are very easily utilized by the bacteria. Earlier studies [159-163] have shown that resin acids can be readily air oxidized in an organic solvent, such as hexane, ethanol, etc. Therefore, the RFA removal in the test should be achieved mainly by air oxidation, confirming the presence of the air oxidation mechanism.

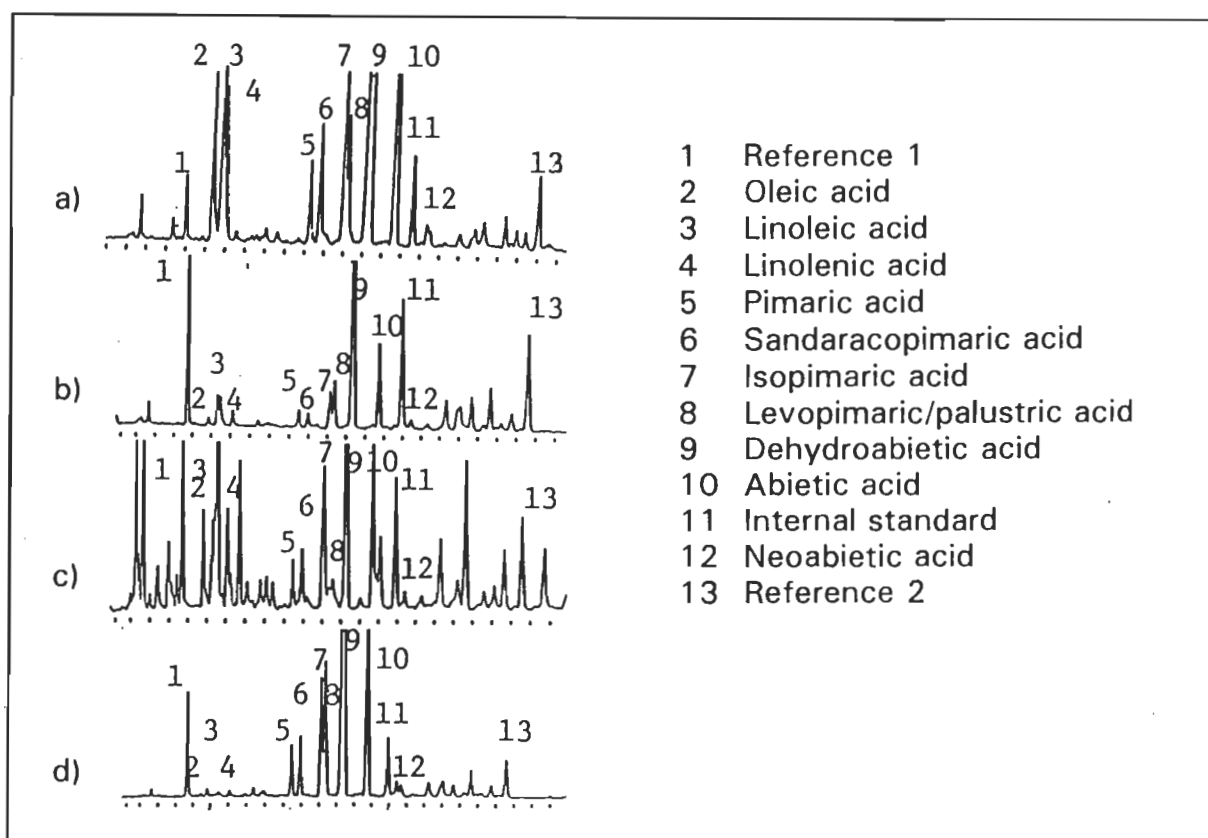


Fig. 9.3 Chromatograph of RFA - a): for the raw CTMP effluent; b) : for the biotreated effluent; c) : for the adsorption onto sludge; d) :for the air oxidized effluent

The results presented in the above two paragraphs indicated that RFA in the CTMP effluent were also removed by both adsorption onto sludge and air oxidation mechanisms proposed previously, in addition to by biooxidation.

#### 9.4.2 Static air oxidation of RFA

Results presented in **Table 9.2** and Fig. 9.4 are the RFA removals by air oxidation. In general, air oxidation rate is low, only about 10% of the RFA was oxidized during a 12-hour aeration period. Therefore, air oxidation of RFA in aerobic biological treatment is not considered as being a major mechanism by which RFA are removed. Studies [159-163] have shown that air oxidation of resin acids initially forms inter-products, such as transannular peroxides, which could be more easily attacked by microorganisms. Thus, it is speculated that the oxygen in biological treatment would also indirectly play an important role in modification of RFA molecular structures for microbiological oxidation, in addition to directly oxidizing RFA and to supplying the oxygen for bacterial growth and synthesis.

**Table 9.2** Static air oxidation of RFA - Experimental results

Sample code	Aeration time	RFA conc.	Removal
	Hours	mg/L	%
AO-0	0	45.5	0
AO-1	1	45.4	1
AO-6	6	42.5	6.5
AO-12	12	40.2	10.5
AO-36	36	39.4	13.4
AO-48	48	38.4	15.6
AO-96	96	36.2	20.3

Under the conditions studied, air oxidation of RFA does not follow a first-order reaction or Monod model while it can be well represented by a zero-order reaction model, implying that oxidation rate is independent of RFA concentration. However, there exist two oxidation rate constants, depending on the range of aeration time shown in Fig. 9.4b. Oxidation rate constant within the first 12 hours of aeration was much greater (about 10 times) than that within the extended aeration, due to the rapid removal of fatty acids in the first hours, as exhibited in Fig. 9.3d. This result further indicated that no bacterial growth in the test would take place; otherwise, the results for the rate constant would be reverse, since the longer the aeration time is, the more the bacteria would grow and the more rapidly the RFA would be removed. Schuller [159] and Moore [160] also observed that the oxidation rate of resin acids was independent of the acids concentrations during photosensitized air oxidation in organic solvents. The results obtained are in agreement with their findings.

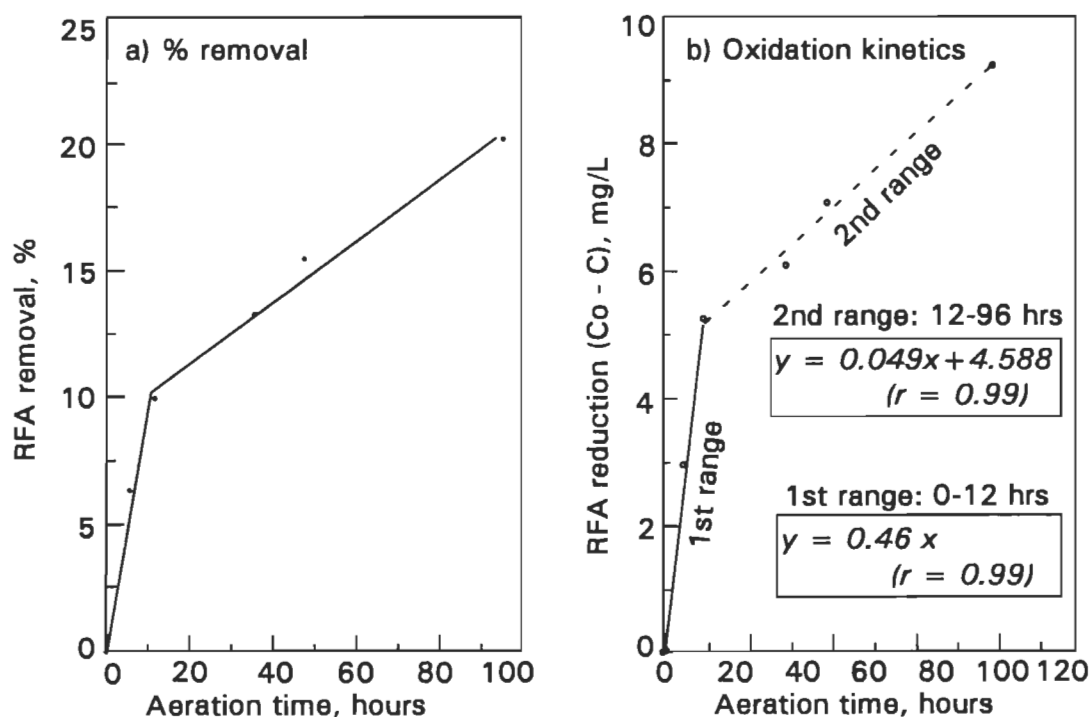


Fig. 9.4 Removal of RFA by static air oxidation

### 9.4.3 Static adsorption of RFA onto sludge

#### 9.4.3.1 Rate of static adsorption of RFA

**Table 9.3.** Static adsorption of RFA - Experimental results

Sample code	Contact time	RFA conc.	Removal
	minutes	mg/L	%
AD-0	0	33.9	0
AD-1	2	17.2	55.6
AD-2	5	15.7	60.7
AD-3	10	12.9	62
AD-4	20	10.3	69.5
AD-5	30	10.1	70.3
AD-6	60	10.2	69.8
AD-7	120	10.7	68.5
AD-8	240	10.3	69.5
AD-9	360	10.5	69.1
AD-10	450	9.2	72.8

Hydrophobic organic compounds usually easily adsorb onto soils and sediments [165-168]. The adsorption of hydrophobic organic compounds, such as chlorophenols, chloroguaicol, etc, generated in pulping and bleaching operations onto pulp-derived solids has also been observed [155]. RFA are highly hydrophobic and may also adsorb onto biosolids during biological treatment. To evaluate the adsorption of RFA onto biosolids, static adsorption of RFA in the CTMP effluent studied was tested using thickened mixed liquor. The experimental results are presented in **Table 9.3** and **Fig 9.5**. The initial concentration  $C_0$  of the RFA in liquid phase in the beaker was cal-

culated from the RFA concentration  $C_o^*$  in the untreated effluent and the concentration  $C_{sl}$  in the liquid phase of the thickened mixed liquor used in the experiment, using the following equation :

$$C_o = (C_o^*v_o + C_{sl}v_s)/v \quad (9.4)$$

As shown in Fig. 9.5, the adsorption of RFA onto the sludge is very rapid at the beginning and completed within about 30 minutes of contact time. After 30 minutes, the adsorption reaches an equilibrium. As observed, as much as about 70% of the RFA in the effluent has been removed, indicating that adsorption of RFA onto sludge would take place.

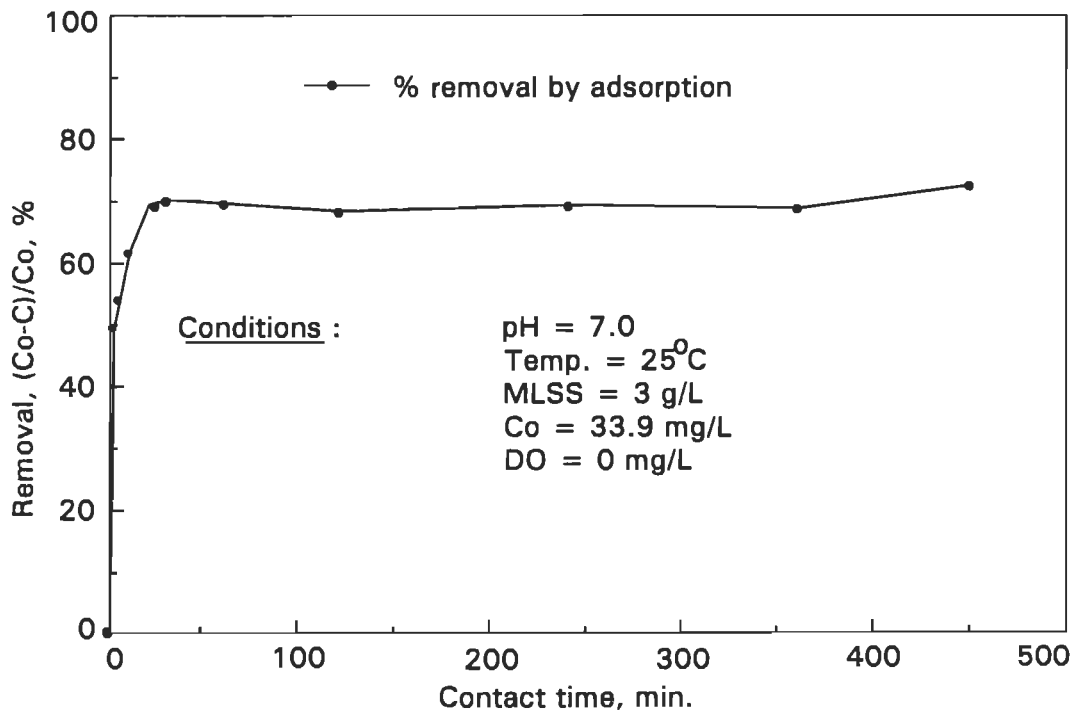


Fig. 9.5 Removal of RFA by static adsorption onto sludge



As there were no nutrient and particularly no oxygen available, theoretically, aerobic biodegradation should not take place. The growth of anaerobic bacteria would also not occur under such unacclimated environment, or, if any, would be negligible within such a short period (30 minutes). An anaerobic treatment operated using very high concentration (10-40 g/L, even higher) of acclimated bacteria and a treatment time of at least one day usually produces low removal of RFA [59, 104, 108], of which a great part would be due to the adsorption onto biosolids. The growth of facultative organisms would most likely occur; however, it would also be quite marginal under the test conditions within such a short contact time. In fact, no more RFA removal after 30 minutes of contact may also indicate that no significant biodegradation of RFA would take place; otherwise, RFA removal would increase continuously. Therefore, biodegradation in the test would not take place, or, if any, would be negligible under the testing conditions.

In order to confirm experimentally no significant occurring of bacterial growth, a further supplemental experiment was run using both dead (sterilized sludge) and live biosludge. The experimental conditions and results are presented in **Table 9.4**. As shown, excellent apparent overall RFA concentration balances between before and after static adsorption were obtained for both cases with extremely small errors of -0.7% and -2.6, respectively. The little higher apparent overall RFA concentration in the tested sample after adsorption might be due to experimental error or, in particular, to the neglected amount of RFA adsorbed onto the suspended solids present in the untreated effluent. Such amount was not determined before adsorption since the suspended solids content was low (0.12 g/L). The corresponding reduction of the RFA in the liquid phase for both cases was also a little less than the amount of net adsorption onto the sludge, still due to the amount of RFA adsorbed onto the suspended solids present in the untreated effluent. These results indicate that the removals observed in both cases are achieved by static adsorption alone, confirming the adsorption of RFA onto biosolids. Somiya *et al* [169] found that about 80% of the particulate COD still adsorbed onto activated sludge after a 27-hour aeration. In the

case of using live biosludge for the test, the amount of the RFA adsorbed onto the MLSS (activated sludge plus suspended solids in the untreated effluent) was about 69% after 2 hours of contact. Therefore, adsorption onto sludge may be a very important mechanism for the removal of RFA by aerobic biological treatment of CTMP effluents.

**Table 9.4.** RFA concentration balance for static adsorption.

Case 1: Dead sludge							Case 2: Live sludge						
Exper. design	V	V <sub>o</sub>	V <sub>s</sub>	X <sub>s</sub>	X	time	Exper. design	V	V <sub>o</sub>	V <sub>s</sub>	X <sub>s</sub>	X	time
	2 L	1.72 L	0.28 L	17.76 g/L	2.5 g/L	2 hrs		3 L	2.4 L	0.6 L	16.24 g/L	3.3 g/L	2 hrs
	Before adsorption			After adsorption		%rem		Before adsorption			After adsorption		%rem
	RFA content, µg/L		%rec	RFA content, µg/L		%rec		RFA content, µg/L		%rec	RFA content, µg/L		%rec
	C <sub>o</sub> : 29402 ± 666 (3)		115 ± 5	C: 15808 ± 810 (2)		115 ± 3		C <sub>o</sub> : 29402 ± 666 (3)		115 ± 5	C: 9845 ± 220 (3)		118 ± 1
	C <sub>el</sub> : 4554 (1)		107	---		--		C <sub>el</sub> : 5788 ± 147 (2)		101 ± 5	--		--
	q <sub>o</sub> : 13655 ± 622 (2)		111 ± 2	q: 17800 ± 12 (2)		107 ± 2		q <sub>o</sub> : 12384 ± 404 (2)		118 ± 2	q: 17391 ± 1068 (2)		111 ± 1
	RFA adsorbed onto in TSS was not determined			RFA adsorbed onto TSS was included in q				RFA adsorbed in TSS was not determined		--	RFA adsorbed in TSS was included in q		--
	$C_o = \frac{29402 \times 1.72 + 4554 \times 0.28}{2} = 25923$			C: 15808		39		$C_o = \frac{29402 \times 2.4 + 5778 \times 0.6}{3} = 24677$			C: 9845		60
	$C_{so} = \frac{13655 \times 0.28 \times 17.76}{2} = 33952$			$C_s = \frac{17800 \times 2 \times 2.5}{2} = 44500$		41		$C_{so} = \frac{12384 \times 0.6 \times 16.24}{3} = 40223$			$C_s = \frac{17391 \times 3.3 \times 3}{3} = 57390$		69
Total	C <sub>ib</sub> = C <sub>o</sub> + C <sub>so</sub> = 59878 µg/L			C <sub>ia</sub> = C + C <sub>s</sub> = 60308 µg/L			Total:	C <sub>ib</sub> = C <sub>o</sub> + C <sub>so</sub> = 64900 µg/L			C <sub>ia</sub> = C + C <sub>s</sub> = 66577 µg/L		
Error : (C <sub>ib</sub> - C <sub>ia</sub> )/C <sub>ib</sub> = - 0.7%							Error : (C <sub>ib</sub> - C <sub>ia</sub> )/C <sub>ib</sub> = - 2.6%						

Remarks:

- 1) The effluent and the thickened mixed liquor used in this supplemental work were different from those employed in the study;
- 2) Unit of q: µg RFA/g MLSS;
- 3) Concentration of TSS in untreated CTMP effluent used was 120 mg/L;
- 4) % rem = (C<sub>o</sub> - C)/C<sub>o</sub> or (C<sub>s</sub> - C<sub>so</sub>)/C<sub>o</sub>;
- 5) % rec: analytical recovery of spiking compound (reference) used in GC-FID analysis;
- 6) (x) --- Number of analysis.

### 9.4.3.2 Adsorption isotherm of RFA

The adsorption isotherm is an important feature of an adsorption process, describing the equilibrium relationship between adsorbent and adsorbate. In order to establish the static adsorption isotherm of the RFA onto the sludge, different initial RFA concentrations  $C_0$  were experimented at a constant temperature with the same amount of sludge. The results are presented in **Table 9.5**. The different initial RFA concentrations were achieved through mixing the untreated CTMP effluent, the thickened mixed liquor and, if needed, fresh distilled water. The plot of initial RFA concentration versus  $q$ , the corresponding amount of adsorption onto unit dry mass of sludge, presents the isotherm.

**Table 9.5.** Adsorption isotherm of RFA at 25°C and MLSS = 3 g/L

Sample code	Initial conc.	Equilibrium conc.	Amount adsorbed
	$C_0$ , mg/L	$C$ , mg/L	$q$ , mg RFA/mg mlss
ISO-1	10	6.64	1.12
ISO-2	15	8.52	2.16
ISO-3	20	9.95	3.35
ISO-4	25	10.4	4.87
ISO-5	30	10.7	6.41
ISO-6	33.86	11.2	7.55

Fig. 9.6 displays the isotherms of the RFA and DHA at 25 °C. In the range of the concentration studied, the isotherm of the RFA was found to be almost linear while that of DHA appeared to be curved, as shown in the figure. Since the properties of DHA are generally similar to those of RFA, its adsorption isotherm would be in principle similar to that of RFA. The different behaviour in isotherm of DHA is probably due to the isomerization of other resin acids [163, 170] to DHA during

experiment, sample preparation, and GC analysis. As shown in Figs. 9.7a and 9.7b as well as 9.8a and 9.8b, the isotherms for both RFA and DHA at 25 °C can be well represented by both the Langmuir and the Freundlich models with  $r$ 's greater than 0.97, except for the DHA Freundlich isotherm ( $r = 0.9$ ).

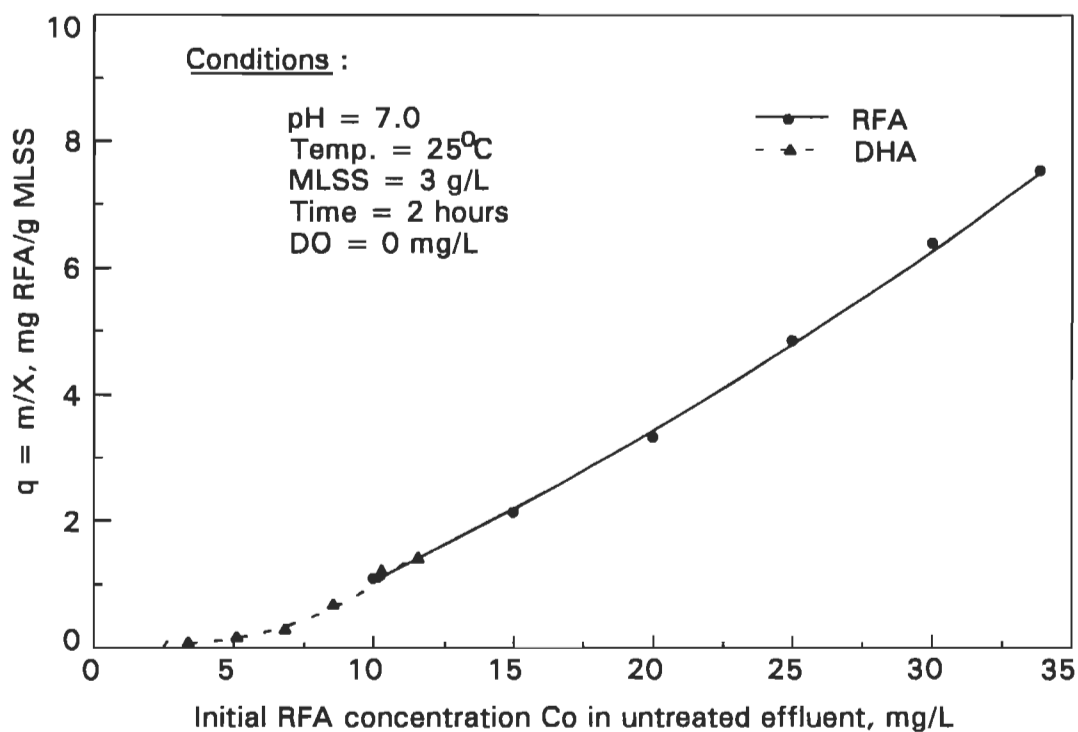


Fig. 9.6 RFA and DHA isotherms at 25°C for static adsorption onto sludge

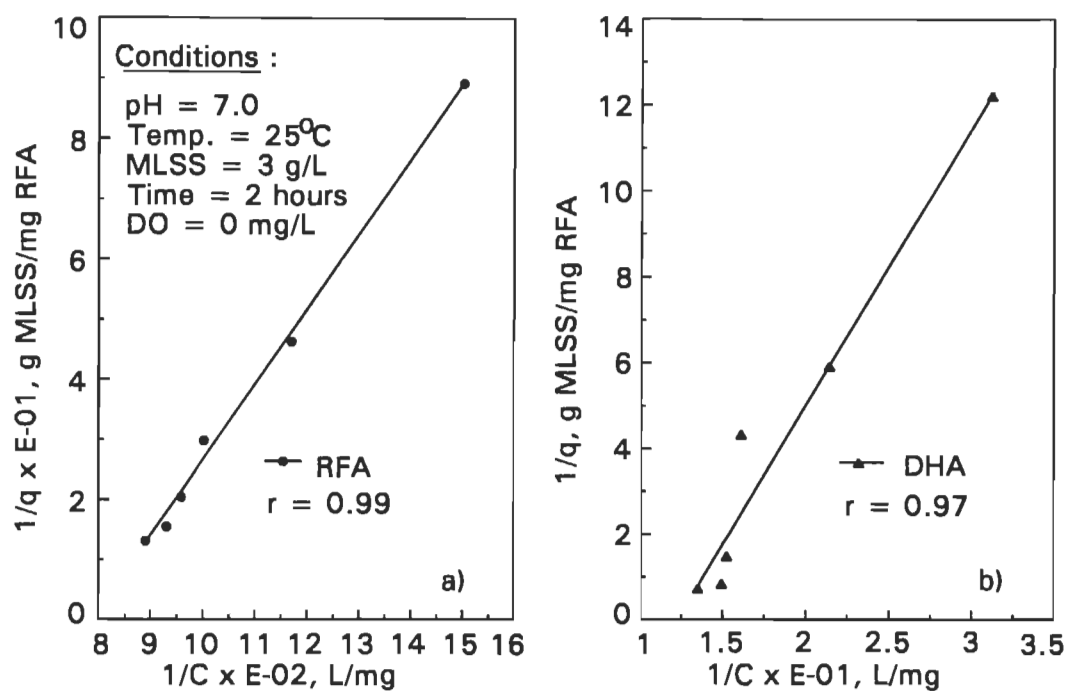


Fig 9.7 RFA and DHA isotherms at 25°C expressed by Langmuir model for static adsorption onto sludge

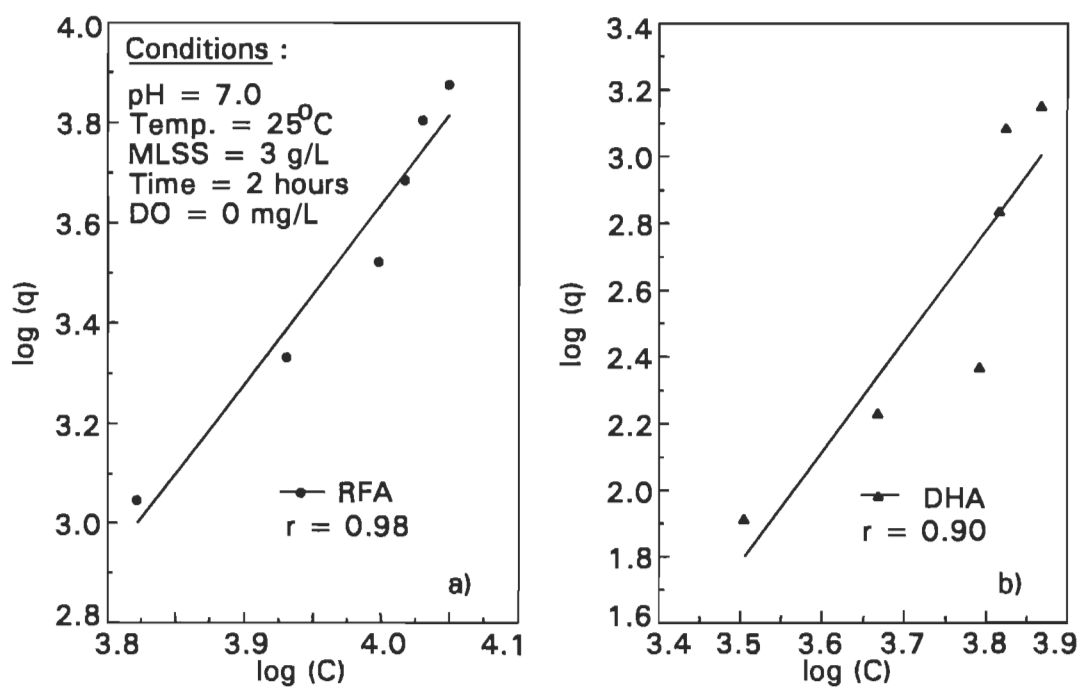


Fig 9.8 RFA and DHA isotherms at 25°C expressed by Freundlich model for static adsorption onto sludge

#### 9.4.4 Biooxidation and dynamic adsorption of RFA during aerobic biological treatment

**Table 9.6** and Fig. 9.9 present the removals of the RFA by biooxidation and by dynamic adsorption onto sludge as well as the overall removal by the treatment.

**Table 9.6.** Bio-oxidation and dynamic adsorption of RFA - Experimental results

Sample code	Aeration time	RFA conc.	Removal, %		
	Hours	mg/L	Overall	Adsorption	Biooxidation
BIO-0	0	32.5	0	0	0
BIO-0.5	0.5	14.92	54.1	36.1	18
BIO-1	1	13.88	57.3	34.6	22.7
BIO-1.9	1.9	13.36	58.9	28.9	30
BIO-4	4	12.78	60.7	29	31.7
BIO-6.1	6.1	12.45	61.7	27.1	34.6
BIO-7.5	7.5	9.65	70.3	20.6	49.7
BIO-12	12	4.52	86.1	17.9	68.2

The removal of RFA by biooxidation, which is actually the sum of the removals by biooxidation and by air oxidation, was calculated by subtracting the removal by adsorption onto sludge from the overall removal. Because it is impossible to determine the degree of removal by air oxidation in practical aerobic biological treatment, and because the removal of RFA by air oxidation was very low, found from the study of static air oxidation of RFA presented in Sub-section 9.4.2 as presented previously, the removal by this mechanism was neglected in the calculation.

As noted, about 36-18% of the RFA was removed by adsorption in the range of the treatment time studied. The rest was removed by biooxidation and by air oxidation. It seems to be difficult to explain why the removal of the RFA by dynamic adsorption was much less than that by static adsorption.

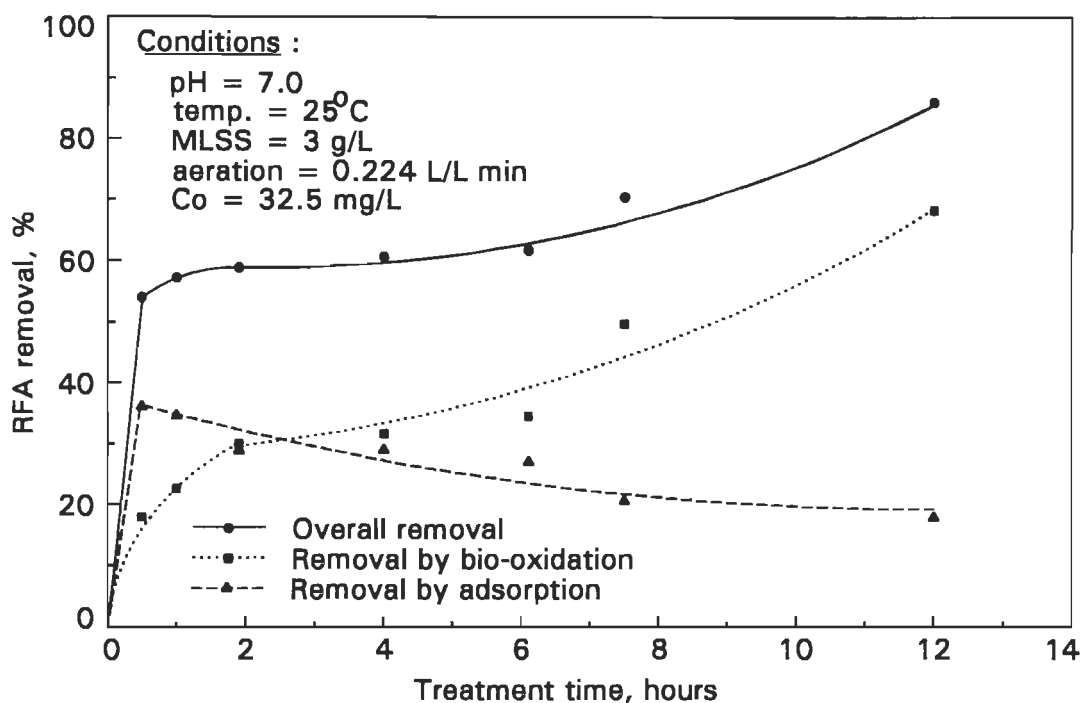


Fig. 9.9 Removals of RFA by bio-oxidation and by adsorption onto sludge in a batchwise aerobic biological treatment

As observed also, both the overall removal and the amount of the RFA adsorbed increase rapidly as the treatment time is increased from 0 to 0.5 hour. The removal by biooxidation also increases rapidly, probably due to the oxidation of the fatty acids. During this 0-0.5 hour period the overall removal is mainly due to the adsorption as shown in the figure. From 0.5 to 6 hours, the removal by biooxidation increases very slowly while the removal by adsorption decreases gradually, resulting in almost no increase in the overall removal of the RFA. The decrease in the removal by adsorption is probably due to the biooxidation of the RFA adsorbed onto the sludge because the overall removal seems to have no increase. From about 6 to 12 hours, the biooxidation of the RFA increases readily and the removal by adsorption still decreases. The overall removal increases following the similar pattern to that of the biooxidation.



There seems to exist a lag phase in the interval from 0.5 to approximately 6 hours, during which the biooxidation of the RFA takes place very slowly. After this lag period, the biooxidation proceeds faster. In a study on the incubation of resin acids with bacteria, Hemingway and Greaves [171] also found that there was a lag period of about 18-20 hours during which negligible resin acids decomposition took place. This lag was followed by a logarithmic growth period in which the resin acids concentration declined precipitously. Caunt and Hester [172] noted in their study of batchwise aerobic treatment of piggery waste that there was a delay of 4 to 6 hours before volatile fatty acids began biodegraded. Our results seem to be in agreement with their findings. As noted in Fig. 9.9, during this lag period, the adsorption greatly contributed to the overall removal. Thus, in high rate biological treatment where hydraulic retention time is usually very short (hours), adsorption mechanism would be expected to play an important role in RFA removal.

#### **9.4.5 Effects of the treatment variables on RFA removals by various mechanisms**

The above results indicate that, in addition to bio-oxidation by microorganisms, adsorption onto sludge is an important mechanism for RFA removal, particularly when treatment time is very short. RFA removals by these two major mechanisms would be affected by the treatment variables. These variables include : 1) MLSS concentration, 2) treatment time, 3) temperature and 4) pH.

pH would induce an effect on the adsorption of an organic compound by changing its hydrophobicity or hydrophilicity. However, pH in a well operated aerobic treatment system normally stabilizes around the value of 7 (6.5 to 7.5) or is controlled at 7. Furthermore, the experimental results reported in Chapter 5 have shown that pH in the range from 5 to 8 has no significant effect on RFA removal by the single stage aerobic treatment. The effects of pH on the removals were thus not investigated. Other variables can vary in real aerobic treatment. The effects of treatment time, temperature and MLSS concentration on the removals of RFA by bio-oxidation

and onto sludge, as well as on the overall removal, were therefore investigated using batchwise aerobic treatment.

To minimize the number of experiments to be run, a factorial central composite design (CCD) [173] was used. The design is both orthogonal and rotatable. With minimum experimental runs, it generates not only the linear main effects of the variables studied but also the interaction effects, which likely exist in the present study; thus, it is very efficient.

To study the effects, a CCD of 3 variables was chosen. This CCD requires fifteen experiments to be run at the conditions shown in the diagram presented in Fig. 9.10. In the design, the levels of each variable are expressed as -1 and +1, zero (0), -1.68 (- $\alpha$ ) and 1.68 (+ $\alpha$ ) to represent the low and high levels, the central point and the two extreme levels (stars). The values of the two extreme levels are normally preset. The real values of the rest levels are determined by the following equations (9.5) and (9.6) :

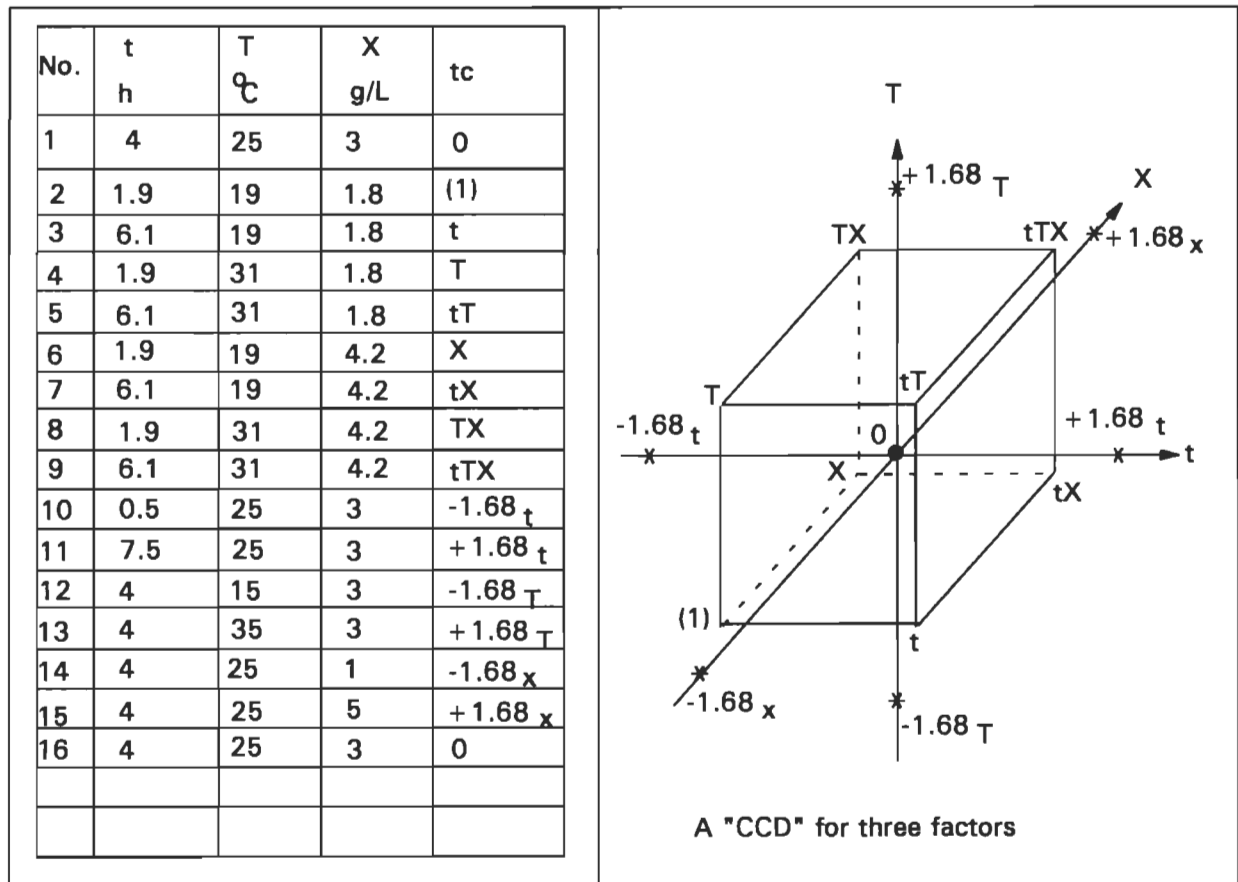
$$Centre(0) = \frac{extremehigh(+\alpha) + extremelow(-\alpha)}{2} \quad (9.5)$$

$$\pm 1 Level = Centre \pm \frac{(extremehigh - centre)}{\alpha(1.68)} \quad (9.6)$$

The real values of each level of the three variables are presented in **Table 9.7**. The experiment at the central point was run twice to provide the experimental error for statistic analysis.

**Table 9.7.** Levels of the three variables used in the CCD

Factors	Levels				
	$-a$	-1 (low)	0 (centre)	+1 (high)	$+a$
MLSS concentration (X), g/L	1	1.8	3	4.2	5
Treatment time (t), hours	0.5	1.9	4	6.1	7.5
Temperature (T), °C	15	19	25	31	35

**Fig. 9.10** Experimental design for the effects of treatment variables on RFA removals by the various mechanisms during batchwise aerobic treatment

**Table 9.8.** Experimental results for the effects of the three treatment variables on RFA removals by the various mechanisms

Run No.	Combinations	% overall	% adsorption	% bio-oxidation
1	0 (Zero)	62	25	37
2	(1) (1)	43	33	10
3	t (a)	62	26	36
4	T (b)	63	29	34
5	tT (ab)	77	22	55
6	X (c)	67	48	19
7	tX (ac)	80	41	39
8	TX (bc)	64	37	27
9	tTX (abc)	82	31	51
10	-1.68 <sub>t</sub> (- <i>aa</i> )	54	35	19
11	+ 1.68 <sub>t</sub> (+ <i>aa</i> )	68	21	47
12	-1.68 <sub>T</sub> (- <i>ab</i> )	55	35	20
13	+ 1.68 <sub>T</sub> (+ <i>ab</i> )	80	27	53
14	-1.68 <sub>x</sub> (- <i>ac</i> )	41	30	18
15	+ 1.68 <sub>x</sub> (+ <i>ac</i> )	85	31	54
16	0 (Zero)	63	29	34

The experimental results obtained are presented in **Table 9.8**. Statistic analysis of the experimental results was performed using the program "Stagraphics "(version 5.0). The significance of the main effect of each variable was analyzed on the basis of the total error, using the F-test technique. Results from the statistic analysis are presented in **Table 9.9**, and plotted in Figs. 11, 12, and 13 using the correlations 9.7 - 9.9 between the responses and the variables in real value.

#### 9.4.5.1 Effects of treatment variables on overall removal of RFA

Statistical analysis of the results (**Table 9.9**) shows that treatment time, temperature and MLSS concentration in the ranged studied significantly (at 5%) affect the overall removal; increasing these three variables in the range studied generally enhanced the overall removal of the RFA (Fig. 11a to c). The latter two variables also produced a significant interaction effect (at 10%) on the removal (Fig. 11c). Other effects on the removal were not significant.

By removing and combining the non-significant effects into the estimated total error and re-analyzing the results, the following relationship between the overall removal and the treatment variables, as expressed by equ. (9.7), was obtained with a correlation coefficient of 0.95.

$$\begin{aligned} \text{Overall removal (\%)} = & - 38.02 + 3.09[\text{time}] + 2.74[\text{temp}] + 22.70[\text{MLSS}] \\ & - 0.61[\text{temp}][\text{MLSS}] \end{aligned} \quad (9.7)$$

#### 9.4.5.2 Effects of treatment variables on sludge adsorption :

Treatment time, temperature and MLSS concentration induced a significant linear main effect on RFA adsorption in the range studied (at 5, 5 and 1 %, respectively, in **Table 9.9**). An increase in MLSS concentration significantly enhanced the adsorption (Fig. 9.12c); however, prolonging treatment time and raising temperature reduced the adsorption (Figs. 9.12a and b). The interaction effects among these three variables in the ranges studied were not significant. The correlation ( $r = 0.92$ ) between the adsorption and the treatment variables can be expressed by the following equ. (9.8) :

$$\begin{aligned} \text{\% Removal of RFA by adsorption mechanism} \\ = 39.67 - 1.73[\text{time}] - 0.53[\text{MLSS}] + 3.75[\text{temp}] \end{aligned} \quad (9.8)$$

#### 9.4.5.3 Effects of treatment variables on bio-oxidation of RFA

Both treatment time and temperature brought about a significant linear main effect at 1% on the bio-oxidation of RFA; prolonging treatment time or raising temperature in the range studied enhanced bio-oxidation of RFA (Fig. 9.13). The effect of MLSS concentration on the bio-oxidation was also distinct (at 10%). Increasing MLSS concentration improved the removal by bio-oxidation. The following equation (9.9) was obtained for expressing the relationship between the bio-oxidation and the treatment variables :

$$\% \text{ bio-oxidation} = -32.36 + 4.81[\text{time}] + 1.45[\text{temp}] + 3.86[\text{MLSS}] \quad (9.9)$$

### 9.5 Conclusions

The following conclusions can be drawn based on the results presented.

- 1) The RFA in the CTMP effluent, and also possibly in other pulp and paper mill effluents, during aerobic biological treatment are removed by three mechanisms : biooxidation by microorganisms, adsorption onto sludge and air oxidation. Biooxidation is the main removal mechanism. The removal mechanism of adsorption onto sludge is very important when the treatment time is very short. Air oxidation plays a minor role for the elimination of RFA.
- 2) The adsorption isotherm of RFA onto sludge can be represented by both Langmuir and Freundlich models. The overall RFA removal rate in batch aerobic biotreatment followed a zero order reaction model under the conditions studied.
- 3) Increase in MLSS concentration significantly enhances the adsorption of RFA onto the sludge. However, extending treatment time and raising temperature enhance the bio-oxidation of RFA but proportionally reduce the adsorption.

**Table 9.9.** Effects of the treatment variables on the RFA removals by the various mechanisms  
- Results of statistical analysis

Effect	Estimated effects						df	Mean squares			F-ratios calculated			Significance		
	% overall		% ad		% bio			% Overall	% ad	% Bio	% overall	% ad	% Bio	% overall	% ad	% Bio
	Effect	Std Er	Effect	Std Er	Effect	Std Er										
Average	62.2	± 4.9	26.6	± 3.2	35.6	± 6.1										
t : time	13.0	± 3.8	-7.3	± 2.5	20.2	± 4.75	1	574.1	179.7	1396.3	11.79	8.67	18.35	2.5%	5%	1%
T : temperature	11.0	± 3.8	-6.4	± 2.5	17.4	± 4.7	1	412.4	138.3	1028.2	8.47	6.67	13.52	5%	5%	1%
X : MLSS	18.0	± 3.8	9.0	± 2.5	9.3	± 4.7	1	1107.8	276.5	292.7	22.76	13.34	3.85	1%	1%	10%
tT	0.3	± 4.9	0.5	± 2.5	-0.3	± 6.2	1	0.1	0.5	0.1	0	0.02	0.00	n.s	n.s	n.s
tX	-0.7	± 4.9	0	± 3.2	-0.7	± 6.2	1	1.1	0	1.1	0.02	0	0.01	n.s	n.s	n.s
TX	-8.7	± 4.9	-3.0	± 3.2	-5.8	± 6.2	1	153.1	18.0	66.1	3.15	0.87	0.87	10%	n.s	n.s
tt	-0.4	± 4.6	2.8	± 3	-2.4	± 5.7	1	0.5	18.1	13.8	0.01	0.87	0.18	n.s	n.s	n.s
TT	5.0	± 4.6	4.9	± 3.0	0.1	± 5.7	1	58.6	55.9	0	1.20	2.7	0	n.s	n.s	n.s
XX	1.8	± 4.6	2.1	± 3.0	0.1	± 5.7	1	7.9	10.1	0	0.16	0.49	0	n.s	n.s	n.s
Total error	--	--	--	--	--	--	6	48.7	20.7	76.1	--	--	--	--	--	--
R <sup>2</sup>	0.942		0.984		0.954											
R <sup>2</sup> -adjusted	0.851		0.960		0.884											

$$F_{0.01,1,6} = 13.75; \quad F_{0.05,1,6} = 5.99; \quad F_{0.1,1,6} = 3.78$$

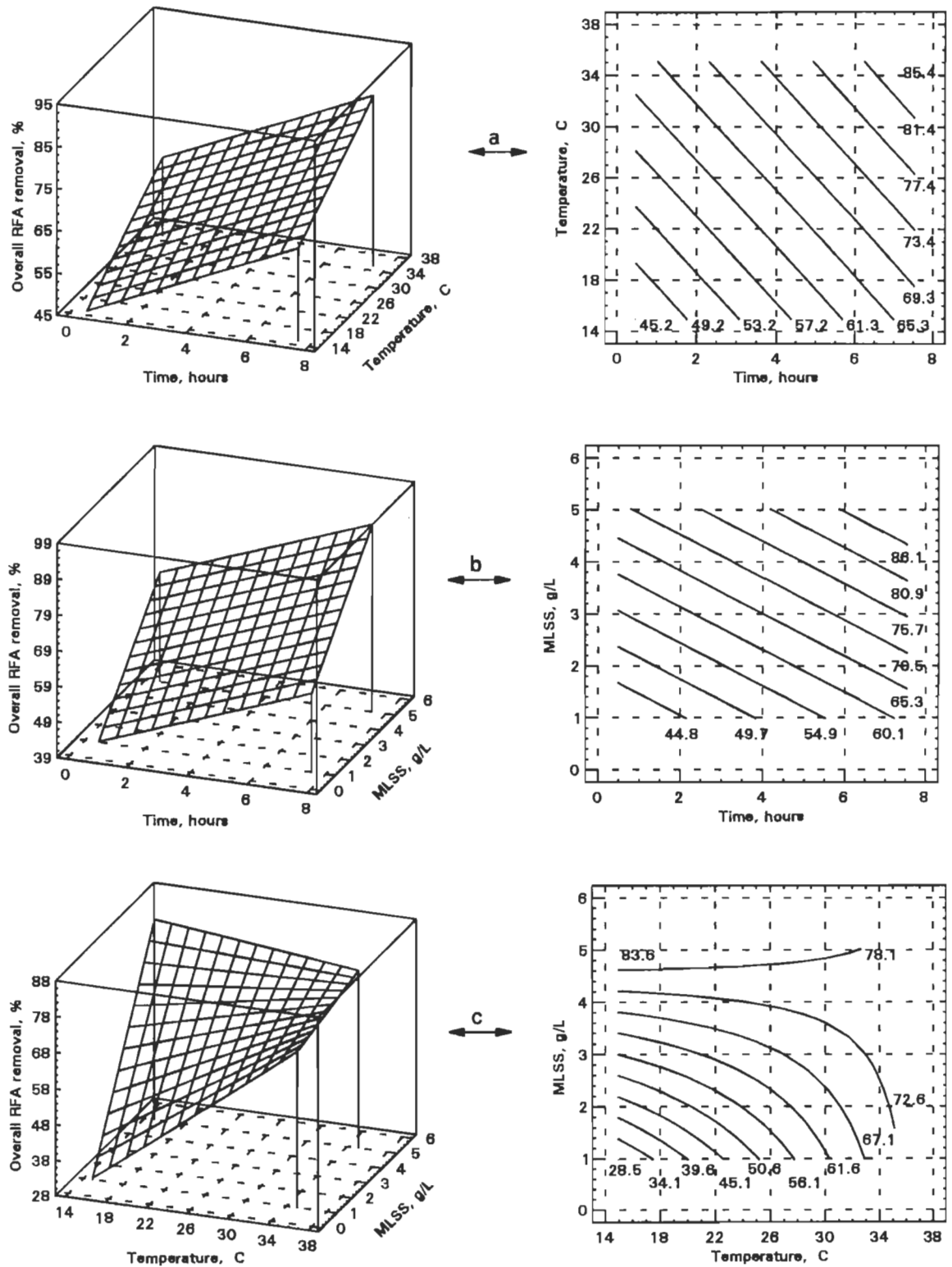


Fig. 9.11 Surface and contour of overall RFA removal - Effects of treatment time, temperature and MLSS concentration



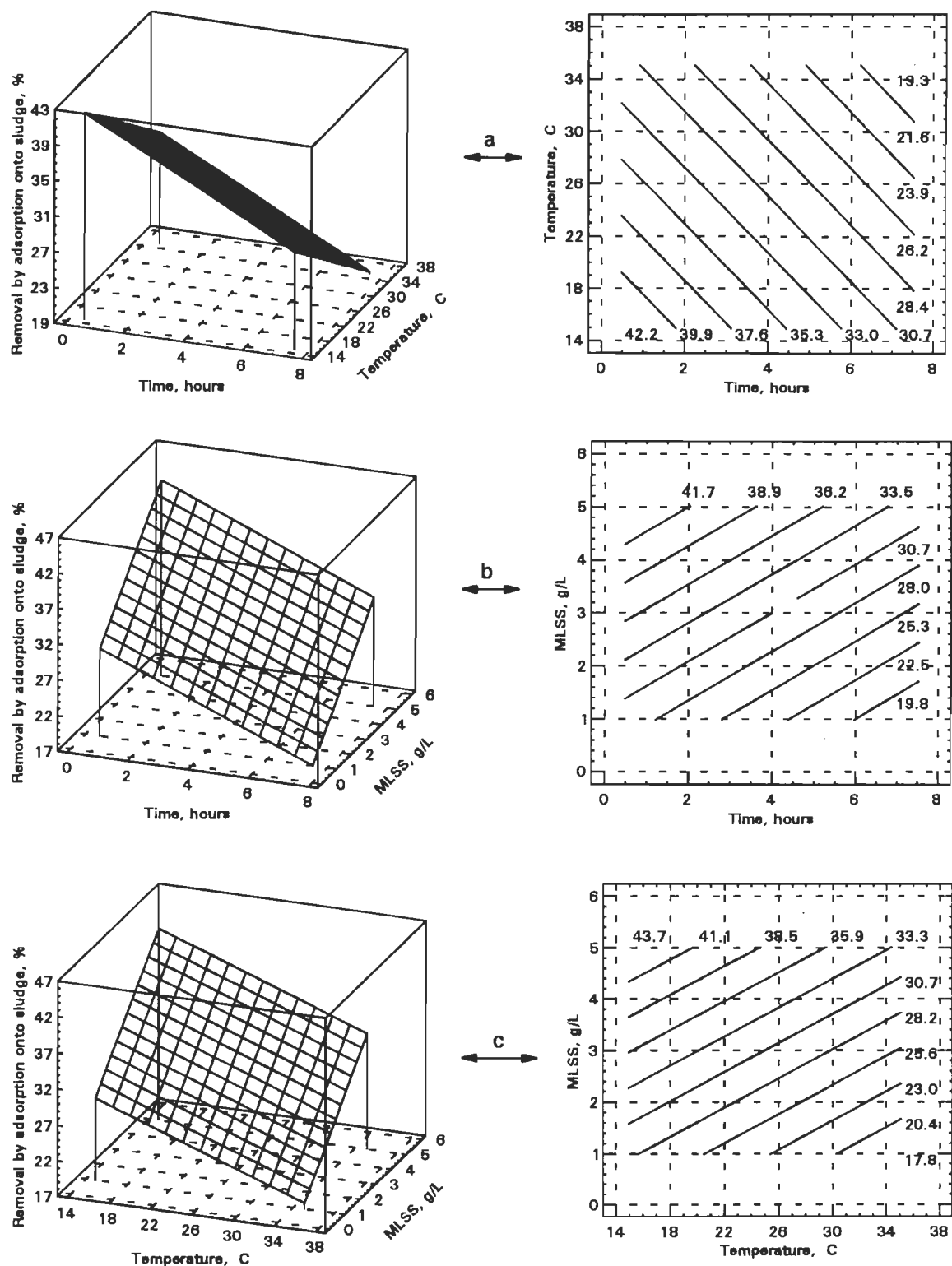


Fig. 9.12 Surface and contour of RFA removal by adsorption onto sludge  
- Effects of treatment time, temperature and MLSS concentration

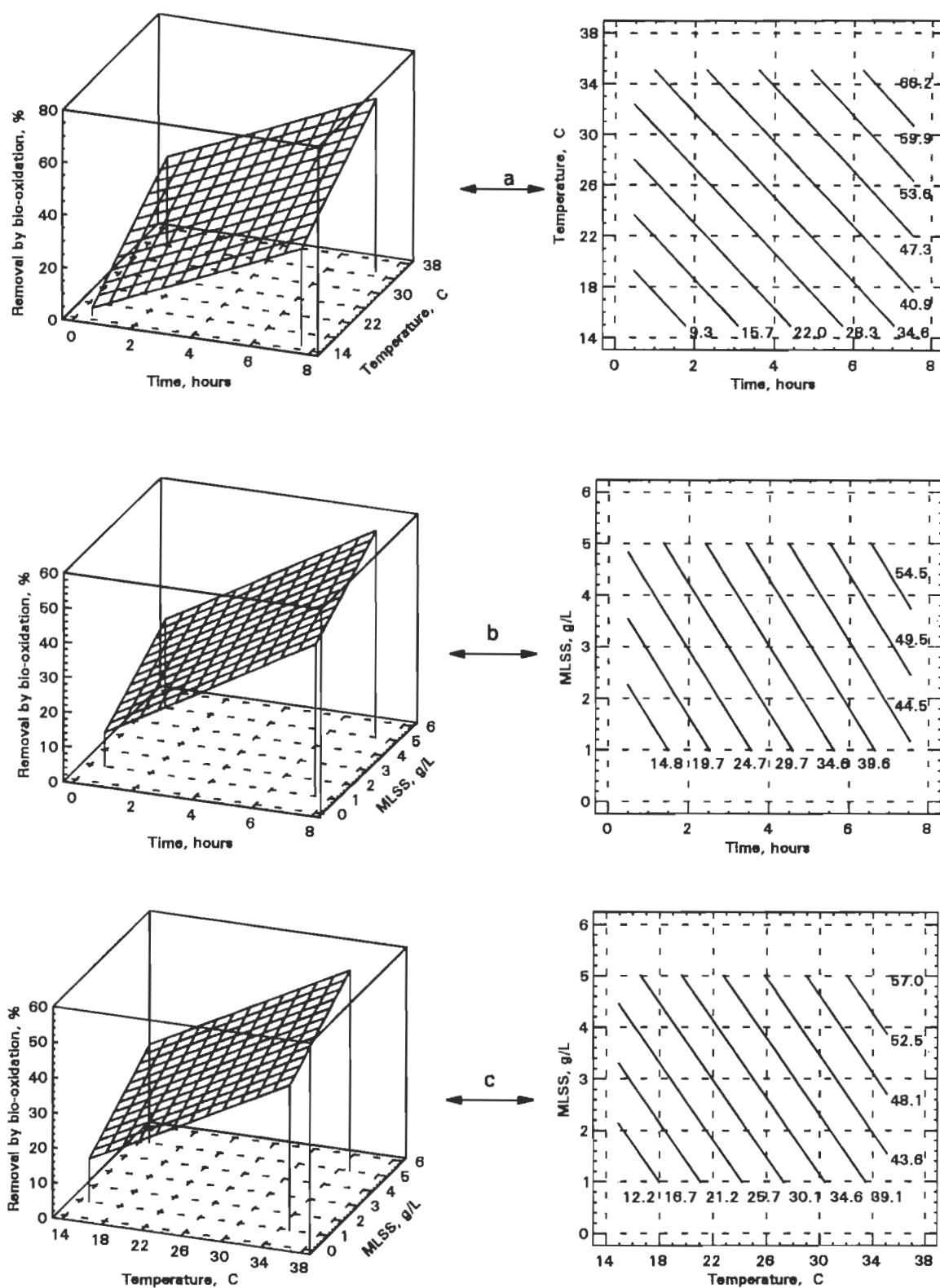


Fig. 13 Surface and contour of RFA removal by bio-oxidation - Effects of treatment time, temperature and MLSS concentration

## CHAPTER 10

### GENERAL CONCLUSIONS

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Results of this research have shown that the operating conditions affect significantly the design, operation and behaviour of the two-stage anaerobic-aerobic system for the CTMP effluents studied. In general, operating the anaerobic stage in a sensitive hydraulic retention time range, in which the operation is very sensitive to the variation of the time caused by the change in feed flowrate, could be one of the reasons for unstable operation encountered sometimes during the treatment.

Either the total hydraulic retention required for or the overall  $BOD_5$  removal achieved from the two-stage treatment of the CTMP effluent can be optimized (i.e, minimized or maximized) with respect to the removal of  $BOD_5$  in the anaerobic stage. The corresponding optimal reactor volume ratio can thus be determined.

The resin and fatty acids in the CTMP effluent are removed by three mechanisms occurring at the same time during aerobic biological treatment; they are : bio-oxidation by microorganisms, adsorption by biosolids and air oxidation.

The CTMP effluent  $BOD_5$  removal rates in both anaerobic treatment (stage) and aerobic treatment (stage) follow well a first order reaction kinetics. The RFA removal rate in aerobic treatment (stage) can be well described by the kinetics of a first order reaction whereas that in anaerobic treatment (stage) follows approximately only the Monod model. Anaerobic treatment (stage) produces poor RFA removal whereas aerobic treatment (stage) is very effective for this removal from the CTMP effluent.

The following specific conclusions can be drawn from the results of this research.

### **10.1 Characterization of pollutants at source for the first mill studied**

- 1) For the first mill investigated, there were four source effluents containing very high concentrations of BOD<sub>5</sub>, COD and RFA. They were the CTMP washing effluent, clear and cloudy filtrates from vacuum disc filter, and dilution water. Among these effluents, the CTMP washing effluent has the highest concentration (45 mg/L) and loading (3.3 mt/d) of RFA and thus was selected for biological treatment in this research.
- 2) The mill discharges about 38 t/d (63.3 Kg/ADT) BOD<sub>5</sub>, 0.26 t/d (0.43 Kg/ADT) RFA, 54 t/d (90 Kg/ADT) COD and 7.5 t/d (12.5 Kg/ADT) TSS. from its primary clarifier to the receiving water.
- 3) The ratio of BOD<sub>5</sub>/COD in the effluent from this mill is about 0.5. Thus, the effluents can be easily biotreated.
- 4) The relative proportions of individual resin and fatty acids in the seventeen source effluents are quite constant with a little variability. Among the resin acids, dehydroabiatic acid is the dominant specie, accounting for about 37% of the total amount.

### **10.2 Aerobic and anaerobic treatments**

#### **10.2.1 Aerobic Treatment**

- 1) An hydraulic retention time longer than two days is not required for better pollutant removals. A decrease of hydraulic retention time in the range of 0.5 to 2 days results in a significant drop in the removals of pollutants, except that for RFA. About 88% of BOD<sub>5</sub> and 95% of RFA can be removed from the CTMP effluent using a short hydraulic retention time of 0.5 day.

pH in the range of 5 to 8 has no negative effect on the removals of BOD<sub>5</sub> and RFA.

In the range of 10 and 50 °C, temperature has no influence on RFA removal, however, it exerts significant effects on the removals of other pollutants, as expected. From 40 to 50°C, the removals of pollutants except that for RFA decrease drastically and filamentous bacteria developed in the system. Therefore, temperature above 40°C is not suitable for aerobic treatment of the CTMP effluent treatment.

The level of dissolved oxygen in the range studied does not have influence on the removals of BOD<sub>5</sub> and RFA. An increase in dissolved oxygen level always induce better removals of COD, LS and effluent colour.

- 2) Good sludge settling prevails for all the treatment conditions studied. The sludge volume indices obtained are low and range from 30 to 140 mL/g.
- 3) pH 7 and temperature 20 to 30°C appear to be the favourable environment conditions for aerobic biological treatment of the CTMP effluent. A dissolved oxygen level of about 2.5 mg/L is required for aerobic treatment of the effluent.

### 10.2.2 Anaerobic treatment

- 1) About 70 to 83 % of the BOD<sub>5</sub> and 55 to 65 % of the COD in the CTMP

effluent can be removed by the anaerobic treatment with a normal HRT of 0.5 to 1 days under the conditions studied. These levels of removals are comparable to those reported for full scale anaerobic treatments of pulp and paper mill effluents.

- 2) Anaerobic treatment was ineffective for RFA removal. With a normal HRT of 0.5 to 2 days, RFA removal by the treatment ranges from about 20 to 50%.
- 3) The biogas yield from the treatment ranges from 0.23 to 0.33 m<sup>3</sup>/kg of COD removed, with an average of around 0.26. The biogas produced contains 70 to 80% of methane.

### 10.3 Kinetics and design parameters

#### 10.3.1 Kinetics and design parameters for aerobic treatment

- 1) Removals of both BOD<sub>5</sub> and RFA by aerobic treatment (stage) can be described better by a first order reaction kinetics than by the Monod model.
- 2) The sludge yield coefficient found for the aerobic treatment of the CTMP effluent studied was 0.54 g MLSS/g BOD<sub>5</sub> removed.
- 3) The values of the other two design parameters  $a$  and  $b$ , for the evaluation of oxygen requirement, were 0.36 g O<sub>2</sub>/g BOD<sub>5</sub> removed and 0.28 g O<sub>2</sub>/g MLSS oxidized/day, respectively.
- 4) The coefficient obtained for the temperature effect for the treatment of the CTMP effluent studied is 1.028

### 10.3.2 Kinetics and design parameters for anaerobic treatment

- 1) Removal of  $BOD_5$  by anaerobic treatment of the CTMP effluent studied can be represented by a first order reaction kinetics, while RFA removal follows approximately the Monod model.
- 2) The sludge yield coefficient found for the anaerobic treatment of the CTMP effluent studied was about 0.08 g MLSS/g  $BOD_5$  removed

### 10.4 The behaviour and optimization of the two-stage treatment system

- 1) From the results of the effects of operating conditions on the behaviour of the treatment system, it would not be expected to obtain a high RFA removal from the CTMP effluent with a normal HRT of one or two days in the anaerobic stage.
- 2) In general, unstable operation of an anaerobic process could be due to the treatment carried out in an HRT range in which the operation is very sensitive to the variation in HRT caused by the change in feed flowrate.
- 3) Although the methods presented for both simulation of system behaviour and optimization of system design and operation were established for the two-stage treatment system studied, they should be also applicable to other types of two-stage anaerobic-aerobic treatment systems, provided that substrate removal rate in each stage follows either the kinetics of first order reaction or the Monod model.
- 4) If the above kinetic models are applicable, the simulation and optimization methods developed in this study can be applied to the two-stage treatment of other types of pulp and paper mill effluents as well.

### 10.5 Mechanisms of removing resin and fatty acids in the CTMP effluent during aerobic treatment

- 1) The RFA in the CTMP effluent during aerobic biological treatment are removed at the same time by three mechanisms : biooxidation by microorganisms, adsorption onto sludge and air oxidation. Biooxidation is the main removal mechanism. The removal mechanism of adsorption onto sludge is very important when the treatment time is very short. Air oxidation plays a minor role for the elimination of RFA.
- 2) The adsorption isotherm of RFA onto sludge can be represented by both Langmuir and Freundlich models.
- 3) Increase in MLSS concentration significantly enhances the adsorption of RFA onto the sludge. Extending treatment time and raising temperature enhance the bio-oxidation of RFA, but proportionally reduce the adsorption.



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