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EFFECT OF OPERATING CONDITIONS ON STEADY-STATE BEHAVIOR OF ACTIVATED SLUDGE IN PHENOLIC WASTEWATER TREATMENT

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Abstract

Steady-state behavior of activated sludge in phenolic wastewater treatment was observed and theoretically considered. The apparatus used in this experiment was a continuous perfect mixing tank where activated sludge was withdrawn continuously and auto-returned from a settling tank. To explain the data well, it must be taken into consideration that activated sludge consists of various species of microorganisms. Therefore, ecosystem and whole metabolism of activated sludge would be affected not only by environmental conditions (pH, temperature, DO, etc), but also by operating variables (dilution rate, inlet substrate concentration, etc.). In this study, the relation of whole metabolism of activated sludge between the case which activated sludge is regarded as a single species of microorganism and the case which activated sludge is regarded as various species of microorganisms was obtained. Seven empirical parameters in the kinetic equations which were introduced from the predator-prey interaction model were considered to be a function of various operating variables. By using this method, steady-state behavior of activated sludge in the phenolic wastewater treatment could be well explained; moreover, important information to design a practical process for phenolic wastewater treatment with activated sludge was obtained.

Key words : *phenolic wastewater treatment, activated sludge, effect of operating conditions, predator-prey interaction model, kinetic model.*

Introduction

The analysis of the behavior of activated sludge in wastewater treatment has been studied by many researchers. In most of these studies, activated sludge was regarded as a single species of microorganism. The kinetic models for a single species (Beltrame, *et al*, 1979; Monod, 1949) were used in these studies. In actuality activated sludge consists of various species of microorganisms. Therefore, ecosystem and whole metabolism of activated sludge would be affected not only by environmental conditions (pH, temperature, DO, etc.) but also by operating variables (dilution rate of wastewater, withdrawing rate of activated sludge, inlet substrate concentration, etc.) Furthermore the predator-prey interaction relation between two inhabitants in activated sludge should be considered to explain its steady-state behavior in wastewater treatment.

In this paper, we deal with phenolic wastewater, an example of industrial waste water including slowly-biodegradable and toxic materials. There has been analysis of the biological treatment of phenolic wastewater with a single species of microorganism (Howell and Jones, 1980; Simizu, *et al*, 1973) However, the studies on phenolic wastewater treatment with activated sludge concerned only with the basic data, and were not sufficient for theoretical analysis (Beltrame, *et al*, 1979; Fukuoka, *et al*, 1965; Radhakrishman and Sinha, 1974)

In this study, experiments were carried out with a continuous perfect mixing tank where activated sludge was withdrawn continuously and auto-returned from a settling tank. The steady-state behavior of activated sludge was observed and theoretically considered. The relation of whole metabolism of activated sludge between the case in which activated sludge is regarded as a single species of microorganism and the case in which activated sludge is regarded as various species of microorganism was obtained. Seven empirical parameters in the kinetic equations introduced from the predator-prey interaction model were considered as a function of various operating variables. By using this method, the experimental results could be well explained.

Experimental

A schematic of the apparatus is shown in figure 1. The aeration tank was a continuous perfect mixing tank. Activated sludge was auto-returned from the settling tank to the aeration tank by furnishing the inclined plate with the settling tank, and was also withdrawn continuously from the aeration tank. Activated sludge used in this experiment was collected from the drainpipe of the school of Science and

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Engineering, Waseda University, and acclimated to phenol.

The experimental conditions are shown in table 1. In this experiment, dilution rates of wastewater D $(=Q/V_a)$ were set at 0.20 and 0.28 h^{-1}. In each dilution rate, inlet phenol concentrations were varied for five levels from 200 to 1000 mg/l. Withdrawing rates of activated sludge from the aeration tank D_w $(=Q_w/V_a)$ were set from 0.047 to 0.070 h^{-1}. A steady state is reached when substrate concentration S, total MLSS concentration in the aeration tank X_T, and outlet MLSS concentration X_e are constant.

Phenol concentration was measured by the 4-aminoantipyrine method, and COD by the $KmnO_4$ method. Figure 8 in appendix shows the relation among phenol concentration, COD by the $KMnO_4$ method and COD by the $K_2Cr_2O_7$ method.

Result And Discussion

1. Initial arrangement of the experimental results.

The calculation of the overall specific growth rate (μ_T) and the overall specific COD removal rate $(\dot{V}_T)$ in the steady state were based on the following assumptions. Assumptions:

- The fluid in the aeration tank is perfectly mixed.
- The removal rate of phenol and the growth rate of activated sludge in the settling-tank are negligible compared to those of in the aeration tank.
- Bacteria are mainly washed out with effluent water from the settling tank; while-protozoa are negligible in effluent water.

On these assumptions, the equations of mass balance in the overall system in steady-state are given as follows.

Total activated sludge balance:

$$Va\mu_T X_T = QwX_T + (Q - Qw)\,Xe \qquad (1)$$

$$\mu_T = Dw + (D - Dw)\,\grave{E} \qquad (2)$$

Total substrate balance:

$$Qso = Va\surd_T X_T + QwS + (Q - Qw)\,S \qquad (3)$$

$$\gamma_T = \frac{D(S_o - S)}{X_T} \qquad (4)$$

The values of μ_T and $\surd_T$, respectively, were calculated from Eq.(2) and Eq (4), respectively.

When the total MLSS concentration in the aeration tank (X_T), the outlet MLSS concentration (Xe), the inlet COD concentration (S_o) and the outlet COD concentration (S) were measured.

The Monod model was hitherto applied for the analysis of kinetics concerned with a single species of microorganism.

$$\mu_T = \frac{\mu_{max}\,S}{K + S} \qquad (5)$$

According to Monod's equation (5), the relation between S and μ_T is shown in Figure 2. Eq (6) is derived by taking the reciprocal of both sides of Eq. (5).

$$\frac{1}{\mu_T} = \frac{K}{\mu_{max}}\left(\frac{1}{S}\right) + \frac{1}{\mu_{max}} \qquad (6)$$

The Lineweaver-Burk plot is shown in Figure 3. A plot of $1/\mu_T$ versus l/S did not yield a straight line, and it is difficult to derive the maximum value of overall specific growth rate (μ_{max}) and bacteria saturation constant (K) from Figure 3. If a straight line was forcibly drawn, μ_{max} and K, respectively, might be given as 0,16 h^{-1} and 7.1 mg/l. The sludge yield factor (Y) is obtained from a plot of μ_T against $\surd_T$.

$$\mu_T = Y \cdot \surd_T \qquad (7)$$

However, Figure 4 shows that their interrelation is also ambiguous. It is impossible to determine the accurate value of Y.

The experimental results could not be adequately analyzed using the Monod model which includes the assumption that activated sludge consists of a single species of microorganism. The cause for the discrepancy from this model is attributable to the fact that ecosystem and whole metabolism of activated sludge are affected by various operating conditions. Actually, this is confirmed by observating ecosystem of activated sludge with a microscope. The examples of photographs of observed activated sludge in the experiment are shown in Figures 5 (a) – (d). Table II shows the operating conditions of the experiment in Figures 5 (a) – (d). Protozoa (especially, *Arcella vulgaris Volticella alba, Epistylis sp*, etc.) inhabited very much under the condition that both the withdrawing rate (D) and inlet phenol concentration (Sp0) are low as shown in Figure 5(a). The number of protozoa decreased and that of zoogloea increased with both Dw and Sp0 increased as shown in Figure 5(d). Under the condition in high phenol concentration and high withdrawing rate, protozoa inhabited very few. Therefore, the data in this experiment are analyzed by the following manner.

2. Kinetic theory for growth of a multiple microorganism system.

Activated sludge consists of various species of microorganism that have various metabolic characteristics and show complex relation among them. In most of previous studies, however, activated sludge was regarded as a single species of microorganism. The monod model has been hitherto used for the analysis of activated sludge behavior by these researchers. This model should be originally applied to each species (shown by suffix i) of bacteria in activated sludge as follows.

$$\frac{dX_i}{dt} = (\mu_{max})_i\,\frac{S}{K_i + S}\,X_i\,, \; (i = 1,2,\ldots,m) \qquad (8)$$

Since the activated sludge consists of various species of bacteria, the overall growth rate of bacteria group which is obtained as experimental result is given by summing up the individual equations for each species as follows.

$$\frac{dX}{dt}=\frac{d}{dt}\left(\sum_{i=1}^{m}X_i\right)=\sum_{i=1}^{m}\left\{(\mu_{max})_i\frac{S}{K_i+S}X_i\right\} \tag{9}$$

Therefore, the relation between the cases which activated sludge is regarded as a single species of bacteria as shown by Eq. (5) and the case which activated sludge is regarded as various species of bacteria is as follows.

$$\mu_T=\frac{1}{X}\frac{dX}{dt}=\mu_{max}\frac{S}{K+S}=Eq\,(9) \tag{10}$$

Here, $(\mu_{max})_i$ and K_i are particular values of i the species of bacteria in the specified environmental condition.

In the case that the value of K_i is identical with regard to each bacteria, μ_{max} is given by the following equation :

$$\mu_{max}=\sum_{i=1}^{m}\left\{(\mu_{max})_i\frac{X_i}{X}\right\} \tag{11}$$

If individual values of $(\mu_{max})_i$, K_i and X_i of each bacteria can be measured, the overall growth rate of bacteria group would be calculated. But, these are unmeasureable as yet. Consequently, it may be forced to measure the overall metabolic characteristic such as μ_{max} which means the weighted average of $(\mu_{max})_i$ multiplying X_i/X, the existence ratio of each bacteria in the bacteria group. It is considered that the existence of each bacteria is affected by various operating conditions – for example, if retention time is very short, bacteria with a low growth rate are washed out from the aeration tank. In case of long retention time, however, bacteria with a low growth rate can also remain.

In the case that the value of $(\mu_{max})_i$ is also identical as well K_i, μ_{max} is not affected by any operating conditions. However, in the case of treatment for toxic wastewater like phenolic wastewater, the metabolic characters of each bacteria ($(\mu_{max})_i$ and K_i) are quite different one to another. In the latter case, since the existence ratio of each bacteria is affected by various operating conditions, the overall growth rate (μ_T), i.e. the overall metabolic characteristic (μ_{max} and K), of the bacteria group shown by Eq. (5) are apparently affected by various operating conditions according to Eq. (10).

Further, activated sludge consists of various species of protozoa as well as bacteria, and predator-prey interaction exists between bacteria and protozoa. It is more general that the predator-prey interaction model is taken into consideration. In this model, substrate is removed by bacteria, and bacteria are taken by protozoa. It should be considered that the predator-prey interaction is originally the relation between each species of bacteria and each species of protozoa. Assuming that Monod's equation can be applied to the growth rate of each species of protozoa in the same way as applied to that of bacteria, the equation for the growth rate of each species (shown by suffix j) of protozoa becomes:

$$\frac{dP_j}{dt}=\sum_{i=1}^{m}\left\{(\eta_{max})_{ij}\frac{X_i}{L_{ij}+X_i}\right\}P_j\,,\ (j=1,2) \tag{12}$$

where $(\eta_{max})_{ij}$ and L_{ij}, respectively, are the maximum value of specific growth rate and saturation constant in combination of i the species of bacteria (prey) and j the species of protozoa. Summing up the individual equations for each species of bacteria and protozoa, the overall growth rate of the protozoa group is given by:

$$\frac{dP}{dt}=\frac{d}{dt}\left(\sum_{j=1}^{n}P_j\right)=\sum_{j=1}^{n}\sum_{i=1}^{m}\left\{(\eta_{max})_{ij}\frac{X_i}{L_{ij}+X_i}P_j\right\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(13)$$

Therefore, the relations between the case which activated sludge is conventionally considered to consist of only two inhabitants (a single species of bacteria and protozoa) and the case which activated sludge is considered to consist of various species of bacteria and protozoa are as follows.

The relation of the protozoa growth rate :

$$\frac{dP}{dt}=\eta_{max}\frac{X}{L+X}P=\sum_{j=1}^{n}\sum_{i=1}^{m}\left\{(\eta_{max})_{ij}\frac{X_i}{L_{ij}+X_i}P_j\right\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(14)$$

The relation of the bacteria growth rate:

$$\frac{dX}{dt}=\mu_{max}\frac{S}{K+S}X-\frac{\eta_{max}}{W}\frac{X}{L+X}P$$
$$=\sum_{i=1}^{m}\left\{(\mu_{max})_i\frac{S}{K_i+S}X_i\right\}-\sum_{j=1}^{n}\sum_{i=1}^{m}\left\{\frac{(\eta_{max})_{ij}}{W_{ij}}\frac{X_i}{L_{ij}+X_i}P_j\right\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(15)$$

The relation of the specific growth rate of total MLSS:

$$\mu_T=\frac{1}{X_T}\frac{dX_T}{dt}=\frac{1}{X_T}\left(\frac{dX}{dt}+\frac{dP}{dt}\right)$$
$$=\mu_{max}\frac{S}{K+S}\Phi_B+\frac{W-1}{W}\eta_{max}\frac{\Phi_B X_T}{L+\Phi_B X_T}(1-\Phi_B) \qquad \ldots\ldots\ldots\ldots\ldots\ldots(16)$$

Consequently, η_{max} means that weighted average of $(\eta_{max})_{ij}$ multiplying P_j/X_T, the existence ratio of each protozoa in total MLSS. W is an average of W_{ij}, yield factor of each protozoa, which also means the weight for η_{max}. Therefore, in the case that the respective metabolic characteristic ($(\eta_{max})_{ij}$, L_{ij}, and W_{ij}) of each protozoa have definitely various values in combination of i^{th} species of bacteria and j th species of protozoa, since the existence ratio of each bacteria and protozoa are affected by various operating conditions as mentioned previously, the overall specific growth rate (μ_T), i.e. the overall metabolic characteristic (μ_{max}, K, η_{max}, L, and W), of activated sludge are apparently affected by various operating conditions according to Eq. (16).

The specific substrate removal rate (v_T) can also be written as follows.

$$v_T = -\frac{1}{X_T}\frac{dS}{dt} = \frac{\mu_{max}}{Y}\frac{S}{K+S}\Phi_B = \sum_{i=1}^{m}\left\{\frac{(\mu_{max})_i}{Y_i}\frac{S}{K_i+S}\frac{X_i}{X_T}\right\} \qquad (17)$$

Y is an average of Y_i, yield factor of each bacteria, which means the weight for μ_{max}.

It can be concluded according to Eq. (16) and Eq. (17) that the seven empirical parameters of the overall metabolic characteristics of activated sludge (μ_{max}, K, η_{max}, Φ_B, and Y) are affected by various operating conditions such as dilution rate of wastewater (D), withdrawing rate of activated sludge (D_w), inlet substrate concentration (S_0).

3. Rearrangement of the experimental result and discussion

The following consideration is based on the predator-prey interaction model mentioned above. If the microbiological ecosystem is affected by various operating conditions such as dilution rate of wastewater (D), withdrawing rate of activated sludge (D_w) and inlet substrate concentration (S_0) whole metabolism of microorganism in activated sludge should be transformed. Therefore, we interrelate the seven parameters of metabolic characteristic (μ_{max}, K, η_{max}, L, W, Φ_B, and Y) given in Eq. (16) and Eq. (17) to the various operating conditions according to the curve-fitting method using a computer. In this study, to acquire a sense of apparent value corresponding to the parameters defined in the predator-prey interaction model, we put a prime after the seven parameters experimentally given by curve-fitting method. This is because the latter parameters might be physically far from the original meaning of the former parameters. The equations given by the curve-fitting method are shown in table III.

The comparisons of experimental data with the values calculated according to this method are shown in Figures 6 (a) – (e). After all, the experimental results were clearly explained by this method where it was taken into consideration that ecosystem and whole metabolism of activated sludge was affected by operating conditions.

Further, we should like to add that the equations estimated above have no theoretical basis in particular, and that they vary with differences of characteristics in the system, such as a variety of activated sludge, a kind of wastewater. Consequently, it is meaningless to apply the parameters and equations obtained in this study to another system.

However, it is very important to make it clear that the various parameters in the kinetic equations based on predator-prey interaction models are affected by various operating conditions – dilution rate of wastewater, withdrawing rate of activated sludge, inlet substrate concentration, etc, the information useful for the design of the equipment in this system can be obtained from these equations. Examples are shown in Figure 7 (a) – (d). The plot of the MLSS ratio (ξ) versus the total MLSS concentration (X_T) at given inlet COD concentration (S_0) is shown in Figure 7 (a). The increase in S_0 at given X_T causes the increase in ξ, which means that the sedimentation characteristics of activated sludge goes into the unfavorable condition. The bacteria ratio (Φ_B) increases with the increase in ξ as shown by Eq. (23) in table III. This result could well explain that the number of protozoa decreased in high phenol concentration. The relation between the overall specific growth rate (μ_T) and S_0 at given X_T is shown in Figure 7 (b). The value of μ_T increases until S_0 goes up to 800 mg/l, while it is nearly constant above this concentration. In contrast, the effect of X_T on μ_T is marked. Within the range used in this experiment, the value of μ_T is inversely proportional to X_T. It is considered that the bacteria ratio (Φ_B) increases with the decrease in X_T at given S_0, from the viewpoint of Figure 7 (a), and hence tahe value of μ_T increases because of the increase in dispersed bacteria which removes the substrate at the grate rate. The relation between the overall specific COD removal rate (v_T) and S_0 at given X_T is shown in Figure 7 (c). The value of v_T increases with the increase in S_0 at given X_T. The plot of outlet COD concentration (S) versus S_0 at given X_T is shown in Figure 7 (d). The value of S increases with the increase in S_0 at given X_T, as well known.

Conclusions

1. The data concerning the steady-state behavior of activated sludge in phenolic wastewater treatment could not be adequately explained by the Monod model, which includes the assumption that activated sludge consists of a single species of microorganism.
2. The relation of whole metabolism of activated sludge between the cases which activated sludge is regarded as a single species of microorganism and the case which activated sludge is regarded as various species of microorganism was obtained.
3. The kinetic equations were introduced from the predator-prey interaction model, which considered that activated sludge consists of various species of microorganism. Seven empirical parameters in the kinetic equations were estimated from the experimental results and correlated with the operating variables.
4. It is shown that the kinetic equations with the correlation mentioned above explain well the experimental result and give important information to design a practical process for treatment of phenolic wastewater with activated sludge.
5. It is concluded that the overall apparent metabolism of activated sludge is affected not only by environmental conditions (pH, temperature, DO,

etc), but also by operating variables (dilution rate of wastewater, withdrawing rate of activated sludge, inlet substrate concentration, etc.).

Nomenclature

A	defined by Eq. (21)
D	dilution rate of wastewater ($D = Q/V_a$) [h^{-1}]
D_w	withdrawing dilution rate of activated sludge ($D_w = Q_w/V_a$) [h^{-1}]
K	bacteria saturation constant [mg/l]
L	protozoa saturation constant [mg/l]
P	protozoa concentration [mg/l]
Q	volumetric flow rate of wastewater [l/h]
Q_w	volumetric withdrawing flow rate of activated sludge [l/h]
S	outlet COD concentration [mg/l]
S_0	inlet COD concentration [mg/l]
S_p	outlet phenol concentration [mg/l]
S_{p0}	inlet phenol concentration [mg/l]
t	time [h]
V	tank volume [l]
W	protozoa yield factor [-]
X	bacteria concentration [mg/l]
X_e	outlet MLSS concentration [mg/l]
X_T	total MLSS concentration in aeration tank [mg/l]
Y	bacteria yield factor based on COD concentration [-]
η	protozoa specific growth rate [h^{-1}]
μ	bacteria specific growth rate [h^{-1}]
μ_T	overall specific growth rate [h^{-1}]
ν_T	overall specific COD removal rate [h^{-1}]
ξ	ratio of outlet MLSS concentration to total MLSS concentration in aeration tank ($\xi = X_e/X_T$) [-]
Φ_B	ratio of bacteria concentration to total MLSS concentration in aeration tank ($\Phi_B = X/X_T$) [-]

Subscripts

a	aeration tank
cal	calculational value
exp	experimental value
i	species of bacteria
j	species of protozoa
max	maximum value
s	settling tank
'	apparent value

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Appendix

In this paper, inlet and outlet COD concentration were expresed as the values measured by the $KMnO_4$ method according to the Water Pollution Control Law in Japan. However, the $K_2Cr_2O_7$ method is widely used in the world. Figure 8 shows the relation among the inlet phenol concentration, COD_{Mn} by the $KMnO_4$ method and COD_{Cr} by the $K_2Cr_2O_7$ method. The value of COD_{Cr} is 70 mg/l larger than of COD_{Mn} in the range of this experiment.

Tabel 1. Experimental Conditions

(a) Environmental conditions

pH	7.0
Temperature	30° C
DO	> 1 mg/l

(b) Artificial wastewater composition

Components	Concentration [g/l]
C_6H_5OH	0.2 – 1.0
$(NH_4)_2SO_4$	0.5
K_2HPO_4	1.0
$MgSO_4 \cdot 6H_2O$	0.2
$FeCl_3 \cdot 6H_2O$	0.02
Pepton	0.1

Tabel 2. Operating conditions of the experiment in Figure 5

Fig. No.	D [h^{-1}]	D_w [h^{-1}]	S_{p0} [mg/l]	S_0 [mg/l]
5 (a)	0.28	0.047	216	449
5 (b)	0.28	0.047	388	849
5 (c)	0.28	0.070	208	480
5 (d)	0.28	0.070	448	1025

Tabel 3. Equations given by this method

$$\mu'_{max} = f(D) \qquad (18)$$

$$f(D) = D \qquad (\text{at } D = 0.28\ h^{-1}) \qquad (19)$$

$$f(D) = 1.01\ D \qquad (\text{at } D = 0.20\ h^{-1}) \qquad (20)$$

$$-\frac{W'-1}{W'}\eta'_{max} \equiv A = 0.045 + 35.0(D - D_w)^4 \qquad (21)$$

$$L' = \frac{1}{0.0034 + 2.27(D - D_w)^4} \qquad (22)$$

$$\Phi'_B = \xi + a\lambda + b\lambda^2 - \lambda^3\ [c + d\xi + e\xi^2 + f\xi^3] \qquad (23)$$

where : $\xi = X_e / X_T$, $\lambda = 1 - \xi$

$a = 0.28$, $b = 1.07$, $c = 0.90$, $d = 0.90$, $e = 0$, $f = 1.90$

$$K' = 0.2\ \text{mg/l} \qquad (24)$$

$$\frac{1}{Y'} = 5.2\left(\frac{S_0}{X_T}\gamma D_w\right)^{0.78} - \frac{S}{X_T}\sqrt{\frac{S_0 - S}{S}\Phi_B'} \qquad (25)$$

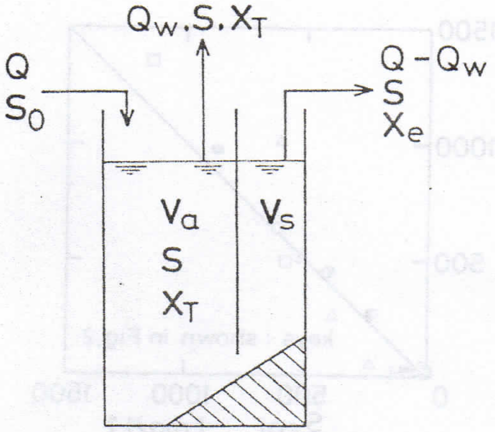

Fig. 1 : Schematic of experimental apparatus

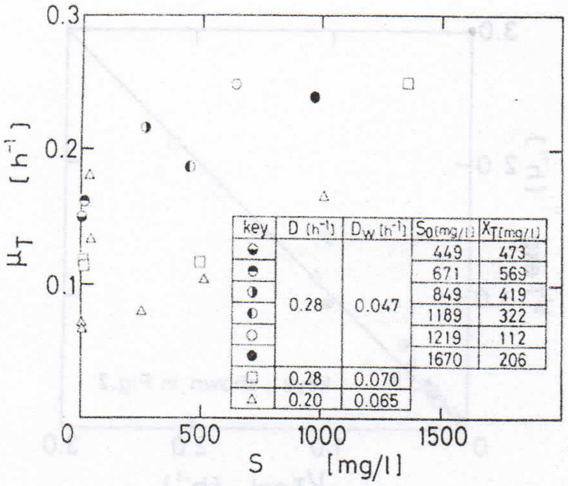

Fig. 2 : Relation between outlet COD conc. and overall specific growth rate.

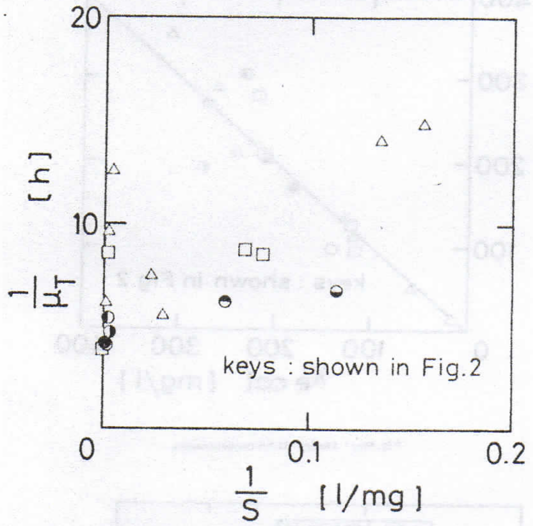

Fig. 3 : Lineweaver-Burk plot experimental data.

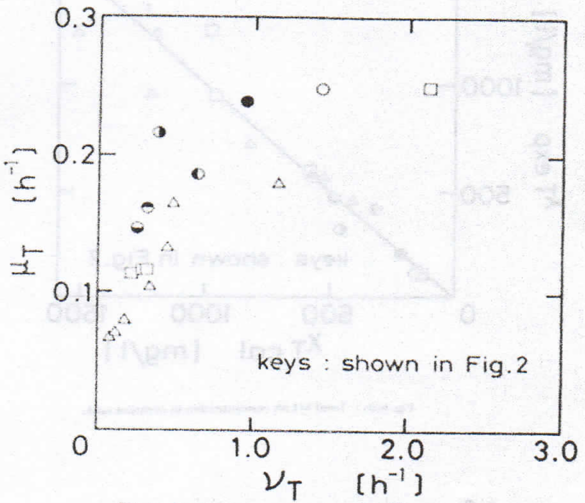

Fig. 4 : Relation between overall specific COD removal rate and Overall specific growth rate.

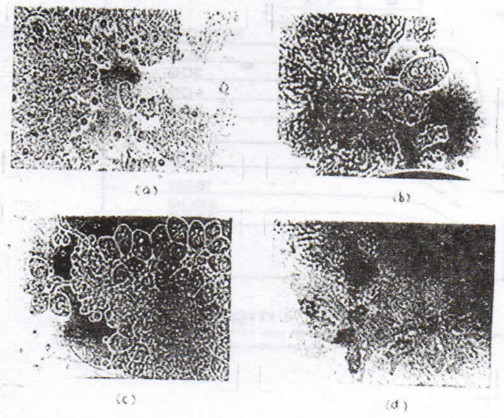

Fig. 5 : Examples of observed activated sludge in the experiment

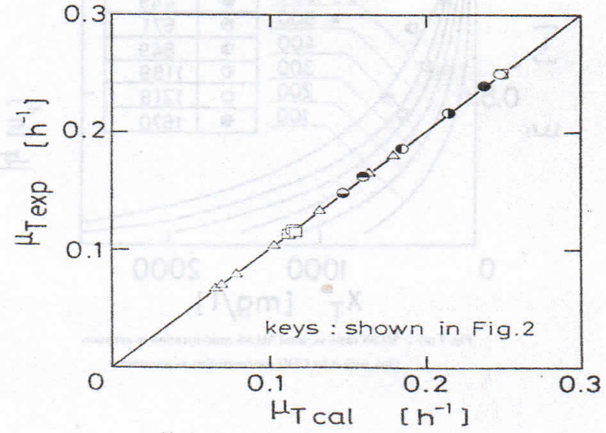

Fig. 6 : Comparison of experimental data with calculation By this method. 6(a) : Overall specific growth rate.

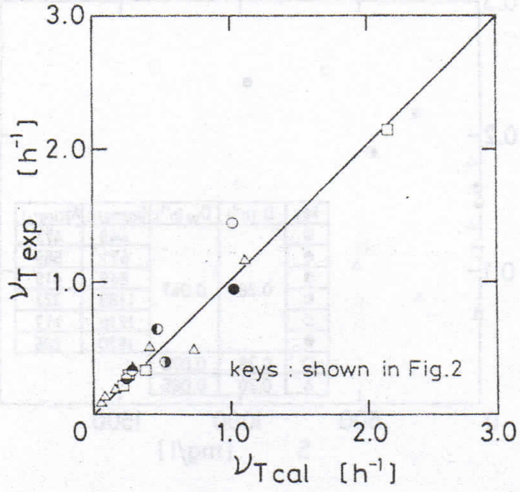

Fig. 6(b) : Overall specific COD removal rate.

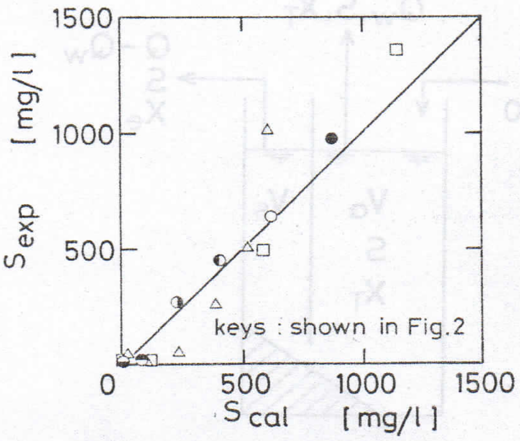

Fig. 6(c) : Outlet COD concentration.

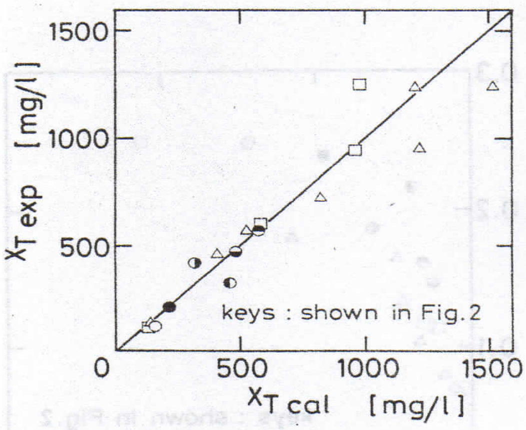

Fig. 6(d) : Total MLSS concentration in aeration tank.

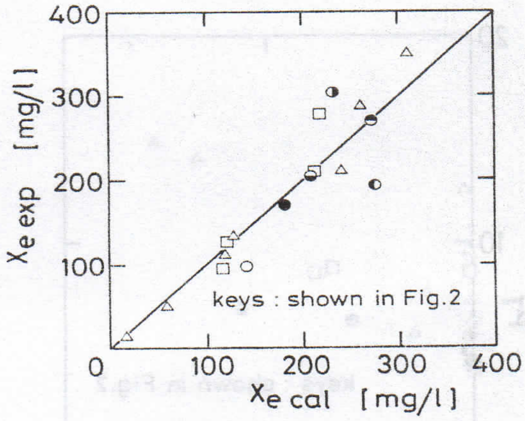

Fig. 6(e) : Outlet MLSS concentration.

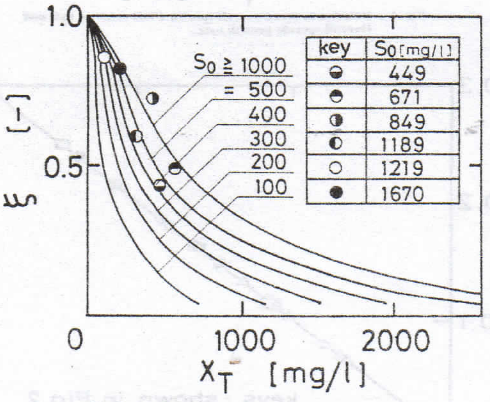

Fig. 7 (a) : MLSS ratio vs. total MLSS concentration in aeration tank with inlet COD concentration as parameter

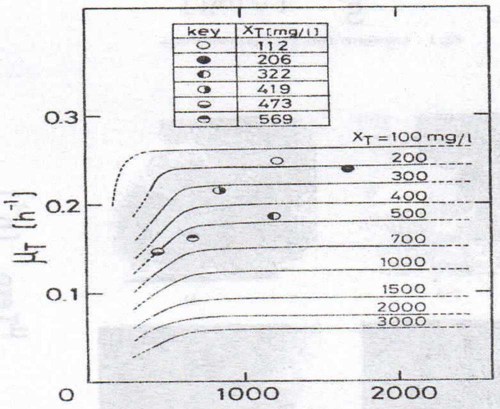

Fig. 7 (b) : Overall specific growth rate vs. inlet COD concentration with total MLSS concentration in aeration tank as parameter

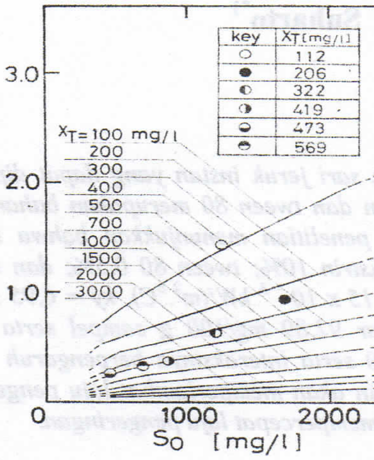

Fig. 7 (c) : Overall specific COD removal rate vs. inlet COD concentration with total MLSS concentration in aeration tank as parameter

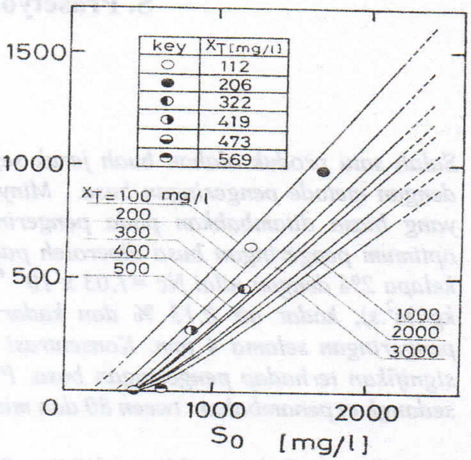

Fig. 7 (d) : Outlet COD concentration vs. inlet COD concentration with total MLSS concentration in aeration tank as parameter

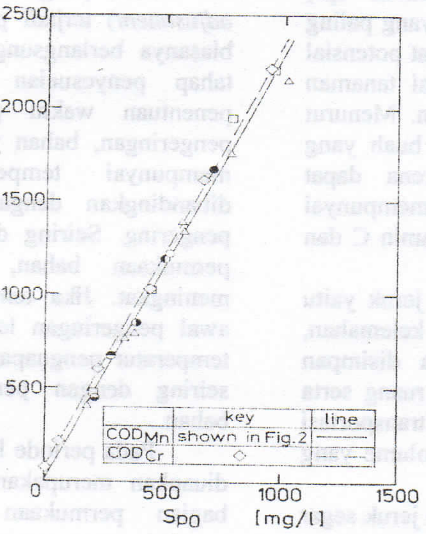

Fig. 8 : Relation among phenol concentration, COD_{Mn} by $KMnO_4$ method and COD_{Cr} by K_2Cr_2O-method