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Kinetic study of anaerobic suspended growth reactor for the treatment of oily wastewater

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The present work reported on determination of the kinetic parameters for biological treatment of synthetic oily wastewater (petroleum based) under batch mode in a laboratory scale anaerobic suspended growth reactor. In this context, a comparison was made using the literatures on various experimental conditions. The increase in the concentration of biomass was marginal in each batch as the growth rate of the same is slow in oily wastewater. It is essential to determine the biochemical kinetic constants in order to understand the degradation potential of biological treatment process. As per the experimental results for the removal of oil from synthetic oily wastewater in anaerobic reactor, various kinetic constants were determined using Monod's approach. The values of half saturation constant (K_s), maximum specific substrate utilization rate (k), yield coefficient (Y) and endogenous decay constant (k_d) were found to be about 202.23 mg/L, 0.01/d, 0.98 mg MLSS/mg oil and 0.001/d respectively.

Keywords: Anaerobic treatment, suspended growth reactor, oil removal, kinetic study, Monod's kinetic model.

Introduction

Anaerobic treatment is a viable technique which has been widely utilized for the treatment of wastewater over a century. Wastewater treatment through anaerobic process has numerous advantages over conventional aerobic treatment process, i.e. less requirement of nutrient, limited cost, formation of methane gas from the organic pollutants and energy saving[1,2]. It has been studied in the literature that oil carrying wastewater can be treated effectively by anaerobic process because of its exceptional capability for degradation of complex waste matter. Various anaerobic reactors which have been utilized for the treatment of oil containing wastewater in the literature include anaerobic filter, upflow anaerobic sludge fixed film reactor (UASFF), upflow anaerobic sludge blanket (UASB), stationary packed bed, expanded bed and fluidized bed reactors[3–5].

The function as well as development of various anaerobic treatment systems can be governed by process kinetics which helps in optimizing the performance as well as reactor design, stability in operation and better process control[6,7]. Basically, the relationship between the rate of growth as well as substrate utilization relates biological growth kinetics and has been utilized in most of the earlier studies[8]. Monod's model is the most commonly used kinetic model, which explains the association of specific growth rate of microorganisms with growth limiting substrate[7]. In this model, substrate concentration of effluent is independent of that of influent. As per Contoise model, growth rate was considered as a function of necessary nutrients as well as population density and half velocity coefficient was proportional to the substrate concentration of the influent. Chen and Hashimoto also established a model by using Contoise model. As per Chen and Hashimoto model, effluent substrate concentration is considered as a function of substrate concentration present in influent[7].

Kinetics is the essence of process analysis, design and control in anaerobic process[6,9]. The information on the substrate consumption and microbial growth rate can be obtained from the bio-kinetic coefficients which help in the determination of reactor volume, for developing the factors relating process design and the impact of the kinetic coefficients on process design[10,11].

Lai *et al.* (1999) employed Monod, Contoise and Chen and Hashimoto models for the treatment of palm oil mill effluent (POME) in membrane anaerobic system and all the three models represented good fitting with the experimental result[7]. Another study was performed by Faisal and Unno (2001) for the treatment of POME through modified anaerobic baffled reactor in which cell growth was assumed to follow Monod kinetics[2]. Again, Zinatizadeh *et al.* (2006) utilized Monod's model for evaluating the performance of upflow anaerobic sludge fixed film reactor to treat POME[12].

It was confirmed from thorough investigation of literature that there was availability of hardly any bio-kinetic study associated with the treatment of petroleum based oily wastewater in suspended growth type anaerobic reactor considering substrate utilization and biomass production. Hence, the purpose of the present work is to study the biodegradation kinetics as per Monod equation for the treatment of petroleum based synthetic oily wastewater in anaerobic suspended growth reactor.

Materials and methods

Acclimatization of biomass:

The anaerobic seed, used in the present work was previously collected and preserved from another anaerobic reactor maintained in the Environmental Engineering Laboratory, Civil Engineering Department, IIEST, Shibpur. The biomass was acclimatized with synthetic dextrose and oil feed in lab scale anaerobic acclimation reactor of capacity 4 L[3]. After acclimatization, several batch studies were performed by adding varying concentration of synthetic oily wastewater in different batches. The synthetic oil feed used in acclimation and batch study was prepared by adding and mixing 1.11 mL of Castrol CRB prima diesel engine oil, 0.1364 g of NH_4Cl and 0.0313 g of KH_2PO_4 to 1 L of distilled water. Again, the composition of synthetic dextrose feed used for acclimation include mixing of 10 g of glucose, 0.7642 g of NH_4Cl and 0.1754 g of KH_2PO_4 to 1 L of distilled water. During acclimation, the range of pH was maintained in between 7 and 7.8. The removal of oily substance was obtained with regard to oil and grease as well as COD and the growth of biomass in terms of mixed liquor suspended solids.

Batch kinetic study:

During batch study, the quantity of synthetic oily wastewater added to the reactor was started from 110 mL, which increased in subsequent batches and the range of initial concentration of oil was between 65–145 mg/L. The values of initial concentration of oil against corresponding batches selected for kinetic study are presented in Table 1. pH, MLSS as well as oil and grease were measured during batch study as per the procedure mentioned in APHA[13]. pH of the anaerobic reactor was maintained in the range of 7–7.8. During batch study, the sample of total volume 50 mL (25 + 25 mL) was collected from the anaerobic acclimation reactor at time interval of minimum 24 h. Here, the sample for determination of pH and oil is the filtered supernatant and that for biomass is the sludge settled at the bottom of the reactor.

Table 1. Specifications for batch study in anaerobic suspended growth reactor

Batch no.	Initial concentration of oil and grease (mg/L)
1	70
2	80
3	90
4	105
5	120
6	126

Model selection and descriptions:

The information on the substrate consumption and microbial growth rate can be obtained from the bio-kinetic coefficients, which help in the determination of reactor volume, for developing the factors relating process design and the impact of the kinetic coefficients on process design[10,11].

Various models used to determine kinetic parameters for the treatment of oily wastewater are Monod, Chen and Hashimoto and Contois model[7]. It was stated by Krylow and Figiel (2003) that Monod, Chen and Hashimoto as well as Contois kinetic models correctly explain the reactions of anaerobic digestion[14]. Lai *et al.* (1999) reported that Monod, Contois and Chen and Hashimoto model fitted well with the experimental results for the treatment of POME with membrane anaerobic system[7]. It was again studied from the literature that Monod model gives appropriate results in comparison to other computational model[6]. Again, Bhunia and Ghangrekar (2008) reported that Monod equation or the modifications of its equation are the basis of numerous kinetic models used for anaerobic processes[9].

Association of specific growth rate of microorganisms with growth limiting substrate in Monod's model[7] is mentioned in eqs. (1) and (2).

$$\mu = \frac{\mu_m S}{K_s + S} \quad (1)$$

$$U = \frac{\mu_m S}{Y(K_s + S)} = \frac{kS}{K_s + S} \quad (2)$$

where, μ_m = maximum specific growth rate (d^{-1}), K_s = half saturation constant (mg/L), S = concentration of oil and grease at any time (mg/L), U = specific substrate utilization rate (d^{-1}), Y = yield coefficient, mg VSS/mg substrate.

Eq. (3) represents Contoise model, which shows growth rate as the function of necessary nutrients along with population density and half velocity coefficient as proportional to the substrate concentration of the influent,

$$U = \frac{u_m S}{Y(BX + S)} \quad (3)$$

Here, $u_m = \mu_m/[1 + a]$

$B = a/\{Y(1 + a)\}$

a = proportionality constant

$$U = \frac{\mu_m S}{[YkS_0 + (1 - k)SY]} \quad (4)$$

S_0 = influent substrate concentration.

As Monod's approach is the most frequently and widely used and is the simplest type of model[7,10], it has been selected for the present work.

Kinetic study:

The equations of kinetics for substrate utilization and biomass production are derived from the basic Monod's eqs. (1, 2). These two equations of kinetics are expressed as:

$$\frac{\theta X}{S_0 - S} = \frac{K_s}{k}\,\frac{1}{{}^{\bullet}S} + \frac{1}{k} \quad (5)$$

$$\frac{X' - X}{\theta X} = \frac{S_0 - S}{\theta X}\,.Y - k_d \quad (6)$$

Monod's kinetic coefficients can be determined by using the above two equations. The kinetic constants K_s and k can be obtained from eq. (5) and the kinetic constants Y and k_d can be found from eq. (6).

Results and discussion

The plot of pH against batch period is represented in Fig. 1. The range of pH during batch study was between 7.25–7.53. After batch 6, pH showed declining trend which may be due to acidogenic phase and was adjusted by adding 1 *N* Na_2CO_3. The range of pH was observed as 6.9–7.02 without addition of chemicals for pH adjustment while treating palm oil mill wastewater in a modified anaerobic baffled reactor[2].

The performance of anaerobic suspended growth reactor in removing oil during batch kinetic study is represented in Fig. 2. The removal efficiency of oil was found to be in the range of 69–79%, which was the highest at initial oil concentration of 126 mg/L against batch period of 9 days. During

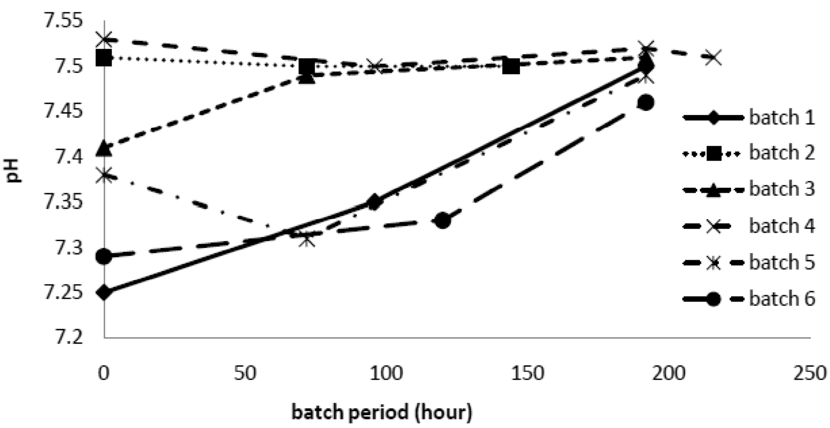

Fig. 1. Trend of pH during batch study in anaerobic suspended growth reactor.

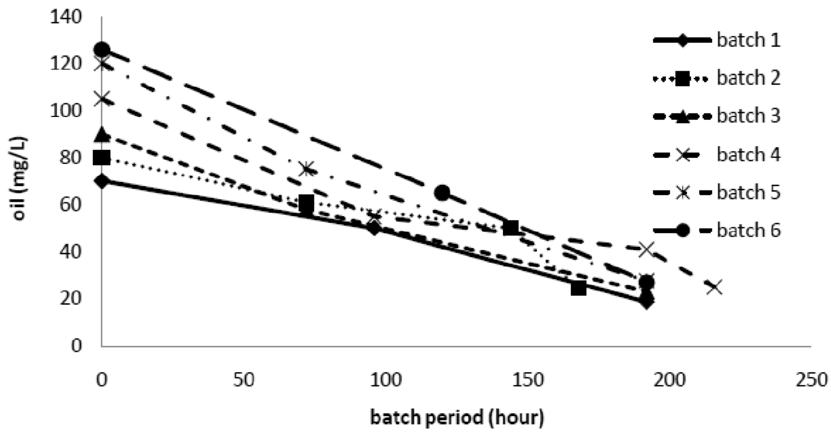

Fig. 2. Trend of oil during batch study in anaerobic suspended growth reactor.

present study, the range of batch period in the anaerobic reactor was 7–9 days and the rate of degradation was found to be enhanced with increase in batch period as oil was degraded slowly. There was inhibition after 100% addition of oil feed, hence the initial batch (1st batch) was repeated several times with increased batch period and nutrient addition. Faisal and Unno (2001) observed that the range of removal of oil was between 44.1–91.3% during treatment of POME in a modified anaerobic baffled reactor and the removal was enhanced with increase in hydraulic retention time[2]. Again, the removal efficiency of COD was found to be between 66.4–85.4% and there is increase in removal efficiency with the rise in hydraulic retention time while treating POME in anaerobic stabilization pond[10].

The bio-kinetic parameters including K_s, k, Y and k_d were obtained by fitting the experimental batch study data to the kinetic model. K_s and k were obtained by plotting $(\theta X)/(S_0 - S)$ against $1/S$ as shown in Fig. 3. Again, Fig. 4 represents plot of $(X' - X)/(\theta X)$ against $(S_0 - S)/(\theta X)$ for determining Y and k_d. The values of K_s, k, Y and k_d were found to be around 202.23 mg/L, 0.01/d, 0.98 mg MLSS/mg oil and 0.001/d respectively, which were obtained from the slope and intercept of the lines as represented in Fig. 3 and Fig. 4.

Table 2 represents values of various kinetic parameters (k, K_s, Y, k_d) found in the present work due to application of Monod's kinetics and also the parameters obtained from the literature.

The value of k and K_s found in the present work is less

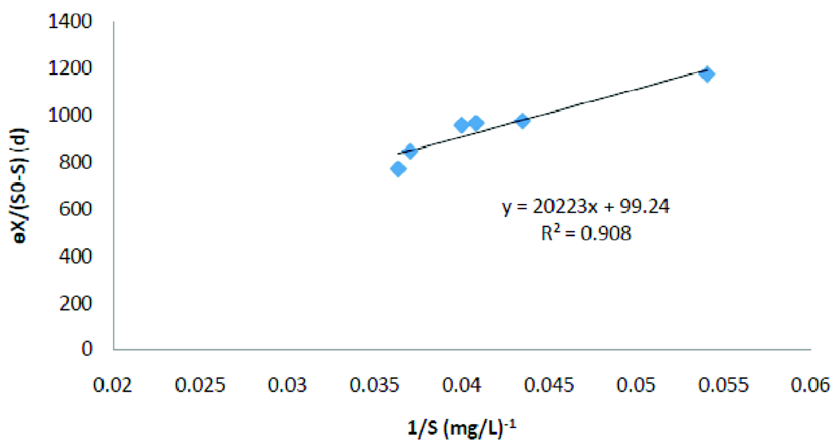

Fig. 3. Plot for determination of k and K_s.

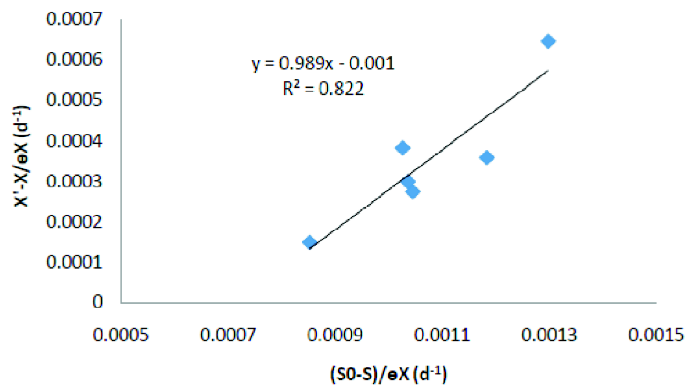

Fig. 4. Plot for determination of Y and k_d.

Table 2. Kinetic parameters during anaerobic treatment of oily wastewater

Type of oily wastewater	Reactor	k	K_S	Y	k_d	References
Palm oil mill wastewater	Anaerobic baffled reactor	–	11.56 g/L	–	–	15
Palm oil mill effluent	Membrane anaerobic system	0.254 mg COD/ mg VSS d	–	0.604 kg VSS/ kg COD	0.099/d	7
Palm oil mill wastewater	Modified anaerobic baffled reactor	–	0.313 g COD/L	–	–	2
Palm oil mill wastewater	Upflow anerobic sludge fixed-film system	–	0.982 g COD/L	–	–	12
Palm oil mill effluent	Anaerobic stabilization pond	0.553/d	203.433 g/L	0.99 g VSS/g COD removed	0.024/d	10
Synthetic oily wastewater (petroleum based)	Suspended growth anaerobic reactor	0.01/d	202.23 mg/L	0.98 mg MLSS/mg oil	0.001/d	Present study

than the values reported by earlier researchers, which may be owing to the variation of the influencing parameters like pH, biomass concentration etc. between the present and past studies. The value of Y obtained in the present study nearly bears out the result obtained by Wong *et al.*[10], but it differs from the value reported by Lai *et al.*[7], which may be due to variation in the ranges of substrate concentration.

Most of the kinetic parameters (k, K_s, Y and k_d) reported for anaerobic treatment of oily wastewater are for palm oil mill wastewater and it has not been reported for petroleum based oily wastewater so far. Hence, the disparity in the values of kinetic parameters may be due to variation in the nature of oily wastewater, concentrations of the substrate and the other experimental conditions. Again, in the earlier studies mentioned in Table 1, COD was considered as the performance parameter, whereas oil and grease is selected as the performance parameter in the present study.

Conclusions

An anaerobic suspended growth reactor was studied for the treatment of synthetic oily wastewater and a kinetic model with Monod's approach was proposed on the basis of experimental results. With initial concentration of oil ranging from 65–145 mg/L, the values of k, K_s, Y and k_d were found to be about 0.01/d, 202.23 mg/L, 0.98 mg MLSS/mg oil and 0.001/d respectively. These values partially corroborate with the literature which may be due to the variation in nature of oil containing wastewater as well as concentrations of the substrate and the experimental condition. These kinetic coefficients are extremely important for the design of anaerobic reactor treating oily wastewater. A good correlation was obtained (R^2 value as 0.908 and 0.822), when the experimental data were plotted in the graph during kinetic analysis with Monod's approach. It can be deduced from the results that synthetic oily wastewater (petroleum based) can be treated effectively by using anaerobic suspended growth reactor by employing properly acclimated biomass. Moreover, Monod's model is again proved to be viable for the kinetic analysis of anaerobic treatment of oily wastewater.

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