Kinetic Modeling of GAC - IFAS Chemostat for Petrochemical Wastewater Treatment

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Abstract-**This paper delivers on the biodegradation kinetics of an integrated fixed film activated sludge (IFAS) reactor using experimental data and a mathematical model under two operational conditions, employing different quantities of granular activated carbon (GAC) as a biological growth support medium. A mathematical model based on Monod kinetics was validated using the experimental data by employing estimated kinetic parameters and values from the literature for other parameters of the process. The mathematical model was found to describe the process well at a steady state and to a lesser extent, at transient state operation. Under chemostat conditions, the process was found to be mainly limited by the high microorganisms decay rate, specific utilization rate and limitation imposed by the substrate availability.**

Keywords- Industrial Wastewater Treatment; Petrochemical Wastewater; Integrated Film Activated Sludge Processes; Granular Activated Carbon; Mathematical Modelling

I. INTRODUCTION

Recently, integrated film activated sludge (IFAS) processes and its variations for the removal of organic compounds have become very attractive especially with the introduction of new support materials for the attached growth and engineering of microorganisms to degrade target organics [1-9]. In an earlier research on synthetic wastewater, a novel hybrid biological reactor which contained both suspended and attached growth biomass was developed by introducing porous materials into a regular activated sludge unit and used for the treatment of domestic wastewater [4]. The total biomass concentration in hybrid reactors increased to 4.30–5.75 g/l-VSS when the volumetric portion of the carrier was 15–30%.

Another hybrid biological reactor was developed by introducing porous ceramic particles into the reactor to provide the surface for biomass attachment [5]. The suspended and attached biomass had approximately the same nitrification activity. The nitrifying kinetic was independent of the initial biomass concentration, and the attached-biomass had a stronger ability to resist the nitrification inhibitor.

Bai et al [6] investigated nitrification and denitrification kinetics of an IFAS process using domestic wastewater and the results revealed that total nitrogen and total phosphorous effluent concentrations of 14 and 0.4 mg/l respectively, could be achieved; while the anoxic phosphorous uptake increased significantly.

In most biological reactors, conventional design procedures are normally sufficient to achieve good results. The activated sludge process (ASP) and rotating biological contactors (RBC) are examples of the suspended growth and attached growth processes. The conventional approach for the design of biological reactors assumes that microorganisms, either in a suspended or attached state, but not both, are responsible for the utilization of organic substrate. This approach is applied for conventional biological reactors, which strongly favour suspended or attached biomass. For example, an ASP has a large aeration basin containing cells in suspension for the degradation of organic compounds. Although attached cells or biofilm exist on the basin wall and diffusers, they are in small amounts and contribute very little to the degradation of the organic substrate. However, in innovative biological reactors, neither suspended nor biofilm kinetics is sufficient. A model incorporating both suspended and attached growth kinetics must be used considering shear losses [7]. Biofilm and its environment is a very complex system and are often very difficult to analyze experimentally [9]. This type of model will improve the understanding of the dynamics of the IFAS process and may lead to more efficient design and operation of IFAS reactors.

Many mathematical models have been developed for similar processes [7-9]; however, these models use estimated values for the model parameters, use synthetic wastewater with one contaminant or are very much simplified. For example, the modeling of the biodegradation kinetics in a laboratory scale biofilm reactor using phenolic wastewater has been conducted by Lin and Hsien [8]. The model results have agreed with the experimental results, and the model was recommended for pilot scale design [8]. However, this model was only valid for phenolic wastewater.

Another model has been developed for a fixed bed biofilm reactor by Kumar and Venkateswarlu [9] using pharmaceutical wastewater and kinetic parameters were approximated using the inverse modeling approach.

The main aim of this paper was to develop a mathematical model for an integrated film activated sludge reactor that can be used to determine the operating parameters for the removal of contaminants in an integrated film reactor for petrochemical wastewater treatment based on a lump sum parameter such as chemical oxygen demand (COD).

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II. METHODOLOGY

The methodology used for the present work was a combination of experimental work and mathematical modelling. The conduct of the experiments was to estimate key kinetic parameters, and then, validate the model using reasonable cited values for other parameters.

A. Experimental Methodology

An industrial wastewater sample was collected and utilised in laboratory reactors in all the experiments. Petrochemical wastewater from the first basin at Al-Wafra industrial wastewater treatment plant was primarily treated at the plant.

The industrial wastewater was utilized in three types of experiments, which were granular activated carbon (GAC) adsorption, suspended growth in a batch reactor, and attached growth on GAC in a batch reactor.

Initially, suspended growth experiments were planned to be conducted in well-stirred controlled containers for a period of 20 to 30 d; however, the observed degradation rates after the first day were more than 95% of the total degradation; and therefore, subsequent experiments were conducted for up to 9 d. Samples were collected daily.

Parameters analysed included temperature, pH, dissolved oxygen (DO), COD, and biomass represented by volatile suspended solids (VSS). Analysis was conducted using standard methods SMWWE 2550 B, SMWWE 4500 - H+ B, SMWWE 4500-O G, SMWWE 5220 B, SMWWE 2540 E of APHA for the previous parameters, respectively [10].

B. Batch Suspended Growth Experiments

In the batch suspended growth experiments, bacterial cultures were acquired from the Al-Wafra industrial wastewater treatment plant, and the industrial wastewater samples were then mixed with cultures in one vessel (one-liter beakers). The parameters mentioned in section 2.1 were monitored daily. The beakers were stirred using a jar-test apparatus.

C. Batch Attached Growth Experiments

In the batch attached growth on GAC experiments, the cultures were allowed to grow on the GAC, and the biological film coverage and homogeneity were observed by microscopic examination. Then, the sample industrial wastewater was added to the 200 g of GAC in one-liter beakers. All parameters mentioned in section 2.1 were monitored daily for each beaker, including the control flask.

III. DEVELOPMENT OF A MATHEMATICAL MODEL

The mathematical model was developed assuming no limitation by oxygen and experimentally, it was found that this assumption was reasonable, as the DO increased from 2.5 to above 4.5 mg/l on the second day for both suspended and attached growth experiments. The model also assumed that no biofilm growth took place on the walls of the chemostat reactor, nor was it comparable to the GAC surface biofilm area. Additionally, the amount of biodegradable organics accumulated in the GAC by adsorption was limited and negligible compared to the total amount of biodegradable organics in the bulk wastewater phase.

Finally, in order to simplify the model, the biofilm coverage and thickness were assumed to be uniform over the GAC surface and had constant steady state value.

Under these conditions the chemostat IFAS mathematical model can be solved by the equations described in the following sections.

A. Kinetic Rates for Suspended Cells

The utilisation of substrate by suspended cells can generally be described by the Monod equation [11]. The amount of pollutants removed by suspended cells per day, $r_s\left({}^{M_s}\!/_{T}\right)$ can therefore be calculated by the equation as follows:

$$r_s = \frac{kS_b}{K_s + S_b} X_s V_v \tag{1}$$

Where k is the maximum specific rate constant for substrate utilization $\left({}^{M_s}\!/_{M_x \cdot T}\right)$; K_s is the half saturation constant $\left({}^{M_s}\!/_{L^3}\right)$; S_b is the organic concentration in bulk liquid $\left({}^{M_s}\!/_{L^3}\right)$; and X_s is the concentration of suspended cells $\left({}^{M_x}\!/_{L^3}\right)$.

The concentration of suspended cells in an integrated film reactor changes due to the growth from substrate utilisation, endogenous decay, shear off from biofilm, and washout in the effluent. These four mechanisms can be described as follows, assuming that there are no cells in the influent [7]:

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$$\frac{dX_S}{dt} = \left[\frac{YkS_b}{K_S + S_b} - b\right] X_S + \frac{A}{V_V} b_S L_f X_f \tag{2}$$

Where Y is the yield $(\dim ensional)$ and b is the specific decay (T^{-1}) coefficient for cells; b_s is the shear loss coefficient for attached cells (T^{-1}); A is the biofilm surface area (L^2); L_f is the biofilm thickness (L); X_f is the cell density in biofilm $\left(M_x/L^3\right)$; and t is the time (T). The last term in the equation assumed that sheared-off attached cells become suspended cells.

Two boundary conditions are required for the aforementioned governing equation, one at the exterior $(z = L_f)$ and another at the interior $(z = 0)$ of the biofilm, as follows:

The mass flow that exists from the bulk solution equals to that entering the biofilm.

$$D_f \frac{dS_f}{dz} = k_f [S_b - S_f|_{z=L_f}] \quad \text{at } z = L_f \tag{3}$$

$D_f \frac{\partial S_f}{\partial z}$ = Substrate flux entering the biofilm

$K_f \lfloor S_b - S_f \rfloor$=Substrate flux leaving the bulk solution

The tangent is horizontal at $z = 0$

$$\frac{\partial S_f}{\partial z} = 0 \tag{4}$$

Where k_f is the film transfer coefficient across the boundary layer $\left(L/T\right)$. Microbial cells in the biofilm grow due to substrate utilization, decay due to death, and can be sheared off by the wastewater flowing in the reactor. The biofilm thickness changes as a result of these mechanisms.

B. Integrated Film Reactor Model

The change in the substrate concentration in the bulk phase of the hybrid chemostat is caused by substrate inflow in the influent, substrate outflow from the effluent, substrate utilised by suspended cells, and substrate utilised by the biofilm. The equations for the four mechanisms are assembled as follows:

$$\frac{\partial S_b}{\partial t} = -\frac{kS_b}{K_S + S_b} X_S - k_f \frac{A}{V_V}\left(S_b - S_f|_{z=L_F}\right) \tag{5}$$

Where S_o is the substrate concentration in the influent $\left(M/L^3\right)$. Equations 6 to 10 constitute the nonsteady state model for a hybrid biological reactor in which both suspended and attached cells are responsible for the removal of organic pollutants. The solution to the model yields the time evolution of substrate concentration, suspended cells concentration, and biofilm thickness.

C. Model Solution

Matlab routine was to solve the aforementioned differential equations (1 to 5). The program must be provided with some important parameters listed in Table 1. It is important to know that some of these parameters were estimated in this study, as discussed in section 4.1, and the others are obtained from Chang et al [7].

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TABLE 1. KINETIC PARAMETERS USED IN THE MODEL SOLUTION

Parameter	Unit	Value
Y	1/d	4.59
$1/k$	mg-substrate/mg-VSS/d	0.12
K_s	mg/l	20.00
b	1/d	1.61
b_s	1/d	0.1
D_f	cm^2/d	0.67
k_f	cm/d	250.00
X_f	g-VSS/l	400.00
$L_{f,initial}$	m	10^{-6}

VSS: Volatile suspended solids.

IV. RESULTS AND DISCUSSION

A. Estimation of Key Kinetic Parameters

Suspended growth experiments results (Table 2) are fitted to Monod reaction kinetic Equation 6, to estimate the biodegradation parameters. It is important to note that the initial biomass is not fully active, and therefore, a correction to the initial biomass value is usually done using the model itself.

TABLE 2. SUSPENDED GROWTH EXPERIMENTAL RESULTS

Time (d)	COD (mg/l)		VSS (mg/l)	
	Measured	Predicted	Measured	Predicted
0	9545	9545	5745*	5130.00
1	548	500. 88871	110	590.22
2	194	183. 637	66	59.59
3	143	141. 672	50	40.78
6	59	58. 094	20	11.03
9	38	36. 097	6	0.0012

*Corrected initial biomass

The results of the least square fitting are shown in Fig. 1 for COD and VSS, respectively.

$$\frac{dX_S}{dt} = \left[\frac{YkS_b}{K_{S+}S_b} - b \right] X_S \tag{6}$$

Where Y is the yield $\left(T^{-1}\right)$ and b is the decay $\left(T^{-1}\right)$ coefficient for cells; k is the maximum specific rate constant for substrate utilization $\left(M_s / M_x.T\right)$; K_s is the half rate concentration $\left(M_s / L^3\right)$; S_b is the organic concentration in bulk liquid $\left(M_s / L^3\right)$; and X_s is the concentration of suspended cells $\left(M_x / L^3\right)$.

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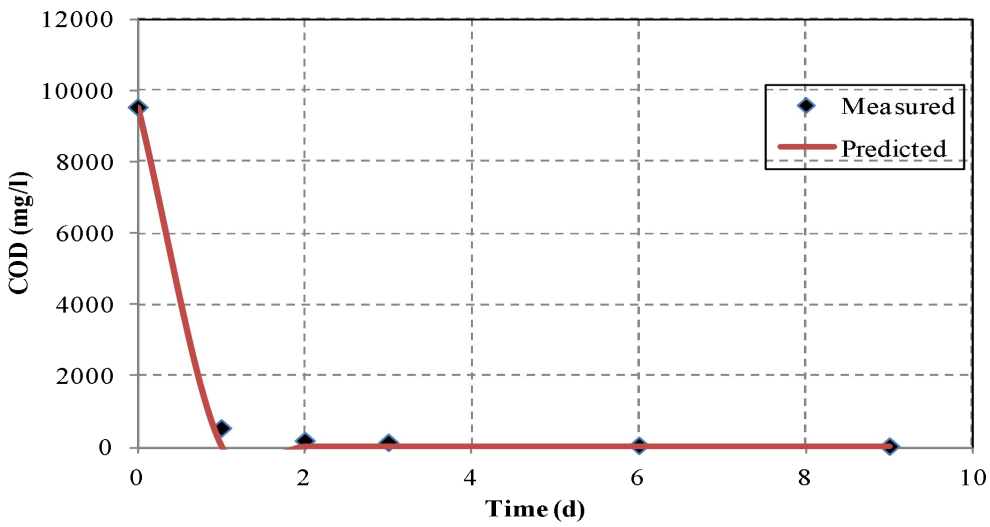
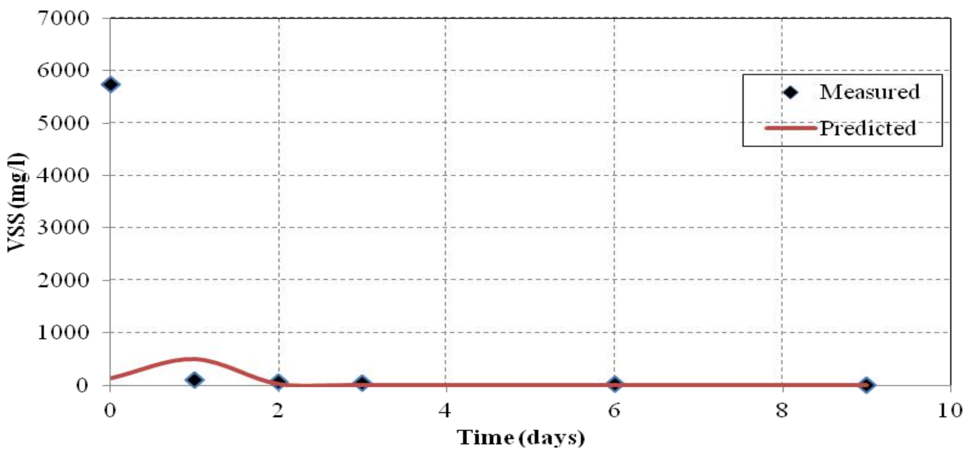


a. Chemical oxygen demand.



b. Volatile suspended solids

COD: Chemical oxygen demand; VSS: Volatile suspended solids

Fig. 1 Fitting COD and VSS suspended growth data to Monod kinetics

The results of the fitting exercise are shown in Table 1. As can be seen, the process kinetics is limited by the high decay rate (b) and the low specific utilisation rate (k). This can be attributed to the toxicity of the wastewater and the availability of the substrate at longer operation of the process [7, 11].

B. Fitting Chemical Oxygen Demand Concentration in Batch Attached Growth Experiments

Using process parameters as per the experimental and results sections and the kinetic data of Table 1, the degradation of organics substrate was simulated using COD as the indicator. The results of the model simulation are given in Figs. 2 and 3.

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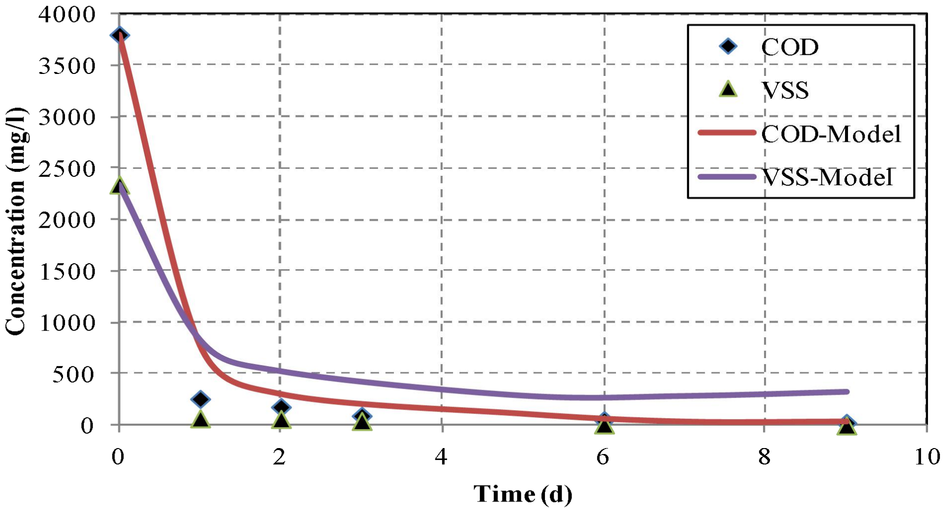
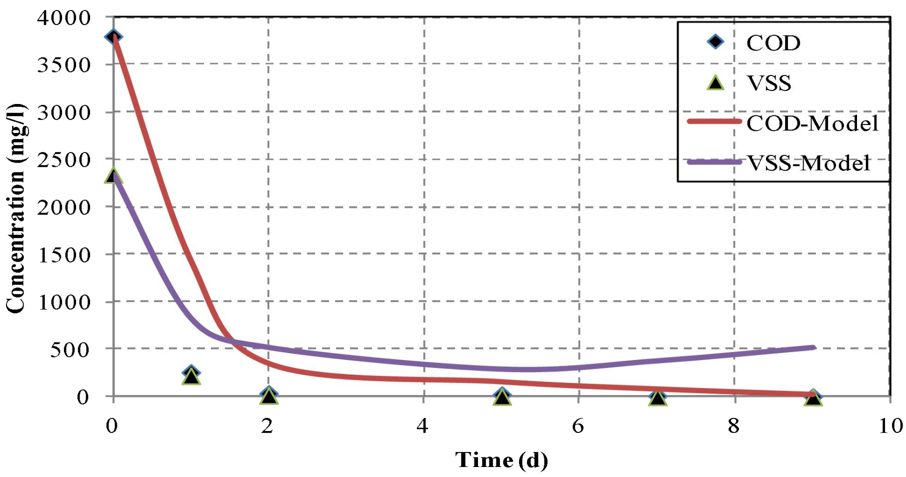


COD: Chemical oxygen demand; VSS: Volatile suspended solids

Fig. 2 Model fitting of COD and VSS concentrations during the attached growth treatment of petrochemical wastewater (GAC 100 g/l)



COD: Chemical oxygen demand. VSS: Volatile suspended solids

Fig. 3 Model fitting of COD and VSS concentrations during the attached growth treatment of petrochemical wastewater(GAC 200 g/l)

Most of the COD utilization occurs during the first 2 d period leading to biomass decay and decreased substrate utilization during the 2-9 d period in both experiments of Fig. 2 and 3.

Additionally, it can be clearly seen that the change in biomass in Fig. 2 and 3 is almost identical beyond the 2 d mark, indicating that the model is more sensitive to the initial degradation rates. This suggests that the sensitivity of model kinetic parameters can be better understood by conducting future experiments focused on the first 2 d behaviour.

Therefore, the model fit appeared to match the overall trend; particularly, at the steady state (beyond the initial 2 d).

However, major discrepancy of the model occurred during the transient state behaviour during the first and second days, and this can be attributed to the imperfections in the kinetic data and other process data, which were not measured such as the initial biofilm thickness.

The estimated decay rate and the shear loss coefficient were estimated to be 1.61 and 0.1/d respectively compared to values of 0.12 and 0.025/d for phenolic wastewater [8]. The high value of the decay rate is probably the key controlling kinetic parameter for the IFAS process. Overall, the model provides a satisfactory behaviour but it is necessary to increase the results in order to make more robust and conclusive interpretation. The literature search for a better kinetic data needs to continue, as new data are published.

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V. CONCLUSIONS

The main conclusions of this study are:

- The treatment of petrochemical wastewater using an integrated fixed film process is viable.
- The mathematical model is very sensitive to kinetic parameters at a nonsteady state operation.

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