

# Simulation of biodegradation process of phenolic wastewater at higher concentrations in a fluidized-bed bioreactor

A. Venu Vinod\*, G. Venkat Reddy

*Department of Chemical Engineering, National Institute of Technology, Warangal 506 004, India*

Received 7 February 2004; received in revised form 4 December 2004; accepted 5 January 2005

---

## Abstract

Experiments were carried out to study the biodegradation of phenolic wastewater using microorganisms in a fluidized-bed bioreactor (FBR). Synthetic wastewater has been used in the study. Experiments were conducted at various conditions of wastewater flow rate, dissolved oxygen (DO) concentration and inlet concentration. The wastewater with feed concentration of phenol as high as 1254 ppm has been successfully biodegraded to 50 ppm in the fluidized-bed bioreactor, whereas feed with concentration up to 1034 ppm could be completely biodegraded (to zero ppm).

Biokinetic parameters for the growth of the cells were determined in batch experiments and they were found to be  $\mu_{\max} = 1.436 \times 10^{-4} \text{ s}^{-1}$ ,  $K_s = 21.92 \times 10^{-3} \text{ kg/m}^3$ ,  $K_i = 522 \times 10^{-3} \text{ kg/m}^3$ . Model equations describing the simultaneous diffusion and reaction of phenol and oxygen in the biofilm of the solid particles, were solved using the orthogonal collocation technique to calculate the rate of biodegradation of phenol. The rate of biodegradation predicted by the model was compared with that observed experimentally and the difference between the two was found to be about 12%.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Biodegradation; Phenol; Biomass; Fluidized-bed bioreactor; Substrate inhibition; Wastewater treatment

---

## 1. Introduction

Fluidized-bed bioreactors (FBR) have been receiving considerable interest in wastewater treatment. A fluidized-bed bioreactor consists of microorganism coated particles suspended in wastewater which is sufficiently aerated to keep the gas, liquid and the solid particles thoroughly mixed. The fluidized-bed bioreactor has been shown [1–5] to outperform other types of reactors. The superior performance of the fluidized-bed bioreactor is due to very high biomass concentration due to immobilization of cells onto the solid particles; intimate contact between gas, liquid and solid phases; decoupling of residence times of liquid and microbial cells due to immobilization.

Extensive information is available in literature on the biodegradation of phenol and fluidized-bed bioreactors

[2,4–12]. Phenolic wastewater treatment is done by using methods like freely suspended cell systems, trickling filters, rotating disc, activated sludge, biological fixed film methods and fluidized-bed bioreactors. Trickling filters are more advantageous over freely suspended cell systems [1]. However, fluidized-bed bioreactors have been found to be superior to other type of reactors [2,3] in relation to volumetric biodegradation capacity. A number of attempts have been made to develop mathematical model for biodegradation of phenolic compounds in wastewater [4,5,12]. Earlier studies [12] using draft tube fluidized-bed bioreactors involved low phenol concentrations (82–131 ppm). The present work reports studies with phenol concentration up to 1254 ppm. In the present work, an attempt has been made to study the influence of various operating parameters, i.e., phenol and oxygen concentrations and feed flow rate on biodegradation of phenol in a draft tube fluidized bioreactor. A model has been used to predict phenol biodegradation and the model predictions compared with experimental findings.

\* Corresponding author. Tel.: +91 870 2459191; fax: +91 870 2459547.

E-mail addresses: avv@nitw.ernet.in (A. Venu Vinod), vreddy@nitw.ernet.in (G. Venkat Reddy).

## Nomenclature

$B_i$	dimensionless group ( $k_o \delta / D_{of}$ )
$B_s$	dimensionless group ( $k_s \delta / D_{sf}$ )
$C$	dissolved oxygen concentration in biofilm ( $\text{kg/m}^3$ )
$C_b$	dissolved oxygen concentration in the bulk liquid phase ( $\text{kg/m}^3$ )
$C_i$	dissolved oxygen concentration at the interface between a bioparticle and the bulk liquid ( $\text{kg/m}^3$ )
$C^*$	dimension less dissolved oxygen concentration ( $c/c_b$ )
$D_{of}$	diffusion coefficient of oxygen in biofilm ( $\text{m}^2/\text{s}$ )
$D_{ow}$	diffusion coefficient of oxygen in water ( $\text{m}^2/\text{s}$ )
$D_{sf}$	diffusion coefficient of phenol in biofilm ( $\text{m}^2/\text{s}$ )
$D_{sw}$	diffusion coefficient of phenol in water ( $\text{m}^2/\text{s}$ )
$k_o$	liquid–solid mass transfer coefficient for oxygen ( $\text{m/s}$ )
$k_s$	liquid–solid mass transfer coefficient for phenol ( $\text{m/s}$ )
$K_i$	inhibition constant for phenol ( $\text{kg/m}^3$ )
$K_o$	monod constant for oxygen ( $\text{kg/m}^3$ )
$K_s$	monod constant for phenol ( $\text{kg/m}^3$ )
$K_i^*$	dimensionless inhibition constant for phenol
$K_o^*$	dimensionless Monod constant for oxygen
$K_s^*$	dimensionless Monod constant for phenol
$N_p$	number of bioparticles in FBR
$Q$	flow rate of synthetic wastewater ( $\text{m}^3/\text{s}$ )
$r$	radial coordinate in biofilm (m)
$r_p$	radius of biomass–free bioparticle (m)
$R_{obs}$	observed rate of phenol removal in the reactor ( $\text{kg/s}$ )
$R_{scalc}$	calculated rate of phenol removal in the reactor ( $\text{kg/s}$ )
$S$	phenol concentration in biofilm ( $\text{kg/m}^3$ )
$S_b$	phenol concentration in the bulk liquid ( $\text{kg/m}^3$ )
$S_I$	phenol concentration in inlet synthetic waste water ( $\text{kg/m}^3$ )
$S_i$	phenol concentration at the interface between a bioparticle and the bulk liquid ( $\text{kg/m}^3$ )
$S^*$	dimensionless phenol concentration ( $S/S_b$ )
$t$	time (s)
$x$	dimensionless distance ( $r-r_p)/\delta$
$Y_{x/s}$	yield coefficient (kg biomass/kg phenol)
$Y_{x/o}$	yield coefficient (kg biomass/kg oxygen)
<i>Greek letters</i>	
$\delta$	biofilm thickness (m)
$\rho_v$	biofilm density ( $\text{kg/m}^3$ )
$\mu$	specific growth rate of biomass ( $\text{s}^{-1}, \text{h}^{-1}$ )
$\mu_{\max}$	maximum specific growth rate of biomass ( $\text{s}^{-1}, \text{h}^{-1}$ )
$\phi_o$	dimensionless modulus for oxygen
$\phi_s$	dimensionless modulus for phenol

## 2. Mathematical model development

A model describing the biodegradation of phenol by bacteria immobilized onto the plastic beads was used which is similar to the one employed by Tang and Fan [5]. Phenol and oxygen were assumed to be simultaneously diffusing into and reacting within the film. There are three basic processes occurring in the biodegradation of phenol in a fluidized-bed bioreactor:

- Transport of oxygen from the gas phase into the bulk liquid.
- Transport of phenol, oxygen and other nutrients from the bulk liquid phase to the surface of the film.
- Simultaneous diffusion and reaction of phenol, oxygen and other nutrients within the biofilm.

Process (a) was not considered in this work, as dissolved oxygen concentration was maintained constant.

A pseudosteady state is reached in the completely mixed draft-tube, three phase fluidized-bed bioreactor when the bulk concentrations of phenol and oxygen are constant and the change in biofilm properties such as the film thickness and density are negligible. Therefore, the concentration profiles of phenol and oxygen in the biofilm are independent of time. The following assumptions were made in the development of the model:

1. The FBR is in backmix condition.
2. Biomass loading is constant at steady state.
3. Plastic bead particles are spherical and inert.
4. Biomass coating on particles is uniform.
5. The growth limiting nutrients are phenol and oxygen. All other nutrients are in excess. The growth kinetics are assumed to follow Monod kinetics with respect to oxygen and substrate inhibited kinetics with respect to phenol.

$$\mu = \frac{\mu_{\max} S}{S + K_s + S^2/K_i} \frac{C}{K_o + C} \quad (1)$$

6. The biofilm has same kind of effect on phenol and oxygen diffusivities, i.e., the ratio of  $D_{of}/D_{ow}$  is the same as the ratio  $D_{sf}/D_{so}$ . The diffusivities of the oxygen and phenol are reduced to the same extent in the biofilm compared to that in water.
7. Immobilization of cells onto the biofilm does not change the kinetic parameters describing the growth.

With these assumptions mass balances of phenol and oxygen across the biofilm have been carried out to get the following two differential equations: (details of the derivation given in [Appendix A](#))

For phenol:

$$\frac{D_{sf}}{r^2} \left[ \frac{d}{dr} \left( r^2 \frac{dS}{dr} \right) \right] - \frac{\rho_v}{Y_{x/s}} \frac{\mu_{\max} S}{S + K_s + S^2/K_i} \frac{C}{K_o + C} = 0 \quad (2)$$

For oxygen:

$$\frac{D_{of}}{r^2} \left[ \frac{d}{dr} \left( r^2 \frac{dC}{dr} \right) \right] - \frac{\rho_v}{Y_{x/o}} \frac{\mu_{\max} S}{S + K_s + S^2/K_i} \frac{C}{K_o + C} = 0 \quad (3)$$

The boundary conditions for these equations are

$$\left(\frac{dS}{dr}\right) = \left(\frac{dC}{dr}\right) = 0 \quad \text{at } r = r_p \quad (4)$$

$$D_{sf} \left(\frac{dS}{dr}\right) = k_s(S_b - S_i) \quad \text{at } r = r_p + \delta \quad (5)$$

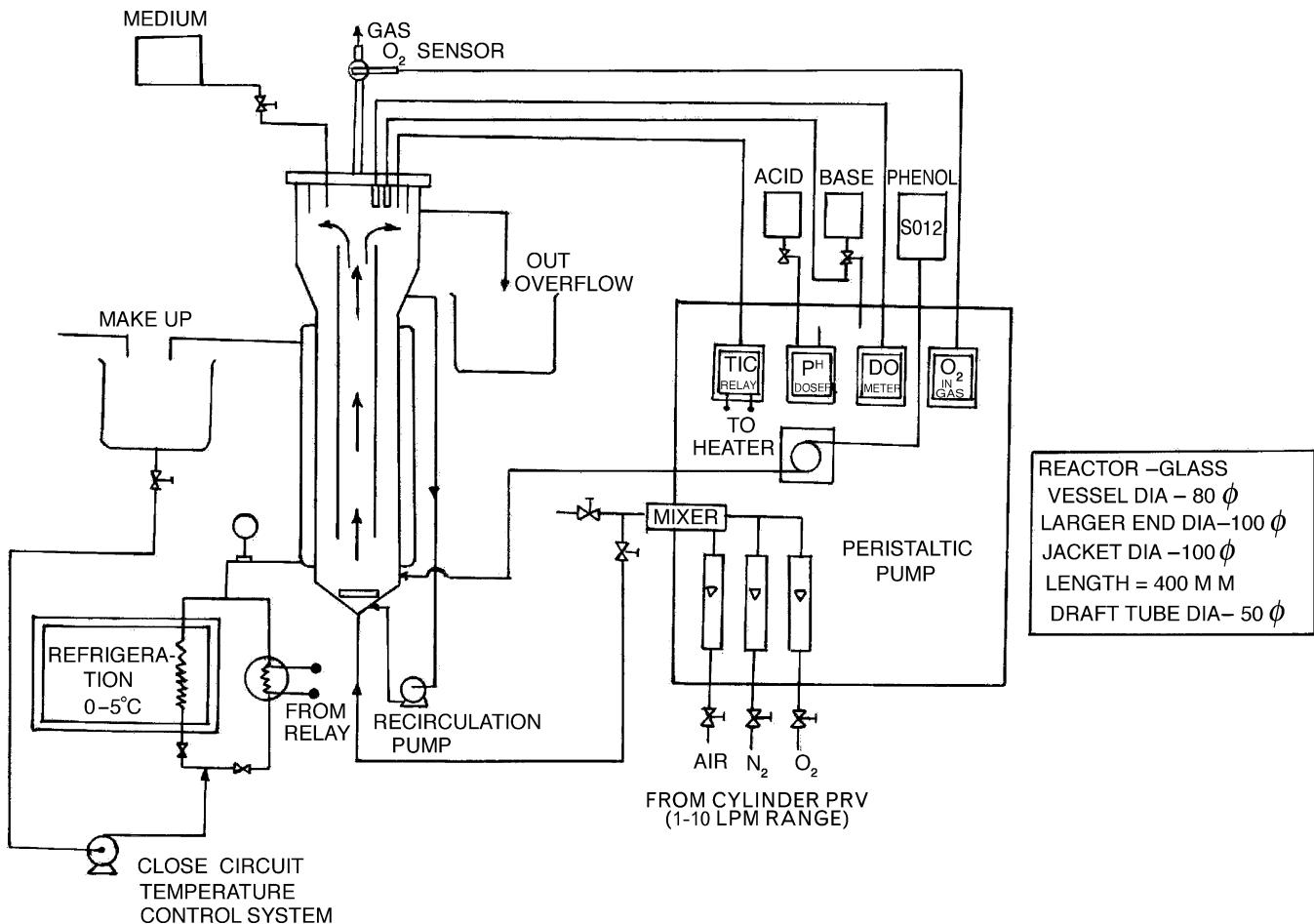
$$D_{of} \left(\frac{dC}{dr}\right) = k_o(C_b - C_i) \quad \text{at } r = r_p + \delta \quad (6)$$

After solving the Eqs. (2)–(6) the rate of phenol degradation from the model can be calculated using the formula

$$R_{scal} = \frac{N_p \rho_v}{Y_{x/s}} \int_{r=r_p}^{r=r_p+\delta} \frac{\mu_{max} S}{S + K_s + S^2/K_i} \frac{C}{C + K_0} 4\pi r^2 dr \quad (7)$$

The above rate of biodegradation can be compared with the experimental rate of biodegradation calculated using the formula

$$R_{Sobs} = Q(S_I - S_b) \quad (8)$$



## 2.1. Numerical method

Eqs. (2)–(6) constitute a set of nonlinear, ordinary differential equations of the boundary value problem type. They were solved using the orthogonal collocation technique. The solution procedure is given in Appendix A.

## 3. Experimental

### 3.1. The reactor set-up

The schematic diagram of a draft tube fluidized-bed bioreactor used in the present work is shown in the Fig. 1.

#### 3.1.1. Reactor and the draft tube

The fluidized-bed bioreactor and the draft tube are made up of glass. A sparger made up of same material has been provided at the bottom of the reactor through which air/oxygen/nitrogen can be sparged into the reactor. The active volume of the reactor is about 2.6 l. The top of the glass reactor is closed with a plate through which all the probes

Fig. 1. Fluidized-bed draft tube bio reactor (FBDTBR).

and sensors are inserted into the reactor. An overflow line has been provided near the top so that, the reaction medium flows out of the reactor in continuous operation.

Plastic beads with a density of 1.05 g/cc are used for immobilization of the microorganism. The average diameter of the beads is 4.31 mm. Two peristaltic pumps one each for media and feed into the reactor have been provided. The flow rate of these pumps can be set at the required value using a flow controller. The capacity of the pumps is 40–3500 ml/h. The reactor is provided with a glass jacket to maintain the temperature of the reactor system above or below the ambient temperature. Depending on the temperature set for the reactor operation, controller switches on either the heating or refrigeration circuit. An additional pump has been provided at the bottom of the reactor to recirculate the reaction medium to supplement the fluidization action of the gas. Separate tanks made of stainless steel have been provided for supplying the feed, medium, acid and base solutions for pH control. Two types of connecting tubing are used in the set-up. One is silicon tubing and the other is PVC.

### 3.1.2. Reactor instrumentation

To maintain the pH of the system a pH meter and a controller has been provided. pH will be maintained by addition of acid or base from the tanks provided at the top. Oxygen will be consumed in the degradation of phenol by microorganism. Oxygen required for the process will be supplied either in the form of air from a compressor or from oxygen cylinder. The oxygen content in the reaction medium can be measured using a DO meter. Phenol present in the feed will be biodegraded and converted to biomass, CO<sub>2</sub>, etc. The gas analyzer will measure the composition of the gas leaving the reactor at the top. To study the biodegradation of phenol at different concentrations of oxygen dissolved in the reaction medium, provisions has been made to pump air, N<sub>2</sub> and O<sub>2</sub> into the reactor through a gas mixer. The flow rates of these gases are measured using rotameters, each with a range of 1–10 lpm (liters per minute).

### 3.2. Microbial culture

A strain of microorganism *Pseudomonas* sp. (SP-1) reported to be capable of utilizing phenol as the sole carbon and energy source was obtained from Regional Research Laboratory, Jammu, India. This was obtained under a Memorandum of Understanding (MoU) signed between National Institute of Technology (Formerly Regional Engineering College) Warangal, India and Regional Research Laboratory (RRL) Jammu, India.

### 3.3. Subculture

The bacterium is subcultured once in a month by preparing slants using nutrient agar. For every 100 ml of nutrient broth/agar the growth medium of the composition mentioned in Table 1 was added. To each of the test tubes 15 ml of this

Table 1  
For 100 ml of nutrient broth/agar

Compound	Concentration (g)
Beef extract	0.3
NaCl	0.5
Peptone	0.5
agar-agar	1.2

nutrient agar solution is added in a tilted position around 30° to the horizontal. After the solidification of the nutrient agar in the test tubes, colonies of bacteria is introduced on it, and is incubated for 24 h at 30 °C and then it is stored at 4 °C in a refrigerator.

### 3.4. Culture preparation

The culture (SP-1) was maintained by periodic subculture on nutrient agar and stored in a refrigerator. The reaction medium was prepared from this strain by growing the bacteria on 2.6 lt of 100 ppm of phenol solution containing growth medium of the composition mentioned in Table 2. Sterilization of the phenol solution was done before inoculation of the organism. This has been done to selectively grow the *Pseudomonas* species.

### 3.5. Growth medium

The growth medium used has the constituents mentioned in Table 2. It was made up using tap water. Sterile conditions were not maintained during the continuous operation of the reactor.

#### 3.5.1. Start-up of the equipment

2.61 of reaction medium was transferred to fluidized-bed bioreactor and the organism was allowed to grow in batch mode for 36 h for immobilization of microorganism on to the solid particles. In the first run thereafter was put in continuous operation with a feed flow rate of 510 ml h<sup>-1</sup> (corresponding to the dilution rate of 0.196 h<sup>-1</sup>) of inlet phenol concentration of about 64 ppm. The dissolved oxygen (DO) concentration in the reactor was maintained at 2 ppm using air initially and subsequently using pure oxygen. The pH in all the runs was maintained at 7.0 using 0.1 N HCl and 0.1 N NaOH. The reaction temperature was maintained at 30 °C in all the runs using a temperature controller provided with a heating/cooling cir-

Table 2  
Composition of growth medium

Compound	Concentration (ppm)
KH <sub>2</sub> PO <sub>4</sub>	420
K <sub>2</sub> HPO <sub>4</sub>	375
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	240
NaCl	15
CaCl <sub>2</sub>	15
MgSO <sub>4</sub> ·H <sub>2</sub> O	30

cuit. The concentration of phenol in the overflow from the reactor was analyzed for every 1 h iodometrically.

### 3.5.2. Analysis for phenol [13]

Samples of the reactor effluent were analyzed for phenol concentration using iodometric method.

### 3.5.3. Determination of kinetic parameters and yield coefficients

Experiments were conducted using SP-1 to measure the biokinetic parameters, viz., maximum specific growth rate ( $\mu_{\max}$ ), inhibition constant ( $K_I$ ) and Monod constant ( $K_S$ ). Experiments were conducted in batch mode in shake flask with different initial phenol concentrations ranging from 64 to 1254 ppm. Nutrients as shown in Table 2 were added to the flasks and the medium was inoculated. Phenol concentration was measured periodically. For each batch run specific growth rate was calculated from the phenol concentration versus time data. The kinetic parameters mentioned above were determined from the data of specific growth rate versus phenol initial concentration obtained above by regression analysis (Fig. 2).

For determination of yield coefficient ( $Y_{X/S}$ , mass of biomass produced per mass of phenol consumed), 25 ml of the reactor medium was taken in every run and filtered through 0.7  $\mu\text{m}$  filter paper to separate the biomass produced. The filter paper was dried and weighed. Phenol concentration was determined and the ratio of the biomass produced to the phenol consumed was determined as the yield coefficient.

### 3.5.4. Determination of biofilm density ( $\rho_v$ )

The biofilm density in terms of mass of dry biomass per volume of biofilm was measured as follows: a sample of biomass-laden particles was withdrawn from the reactor and the volume ( $V_1$ ) of bioparticles was found using a measuring cylinder. The particles were then transferred to a weighed

sample vial and placed in oven at 105 °C to remove all the moisture. The amount of moisture was found from the difference in weights before and after drying. Now the beads were thoroughly washed to remove all the attached biomass and the weight of the biomass was found from the difference in weights before and after washing. Now the volume ( $V_2$ ) of the clean particles was found. The volume of the biofilm is the difference between  $V_1$  and  $V_2$ . The biofilm density was then calculated from the mass of the biomass and the volume of biofilm.

## 4. Studies on synthetic wastewater

Experiments were conducted to study the biodegradation of synthetic wastewater. Synthetic wastewater was prepared by dissolving distilled phenol in tap water. The following studies have been carried out:

1. The effect of dissolved oxygen concentration.
2. The effect of feed flow rate.
3. The effect of feed concentration.

### 4.1. The effect of dissolved oxygen (DO) concentration

The effect of dissolved oxygen concentration on the biodegradation rate phenol in FBR was studied at three DO levels, i.e., at 2, 4 and 6 ppm. The other experimental conditions were maintained at: pH 7.00, temperature = 30 °C, flow rate = 390 ml/h. Fig. 3 shows the effect of DO concentration in the FBR on biodegradation rate. The outlet phenol concentration of phenol remained constant at 51 ppm when the inlet concentration was 1254 ppm. Obviously the DO level at 2 ppm is sufficient for the biodegradation reaction to proceed at its maximum under the given set of conditions. In all subsequent experiments DO level was maintained at 2 ppm only.

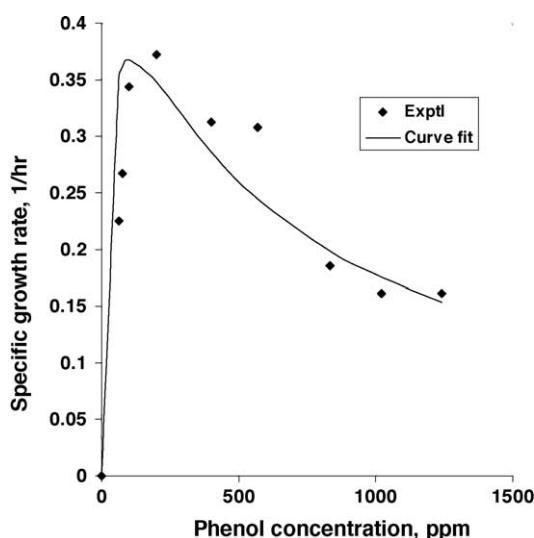


Fig. 2. Specific growth rate as a function of Phenol concentration.

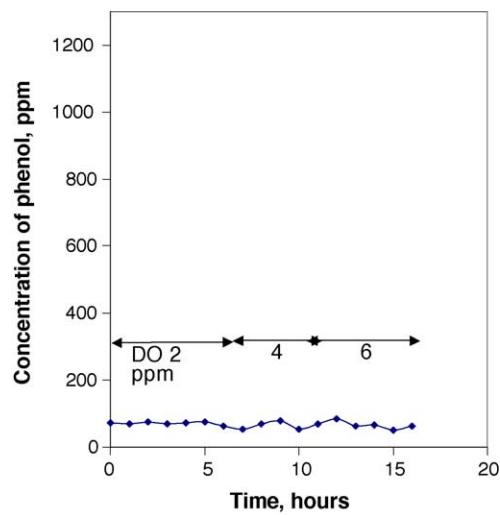


Fig. 3. Effect of dissolved oxygen concentration (feed concentration: 1254 ppm, feed flow rate: 390 ml/h, temperature: 30 °C, pH 7.0).

Table 3  
Composition of growth medium-higher concentration

Constituent	Concentration (g/l)
$\text{KH}_2\text{PO}_4$	1.531
$\text{K}_2\text{HPO}_4$	1.367
$(\text{NH}_4)_2\text{SO}_4$	0.889
$\text{NaCl}$	0.0546
$\text{CaCl}_2$	0.0546
$\text{MgSO}_4$	0.2241

#### 4.2. The effect of feed flow rate

The flow rate of the feed to the reactor changes the rate of biodegradation of phenol as the residence time in the reactor changes with the flow rate. The effect of feed flow rate on the rate of biodegradation of phenolic wastewater was studied at five flow rates viz., 390, 510, 600, 640 and 690 ml/h corresponding to dilution rates of 0.15, 0.196, 0.231, 0.248 and  $0.265 \text{ h}^{-1}$  respectively. The other experimental conditions maintained were pH 7.00, temperature = 30 °C and initial phenol concentration in the reactor at 100 ppm. The initial phenol concentration here refers to the phenol concentration present in the 2.6 l volume fluidized-bed bioreactor at the start of the run. However, the feed concentration remained at 1254 ppm.

#### 4.3. The effect of inlet concentration of phenol

The effect of inlet phenol concentration on biodegradation was studied at eight concentrations viz., 64, 76, 200, 351, 572, 844, 1034 and 1254 ppm. The following experimental conditions were maintained at pH 7.00, temperature = 30 °C, DO = 2 ppm, flow rate 690 ml/h. For the first four concentrations the nutrient concentration was maintained at levels shown in Table 2, but last four concentrations viz., 572, 844, 1034 and 1254 the nutrient concentration was increased to levels shown in Table 3. The reason for increasing nutrient concentration was that at higher inlet phenol concentrations biodegradation was not taking place because of inhibitory effect of phenol, therefore, nutrient concentration was increased to overcome inhibitory effect of phenol.

### 5. Results and discussion

#### 5.1. Biokinetic parameters

As mentioned in experimental procedure batch experiments were carried out to determine the biokinetic parameters. The specific growth rates of the culture at different phenol concentrations were determined from the slopes of linear semi logarithmic plots of biomass concentration versus the elapsed time in the exponential growth phase. The specific growth rates thus obtained were fitted by the Haldane equation using nonlinear least squares method (POLY-FIT function of MATLAB). The variation of specific growth rate with the phenol concentration obtained from these ex-

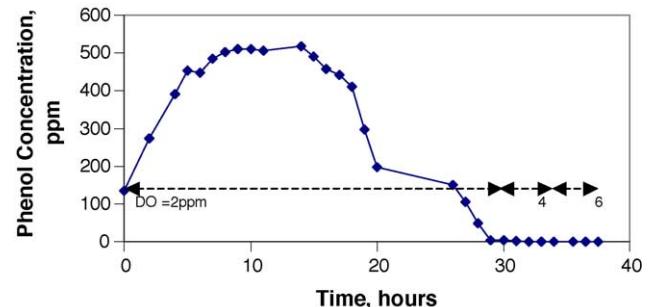


Fig. 4. Effect of dissolved oxygen concentration (feed concentration: 844 ppm, feed flow rate: 510 ml/h, temperature: 30 °C, pH 7.0).

periments is shown in Fig. 2. The growth parameters obtained were  $\mu_{\text{max}} = 0.517 \text{ h}^{-1}$ ,  $K_s = 21.92 \times 10^{-3} \text{ kg/m}^3$  and  $K_i = 522.76 \times 10^{-3} \text{ kg/m}^3$ . These values agree reasonably well with the values reported in literature [5,12] for the microorganism *Pseudomonas* sp. growing on phenol.

Samples were taken from the FBR to determine the yield coefficients. The value of  $Y_{X/S}$  obtained in the study was about  $0.6 \pm 0.1 \text{ kg biomass/kg phenol}$ . This value is close to that reported in literature [5,12] for cultures growing on phenol. The value of  $Y_{X/O}$  was not determined in the study and was taken from literature [12].

#### 5.2. Effect of dissolved oxygen concentration

The results of the study for a feed flow rate of 390 ml/h are shown in Fig. 3. Initially, the DO was maintained at 2 ppm. After steady state is achieved (indicated by the constant outlet concentration from reactor outlet) the DO level was increased to 4 and 6 ppm successively. From the Fig. 3, it can be seen that the increased DO levels have not affected the outlet phenol concentration from the reactor, indicating that the initial DO level of 2 ppm was sufficiently in excess. Similar behavior was observed for other feed flow rates of 510, 600, 690 ml/h. Fig. 4 shows the effect of dissolved oxygen concentration at a feed concentration of 844 ppm and flow rate of 510 ml/h. After the steady state has been established at a DO level of 2 ppm, further increase in the DO level subsequently does not effect the steady state phenol concentration in the FBR.

#### 5.3. Effect of flow rate

Five different feed flow rates viz., 390, 510, 600, 640 and 690 ml  $\text{h}^{-1}$  have been studied. The outlet phenol concentration after steady state for each of the above runs is shown in Table 4. From the Table it can be seen that the steady state outlet concentration in all the runs except at 690 ml/h is almost the same, indicating that the rate of biodegradation increases with increase in feed flow rate.

#### 5.4. Effect of phenol concentration

The various feed concentrations used were 64, 76, 200, 351, 572, 844, 1034 and 1254 ppm at a feed flow rate of

Table 4

Feed flow rate vs. steady state outlet phenol concentration

Inlet feed flow rate (ml/h)	Outlet phenol concentration (ppm)
390	51
510	57
600	50
644	50
690	400

Feed concentration 1254 ppm, temperature = 30 °C.

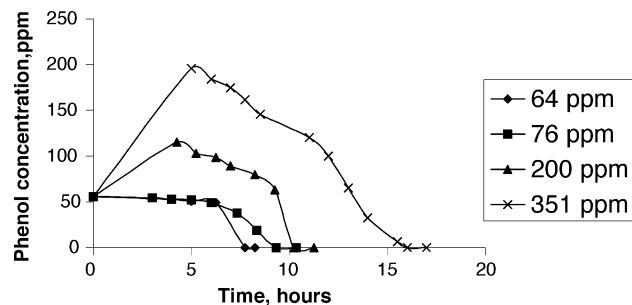


Fig. 5. Phenol outlet concentration from reactor as a function of time at various feed concentrations (feed flow rate: 510 ml/h, temperature: 30 °C, pH 7.0).

510 ml/h. The growth medium of composition shown in Table 2 was used up to inlet concentration of 351 ppm. With this growth medium there was no biodegradation at higher concentrations of phenol. This was due to the inhibitory effect of phenol at higher concentrations. To overcome this, nutrients in larger quantity were tried. This growth medium composition is shown in Table 3. The results of the study are presented in Figs. 5 (64–351 ppm) and 6 (844–1254 ppm) showing outlet phenol concentration as a function of time. From the figures it can be observed that, higher the feed concentration of phenol, longer is the time required to reach steady state. The steady state outlet phenol concentration in all the cases shown in Fig. 5 is zero. Fig. 6 shows similar results at higher inlet feed concentrations viz., 572–1254 ppm. From the figure it can be seen that the steady state outlet concentration is not zero. This indicates a limit on the maximum biodegradation rate for the reactor in the present study. From Fig. 6 for the experimental run with feed concentration 1254 ppm, the steady state reached very quickly compared

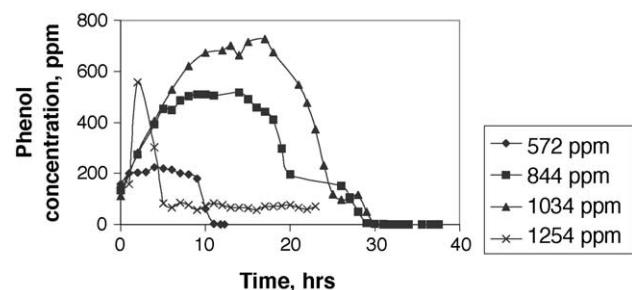


Fig. 6. Outlet phenol concentration from the reactor as a function of time at various feed concentrations (feed flow rate: 510 ml/h, temperature: 30 °C, pH 7.0).

Table 5

Steady state outlet concentration at various inlet concentrations

Inlet phenol concentration (pm)	Outlet phenol concentration (ppm)
64	0
76	0
200	0
351	0
572	0
844	0
1034	0
1254	57

Temperature = 30 °C, flow rate = 510 ml/h.

Table 6  
Model parameters

Parameter	Value	Units
(*) $D_{of}$	$0.356 \times 10^{-9}$	$\text{m}^2/\text{s}$
(*) $D_{sf}$	$0.125 \times 10^{-9}$	$\text{m}^2/\text{s}$
$\mu_{\max}$	$1.436 \times 10^{-4}$	$\text{s}^{-1}$
$K_s$	$21.92 \times 10^{-3}$	$\text{kg}/\text{m}^3$
$K_I$	$522 \times 10^{-3}$	$\text{kg}/\text{m}^3$
(*) $K_o$	$0.26 \times 10^{-3}$	$\text{kg}/\text{m}^3$
$Y_{x/s}$	0.6	$\text{kg}/\text{kg}$
(*) $Y_{x/o}$	0.465	$\text{kg}/\text{kg}$
(*) $k_s$	$0.66 \times 10^{-4}$	$\text{m}/\text{s}$
(*) $k_o$	$1.37 \times 10^{-4}$	$\text{m}/\text{s}$
$N_p$	6369	—
$r_p$	$4.31 \times 10^{-3}$	$\text{m}$
$\delta$	$19 \times 10^{-6}$	$\text{m}$
$\rho_v$	1.7	$\text{kg}/\text{m}^3$

to the other experimental runs. This is due to the fact that in that particular run the feed was given to the reactor containing the biomass generated from the previous run. The reactor would contain large amount of biomass generated in the previous run (feed concentration 1034 ppm) by biodegradation of phenol. This large amount of microbial mass generated from the run with high concentration of 1034 ppm will easily degrade phenol without taking much time for acclimatization to higher concentration 1254 ppm. Table 5 shows the steady state outlet concentrations for various feed concentrations.

#### 5.4.1. Steady state phenol degradation

Mathematical equations, taking into account simultaneous diffusion and reaction of phenol and oxygen in the biofilm

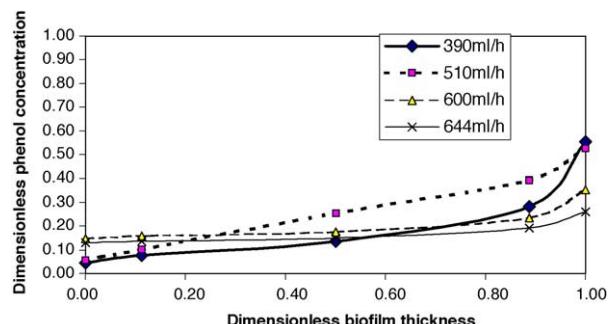


Fig. 7. Concentration profile for phenol in the biofilm.

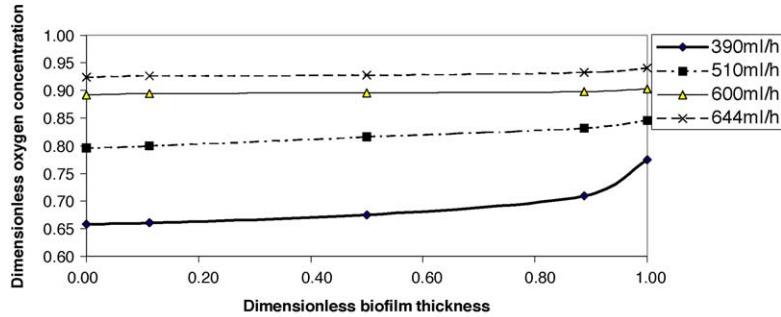


Fig. 8. Concentration profile for oxygen in the biofilm.

of the solid particles, have been derived. The Eqs. (2) and (3) along with the boundary conditions (4)–(6) have been solved using orthogonal collocation technique to determine the phenol and oxygen concentration profiles in the biofilm (the solution procedure is given in Appendix A). The model parameters are given in Table 6. The values with '\*' are taken from literature [12] and not determined in the present work. The profiles for phenol and oxygen, at four different flow rates, have been shown in the Figs. 7 and 8 respectively. From the Fig. 7, it can be seen that the concentration profiles of phenol in the biofilms at four different flow rates are more or less similar. However, the drop in concentration of phenol within the biofilms is steep near the film surface for lower flow rates, whereas at higher flow rates the concentration profiles are almost flat. The oxygen profiles (Fig. 8) show a flat behavior, and it can be seen that the absolute values of oxygen concentration in the biofilm are greater than the value of  $K_o$ . This would explain the independency of the biodegradation rate with respect to DO concentration.

The concentration of phenol within the biofilm, found from the above cited profile, is used in Eq. (7) to calculate rate of phenol degradation. This value is compared with the experimentally observed value from Eq. (8). Such a comparison

for four feed flow rates is shown in Fig. 9. The maximum deviation between the experimental values and that calculated from the model is found to be about 12%, thereby indicating the satisfactory performance of the model.

Earlier studies [4,5,12] using draft tube fluidized-bed bioreactors involved low phenol concentrations (82–131 ppm). In this study phenol up to a concentration of 1254 ppm has been successfully biodegraded in a continuous FBR. This assumes significance in the context of wastewater treatment where high feed concentrations of wastewater would significantly reduce the reactor size and operating time.

Livingston and Chase [12] reported a steady state bulk phenol concentration in the range of 4.24–6.25 ppm, and Tang and Fan [5] reported the same in the range of 2.69–6.49 ppm while in the present work in almost all the runs (except with feed concentration of 1254 ppm) phenol could be biodegraded completely, i.e., a bulk phenol concentration of 0 ppm was obtained as shown in Table 5.

### 5.5. Sensitivity analysis

The sensitivity analysis with respect to  $\mu_{\max}$ ,  $K_s$  and  $K_I$  has been carried out. Fig. 10 shows the effect of variation in  $\mu_{\max}$

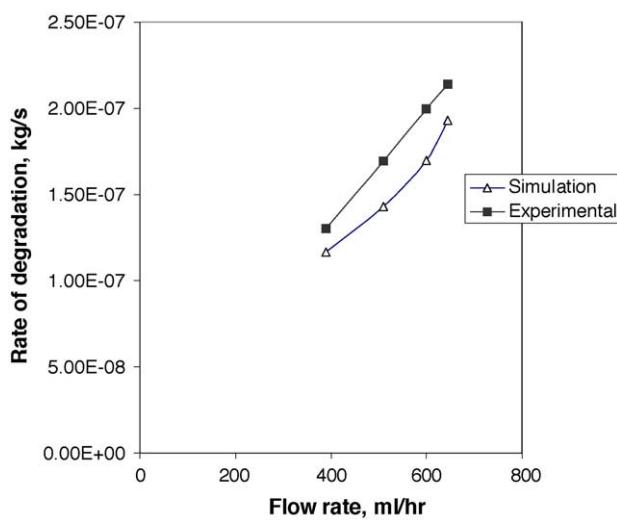


Fig. 9. Effect of flow rate on degradation rate (feed concentration: 1254 ppm).

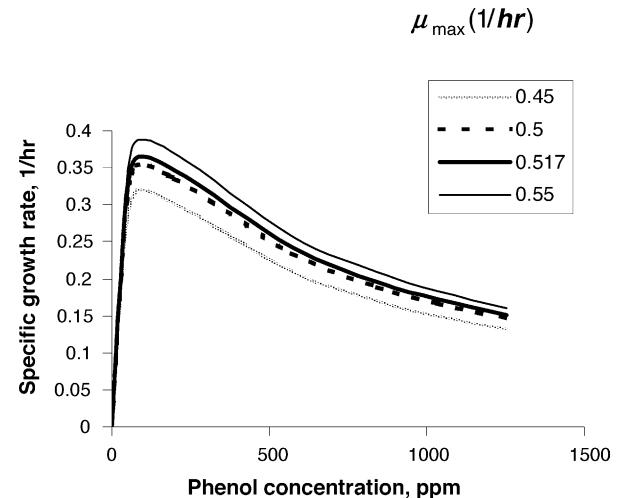


Fig. 10. Sensitivity of specific growth rate to maximum specific growth rate.

on specific growth rate ( $\mu$ ). From the figure it can be seen that for about 10% variation in  $\mu_{\max}$ , specific growth rate changes by 10–12%. The results of analysis with respect to  $K_s$  and  $K_I$  are not shown as they have an insignificant effect on  $\mu$ .

## 6. Conclusions

Synthetic wastewater of higher concentration (1254 ppm) of phenol has been biodegraded in a fluidized-bed bioreactor using the microorganism *Pseudomonas* sp. Steady state biofilm model has been used to describe the biodegradation of phenol using the immobilized bacteria. The model predictions have been found to be satisfactory.

## Acknowledgements

The financial aid provided by the Department of Biotechnology, Government of India (vide letter no. BT/PR 0639/PID/25/002/97 dated 23-10-98) is gratefully acknowledged. The authors are also grateful to RRL Jammu for providing microorganisms used in the present study.

## Appendix A. Mathematical procedure

The modeling equations comprise a nonlinear boundary value problem. This was solved using the method of Orthogonal Collocation Technique [14]. The technique owes part of its popularity to its simplicity and inherent ability to give a stable solution.

The solution of these model equations consists of two steps:

1. Transformation of nonlinear ordinary differential equations into nonlinear algebraic equations using four collocation points.
2. Solving these nonlinear algebraic equations to obtain  $S^*$ ,  $C^*$  at different biofilm radii by simplified Newton–Raphson method.

$$\frac{d^2S^*}{dx^2} + \frac{2}{(x + r_p/\delta)} \frac{dS^*}{dx} = \phi_s \frac{S^*}{(S^* + K_s^* + S^{*2}/K_i^*)} \frac{C^*}{(C^* + K_0^*)} \quad (A.1)$$

$$\frac{d^2C^*}{dx^2} + \frac{2}{(x + r_p/\delta)} \frac{dC^*}{dx} = \phi_o \frac{S^*}{(S^* + K_s^* + S^{*2}/K_i^*)} \frac{C^*}{(C^* + K_0^*)} \quad (A.2)$$

The corresponding boundary conditions are

$$\frac{dS^*}{dx} = \frac{dC^*}{dx} = 0 \quad \text{at } x = 0 \quad (A.3)$$

$$\frac{dS^*}{dx} = Bi_s(1 - S^*) \quad \text{at } x = 1.0 \quad (A.4)$$

$$\frac{dC^*}{dx} = Bi_o(1 - C^*) \quad \text{at } x = 1.0 \quad (A.5)$$

Eq. (A.1) can be written using orthogonal collocation method as

$$\sum_{J=1}^5 B_{KJ} S_J^* + \frac{2}{(x + r_p/\delta)} \sum_{J=1}^5 A_{KJ} S_J^* = \phi_s F(S^*, C^*) \quad K = 1, 2, 3 \quad (A.6)$$

Eq. (A.2) can be written as

$$\sum_{J=1}^5 B_{KJ} C_J^* + \frac{2}{(x + r_p/\delta)} \sum_{J=1}^5 A_{KJ} C_J^* = \phi_o F(S^*, C^*) \quad K = 1, 2, 3 \quad (A.7)$$

Eq. (A.4) can be written as

$$\sum_{J=1}^5 A_{4J} S_J^* = Bi_s(1 - S_5^*) \quad (A.8)$$

similarly, Eq. (A.5)

$$\sum_{J=1}^5 A_{4J} C_J^* = Bi_o(1 - C_5^*) \quad (A.9)$$

The collocation points and the corresponding matrices used in the Eqs. (A.6)–(A.9) are available in reference [14]. The Eqs. (A.6)–(A.9) are solved using Newton–Raphson method. Similar work involving orthogonal collocation has been mentioned in references [5,12].

## References

- [1] J.C. Van Den Heuvel, H.H. Beeftink, Kinetic effects of simultaneous inhibition by substrate and product, *Biotechnol. Bioeng.* 31 (1988) 718–723.
- [2] D.W. Holladay, C.W. Hancher, C.D. Scott, D.D. Chilcote, Biodegradation of phenolic waste liquors in stirred-tank, packed bed and fluidized-bed bioreactors, *J. Water Pollut. Control Fed.* 50 (1978) 2573.
- [3] M. Denac, I.J. Dunn, Packed and fluidized bed biofilm reactor performance for anaerobic wastewater treatment, *Biotechnol. Bioeng.* 32 (1986) 159–173.
- [4] W.T. Tang, K. Wiesecarver, L.S. Fan, Dynamics of a draft tube gas–liquid–solid FBBR for phenol degradation, *Chem. Eng. Sci.* 42 (1987) 2123–2134.
- [5] W.T. Tang, L.S. Fan, Steady state phenol degradation in a draft-tube fluidized bed bioreactor, *AIChE J.* 33 (1987) 239–249.
- [6] A.G. Livingston, H.A. Chase, Development of a phenol degrading fluidized bed bioreactor for constant biomass hold up, *Chem. Eng. J.* 45 (1991) B35–B47.
- [7] L.S. Fan, R. Levy-Ramos, K.D. Wiesecarver, B.J. Zehner, Diffusion of phenol through a biofilm grown on activated carbon particles in a Draft-Tube three phase Fluidized bed bioreactor, *Biotechnol. Bioeng.* 35 (1990) 279–286.

- [8] R.M. Worden, T.L. Donaldson, Dynamics of a biological fixed film for phenol degradation in a FBBR, *Biotechol. Bioeng.* 30 (1987) 398–412.
- [9] A.M.G. Alvaro, Monteiro, R.A.R. Boaventura, A.E. Rodridues, Phenol biodegradation by *Pseudomonas putida* DSM 548 in a batch reactor, *Biochem. Eng. J.* 6 (2000) 45–49.
- [10] C.S.A. Sa, R.A.R. Boaventura, Biodegradation of phenol by *Pseudomonas putida* DSM 548 in a trickling bed reactor, *Biochem. Eng. J.* 9 (2001) 211–219.
- [11] G. Gonzalez, M.G. Herrera, M.T. Garcia, M.M. Pena, Biodegradation of phenol in a continuous process: comparative study of stirred tank and fluidized-bed bioreactors, *Bioresource Technol.* 76 (2001) 245–251.
- [12] A.G. Livingston, H.A. Chase, Modeling phenol degradation in a fluidized bed bioreactor, *AIChE J.* 35 (1989) 1980–1992.
- [13] N.H. Furman, *Standard Methods of Chemical Analysis*, fifth ed., vol. 2, 1959.
- [14] J. Villadsen, M.L. Michelsen, *Solution of Differential Equation Models by Polynomial Approximation*, Prentice Hall, Englewood Cliffs, NJ, 1978.