

Journal of Hazardous Materials B136 (2006) 727-734

www.elsevier.com/locate/jhazmat

Journal of Hazardous Materials

# Mass transfer correlation for phenol biodegradation in a fluidized bed bioreactor

A. Venu Vinod\*, G. Venkat Reddy

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

Received 26 May 2005; received in revised form 6 January 2006; accepted 9 January 2006 Available online 28 February 2006

#### Abstract

Experiments have been carried out in a draft tube fluidized bed bioreactor to study biodegradation of synthetic wastewater containing phenol. The microorganism employed in the study *Psuedomonas putida* has been immobilized on solid support particles. Studies have been carried out at different feed concentrations of phenol, air flow rates and feed flow rates. The mass transfer coefficient for phenol transfer from bulk phase to the surface of the biofilm on the solid particle has been estimated from observed experimental data using the conservation equations. The mass transfer coefficient was found to be in the range of  $0.0726 \times 10^{-5}$  to  $0.2012 \times 10^{-5}$  m s<sup>-1</sup>. It was found to increase with increase in feed concentration, air flow rate and feed flow rate. A dimensionless correlation has been developed for the mass transfer coefficient in terms of Sherwood, Reynolds and Schmidt numbers, and the same has been compared with correlations available in literature.

Keywords: Biodegradation; Wastewater; Phenol; Mass transfer coefficient; Biofilm

#### 1. Introduction

Chemical and petroleum industries generate a wide variety of highly toxic organic wastes. The effluents of these industries often contain aromatic compounds that are resistant to natural degradation and therefore persist in the environment. One of the major organic pollutants found in these wastewaters is phenol. Process industries, which are major sources of phenolic discharges, are petroleum refineries, coal carbonization units, gas and coke industries and fiberglass units. Biodegradation of phenol in fluidized bed bioreactors (FBRs) has been reported because of their superior performance and some inherent advantages [1-6]. The superior performance of FBRs is due to very high concentration of immobilized cells on the solid particles, prevention of washout of the microbes, lack of clogging of the biomass, ease of separation of cells from product stream and elimination of limit on liquid flow rates due to decoupling of residence time of liquid phase and of microbial cells.

0304-3894/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2006.01.043

In an FBR transport of phenol along with oxygen and other nutrients takes place from bulk solution to the surface of biofilm. Therefore, the knowledge of phenol mass transfer coefficient, inter alia, from bulk solution to surface of bioparticle is essential for design and operation of FBRs. Livingston and Chase [2] compared the value obtained from their experiments with that calculated from the correlation of Arters and Fan [7], and found reasonable agreement between the two values. Studies by Tang and Fan [1] and Livingston and Chase [2] did not involve phenol directly in determination of mass transfer coefficient for phenol from bulk phase to the surface of biofilm. In another study [5] phenol mass transfer coefficient was determined for biodegradation of phenol in synthetic wastewater in a differential fluidized bed.

There have been reports of mass transfer correlations for phenol degradation in packed bed bioreactors [8,9]. In literature though there have been reports of mass transfer coefficient for phenol in FBRs, reports of mass transfer correlation for phenol degradation in biofilm in FBRs have been scarce. The present study addresses this issue and reports the work carried out to develop mass transfer correlation for phenol biodegradation in FBR in terms of operating variables, viz., air and feed flow rates, liquid properties.

<sup>\*</sup> Corresponding author. Tel.: +91 870 2462621; fax: +91 870 2459547. *E-mail address:* avv@nitw.ernet.in (A. Venu Vinod).

**Nomenclature**  $A_p$  surface area of the bioparticle (m<sup>2</sup>)  $D_1$  offective diffusion coefficient of pha

- $D_{\rm f}$  effective diffusion coefficient of phenol within the biofilm (m<sup>2</sup> s<sup>-1</sup>)
- $k_s$  mass transfer coefficient for the substrate (phenol) (m s<sup>-1</sup>)
- $K_{\rm s}$  Monod constant (kg/m<sup>3</sup>)
- *K* first order reaction rate constant for phenol degradation  $(kg/m^3)^{-1} - h^{-1} = \mu_{max}/(Y_{x/s} K_s)$
- *N*<sub>p</sub> number of bioparticles in the fluidized bed bioreactor
- Q feed flow rate to the fluidized bed bioreactor (m<sup>3</sup> s<sup>-1</sup>)

$$\bar{r}$$
 characteristic length,  $(r_b^3 - r_p^3)/3r_b^2$  (m)

- *r* radial distance (m)
- $r_{\rm b}$  radius of the biofilm covered support particle (m)
- $r_{\rm p}$  radius of clean support particle (m)
- $R_{\rm s}$  phenol consumption rate (kg s<sup>-1</sup>)
- *S* phenol concentration  $(kg/m^3)$
- *S*<sub>b</sub> steady state bulk phenol concentration in fluidized bed bioreactor (kg/m<sup>3</sup>)
- $S_i$  phenol concentration at the biofilm surface (kg/m<sup>3</sup>)
- $S_{\rm f}$  phenol concentration in feed to fluidized bed bioreactor (kg/m<sup>3</sup>)
- $V_{\rm g}$  superficial velocity of air (m s<sup>-1</sup>)
- $V_1$  superficial velocity of feed (m s<sup>-1</sup>)
- $V_{\rm p}$  volume of biofilm on a particle (m<sup>3</sup>)
- X microorganism concentration (kg/m<sup>3</sup>)
- $X_{\rm f}$  biofilm density (kg/m<sup>3</sup>)
- $Y_{x/s}$  yield coefficient for phenol (kg/kg)

Greek letters

 $\phi_{\rm s}$  Thiele modulus =  $\bar{r}\sqrt{KX_{\rm f}/D_{\rm f}}$ 

- $\eta$  effectiveness factor for the biofilm system
- $\mu_{\text{max}}$  maximum specific growth rate (h<sup>-1</sup>)

# 2. Experimental

#### 2.1. The reactor set-up

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

# 2.2. 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 can be sparged into the reactor. The total volume of the reactor is about  $2.67 \times 10^{-3}$  m<sup>3</sup> (2.671). The top of the glass reactor is closed with a plate through which all the probes 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  $1005 \text{ kg/m}^3$  are used for immobilization of the microorganism. The average diameter of the beads is 3.895 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  $0.11 \times 10^{-7}$  to  $9.7 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$  (40–3500 ml h<sup>-1</sup>). 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. 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.

#### 2.3. Reactor instrumentation

To maintain the pH of the system a pH meter and a controller have been provided. pH has been 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 has been supplied in the form of air from a compressor. The oxygen content in the reaction medium can be measured using a DO meter. The flow rate of air can be measured using rotameter, with a range of  $0.167 \times 10^{-4}$ to  $1.67 \times 10^{-4}$  m<sup>3</sup> s<sup>-1</sup> (1–10 lpm).

# 2.4. Microbial culture

A strain of microorganism *Pseudomonas putida* (NCIM-2176) reported to be capable of utilizing phenol as the sole carbon and energy source was obtained from National Collection of Industrial Microorganisms (NCIM) of National Chemical Laboratory (NCL), Pune, India.

# 2.5. Subculture

The bacterium is subcultured once in a month by preparing slants using nutrient agar [6]. To each of the test tubes 15 ml of this nutrient agar solution is added in a tilted position around  $30^{\circ}$  to the horizontal. After the solidification of the nutrient agar in the test tubes, colonies of bacteria were introduced on it, and incubated for 24 h at 30 °C and then stored at 4 °C in a refrigerator.

#### 2.6. Culture preparation

The culture 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  $2.6 \times 10^{-3}$  m<sup>3</sup> (2.61) of 0.05 kg/m<sup>3</sup> (50 ppm) of phenol solution containing growth medium [2,6]. Before inoculation of the organism sterilization of the phenol solution was done in autoclave at a gage

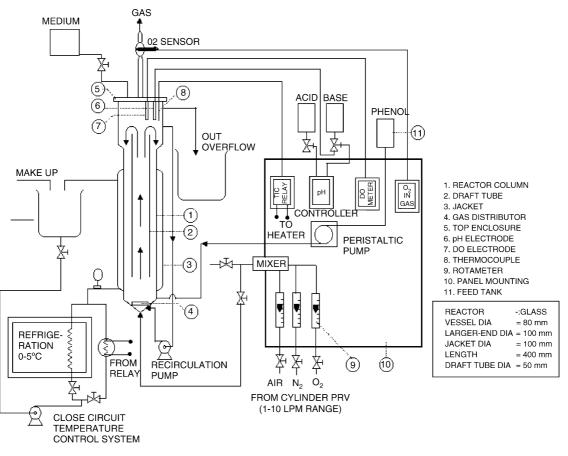


Fig. 1. Schematic diagram of the experimental set-up.

pressure of  $1.034 \times 10^5$  N/m<sup>2</sup> (15 psi) for 20 min. This has been done to selectively grow the *Pseudomonas* species.

#### 2.7. Growth medium

The growth medium was made up using tap water. Sterile conditions were not maintained during the continuous operation of the reactor, to simulate treatment of actual plant wastewater as the latter would contain different contaminants.

## 2.8. Start-up of the equipment

A  $2.6 \times 10^{-3}$  m<sup>3</sup> (2.61) of reaction medium 24 h after inoculation 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 the FBR was put in continuous operation with a feed flow rate of  $0.141 \times 10^{-6}$  m<sup>3</sup> s<sup>-1</sup> (510 ml h<sup>-1</sup> corresponding to the dilution rate of 0.2167 h<sup>-1</sup> with a solid particle volume fraction of 0.1 and gas hold-up of 50 cc). Synthetic wastewater containing phenol has been used as feed. Synthetic wastewater was prepared by distilling phenol to obtain pure phenol and dissolving it subsequently in water. Phenol concentration in feed was 0.05 kg/m<sup>3</sup> (50 ppm). The dissolved oxygen (DO) concentration in the reactor was maintained at 2 ppm using air. The pH in all the runs was maintained at 7.0 using 0.1N HCl and 0.1N

NaOH [1,2]. The reaction temperature was maintained at  $30 \,^{\circ}$ C in all the runs using a temperature controller provided with a heating/cooling circuit. The concentration of phenol in the overflow from the reactor was analyzed every 1 h iodometrically [10].

# 2.9. Determination of biofilm density $(X_f)$

The biofilm density in terms of mass of dry biomass per volume of biofilm was measured as follows: a sample of biomassladen particles was withdrawn from the reactor and was weighed. The particles were then placed in oven at  $105 \,^{\circ}$ 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. The biofilm density was then calculated by dividing the amount of the biomass by the amount of water present in biofilm.

Experiments have been carried out using *P. putida* for determining the mass transfer coefficient for phenol from bulk phase to the surface of the biofilm. Four feed flow rates  $0.11 \times 10^{-6}$ ,  $0.14 \times 10^{-6}$ ,  $0.166 \times 10^{-6}$  and  $0.177 \times 10^{-6}$  m<sup>3</sup> s<sup>-1</sup> (396, 504, 600 and 640 ml h<sup>-1</sup>) have been used. The effect of air flow rate has been examined at three air flow rates of  $0.33 \times 10^{-4}$ ,  $0.5 \times 10^{-4}$  and  $0.667 \times 10^{-4}$  m<sup>3</sup> s<sup>-1</sup> (2, 3 and 4 lpm). The feed concentrations of phenol that have been used in the study are

0.05, 0.1, 0.15, 0.2 and  $0.25 \text{ kg/m}^3$  (50, 100, 150, 200 and 250 ppm). The modeling aspects and the methodology for determining the transfer coefficients are discussed in Section 3.

# 3. Mathematical modeling

There are three basic processes occurring in the biodegradation of phenol in a fluidized bed bioreactor:

- (a) transport of oxygen from the gas phase into the bulk liquid,
- (b) transport of phenol, oxygen and other nutrients from the bulk liquid phase to the surface of the film and
- (c) simultaneous diffusion and reaction of phenol, oxygen and other nutrients within the biofilm.

Since dissolved oxygen concentration in bulk phase could be measured directly with a DO meter, modeling of transport of oxygen from gas phase to bulk phase (process (a)) was not carried out in the present study. Process (c) is not dependent on flow conditions or turbulence in the reactor as it is a molecular phenomenon. Process (b) is important as the rate of transport of phenol from the bulk phase to the surface of the biofilm would directly influence the biochemical reaction (biodegradation of phenol) taking place in biofilm. Hence the knowledge of mass transfer coefficients for the transfer of phenol is imperative in design and modeling of bioreactors.

The measurement of mass transfer coefficient for phenol in fluidized bed bioreactor is based on material balance and kinetics of biodegradation of phenol in the biofilm. Transfer of substrate into biofilm is assumed to occur in two steps:

- 1. transfer of substrate from bulk liquid to the surface of bioparticle and
- 2. diffusion through the microorganism (biofilm) layer.

In the fluidized bed bioreactor, a diffusion-reaction model is supposed to fit on a spherical bioparticle on the basis of following assumptions:

- 1. The bioparticle is spherical in shape.
- 2. Phenol is the limiting substrate, and oxygen and other nutrients are in excess. In the experiments carried out the maximum feed concentration used was 250 ppm. At this level of concentration if substrate inhibition is ignored, then the Haldane expression reduces to Monod equation. Now, the growth expression is of first order with respect to the substrate concentration based on the assumption that  $K_s > S$  and is given by [5]:

$$R_{\rm s} = \frac{\mu_{\rm max} XS}{Y_{x/{\rm s}} K_{\rm s}} = KXS$$

3. Cell growth and substrate utilization kinetics obtained from suspended cell culture can be applied equally well to the immobilized microorganism on the support particles.

- 4. The diffusivity of limiting substrate through the biofilm is assumed to be constant and is independent of radial position.
- 5. Bioadsorption of the limiting substrate onto support particles is negligible.

Based on the continuity equation within the biofilm, the phenol concentration on the surface of the film is calculated. At steady state, the simultaneous transport and consumption of phenol within the biofilm is described in the substrate continuity equation as:

$$\frac{D_{\rm f}}{r^2} \frac{\rm d}{{\rm d}r} \left( r^2 \frac{{\rm d}S}{{\rm d}r} \right) = K X_{\rm f} S \tag{1}$$

with the boundary conditions:

 (i) at the biofilm surface (radius r<sub>b</sub>) the substrate concentration is equal to the interface concentration (S<sub>i</sub>);

$$r = r_{\rm b}, \quad \text{when } S = S_{\rm i}$$
 (2)

(ii) there is no diffusion into the surface of the bare particle (radius  $r_{\rm p}$ ).

$$r = r_{\rm p}, \quad \text{when } \frac{\mathrm{d}S}{\mathrm{d}r} = 0$$
 (3)

Analytical solution of Eq. (1) using boundary conditions (2) and (3) gives [11]:

$$S = \frac{S_{\rm i} r_{\rm b}}{r} \left[ \frac{(nr_{\rm p} + 1){\rm e}^{n(r-r_{\rm p})} + (nr_{\rm p} - 1){\rm e}^{-n(r-r_{\rm p})}}{(nr_{\rm p} + 1){\rm e}^{n\delta} + (nr_{\rm p} - 1){\rm e}^{-n\delta}} \right]$$
(4)

where  $\delta = r_{\rm b} - r_{\rm p}$ .

$$n = \sqrt{\frac{KX_{\rm f}}{D_{\rm f}}}$$

To measure the extent to which the reaction rate is lowered because of resistance to mass transfer (due to of immobilization of microorganism onto the particles), effectiveness factor  $\eta$ , is defined as:

 $\eta = \frac{\text{actual reaction rate}}{\text{reaction rate if not slowed down by diffusion}}$  $\frac{(dS/dr) = A_{\rm P} D_{\rm F} / V_{\rm P}}{(dS/dr) = A_{\rm P} D_{\rm F} / V_{\rm P}}$ 

$$=\frac{(dS/dr)_{r=r_{\rm b}}A_{\rm p}D_{\rm f}/V_{\rm p}}{KX_{\rm f}S_{\rm i}}$$

where  $A_p$  = surface area of bioparticle (m<sup>2</sup>) and  $V_p$  = volume of biofilm on a particle (m<sup>3</sup>).

Using Eq. (4) obtained above for *S*, the effectiveness factor can be derived as [11]:

$$\eta = \frac{1}{\phi_{\rm s}} \left( \frac{1}{\tanh 3\phi_{\rm s}} - \frac{1}{3\phi_{\rm s}} \right) \tag{5}$$

From the above equations it can be seen that the effectiveness factor  $(\eta)$  is a function of physical and biochemical properties in biofilm, viz., biofilm density, diffusion coefficient in biofilm and rate constant. An increase in rate constant (*K*) and biofilm density ( $X_f$ ) would decrease the effectiveness factor, whereas larger values of the diffusion coefficient would result in higher

Table 1a Parameters used for calculation of mass transfer coefficient,  $k_s$ 

Feed concentration, $S_{\rm f}$ (ppm)	Bioparticle radius, <i>r</i> <sub>b</sub> (cm)	$\bar{r}$ (cm)	$\phi_{ m s}$	η	V <sub>p</sub> (cc)	$X_{\rm f}$ (kg/m <sup>3</sup> )	$D_{\rm f} \times 10^9 \ ({\rm m}^2 \ {\rm s}^{-1})$
50	0.1987	0.00387	1.0766	0.638	0.00192	30	0.5
100	0.2021	0.0071	2.715	0.323	0.003644	51	0.45
150	0.2042	0.009	4.367	0.2115	0.00472	73	0.4
200	0.2076	0.0121	6.85	0.1389	0.00655	87	0.35
250	0.2100	0.0142	9.03	0.1066	0.00787	94	0.3

substrate concentrations in the biofilm leading to high reaction rates in biofilm, hence the higher effectiveness factor. The Thiele modulus related to effectiveness factor, is a measure of reaction rate to diffusion rate in biofilm. The characteristic length  $\bar{r}$  given above is the ratio of volume of the biofilm to surface area of the bioparticle. Higher values of  $\bar{r}$  would have an opposing effect on the effectiveness factor. Large values of  $\bar{r}$  are indicative of thicker biofilms, which give lower effectiveness factor.

Under steady state conditions, by equating the rate of phenol degradation in the bioreactor to the total rate of mass transfer to the bioparticles in fluidized bed bioreactor, mass transfer coefficient can be calculated:

$$N_{\rm p}A_{\rm p}k_{\rm s}(S_{\rm b}-S_{\rm i}) = Q(S_{\rm f}-S_{\rm b}) \tag{6}$$

Under steady state conditions, mass balance over all bioparticles results in:

$$N_{\rm p}V_{\rm p}KS_{\rm i}X_{\rm f}\eta = Q(S_{\rm f} - S_{\rm b}) \tag{7}$$

where  $V_p$  = volume biofilm on a particle =  $4/3\pi (r_b^3 - r_p^3)$  (m<sup>3</sup>).

In Eq. (7),  $S_i$  is unknown and can be calculated using corresponding experimental data. Knowing the value of  $S_i$ , Eq. (6) can be used to calculate the external mass transfer coefficient,  $k_s$ . Mass transfer coefficient is determined at different gas and liquid flow rates.

## 4. Results and discussion

The mass transfer coefficient  $k_s$  calculated using Eqs. (6) and (7) has been found to be in the range of  $0.0726 \times 10^{-5}$  to  $0.2012 \times 10^{-5}$  m s<sup>-1</sup>. The model parameters used in the work have been given in Tables 1a and 1b. The phenol concentration at the surface of the biofilm  $S_i$  has been found to be in the range of 0.001078-0.0044 kg/m<sup>3</sup> depending on the feed concentration, feed flow rate and air flow rate. The value of Monod constant  $K_s$  (0.01639 kg/m<sup>3</sup>) for the microorganism employed in the study is very much greater than the surface concentration  $S_i$ , thereby justifying the assumption  $K_s > S_i$  made in modeling.

Table 1b

Model parameters for mass transfer studie
---

Parameters	Value	
$\overline{\mu_{\max} (h^{-1})}$	0.456	
$K_{\rm s}$ (kg/m <sup>3</sup> )	$16.39 \times 10^{-3}$	
$Y_{x/s}$ (kg/kg)	0.6	
Np	8119	
$r_{\rm p}$ (m)	$1.9475 \times 10^{-3}$	

Reynolds number at different air flow rates

Air flow rate, $Q_a$		Superficial velocity, $V_{\rm g} \ (\times 10^3  {\rm m  s^{-1}})$	Reynolds number, <i>Re</i>	
lpm	$\times 10^3 \text{ m}^3 \text{ s}^{-1}$			
2	0.03333	20.08	9.264	
3	0.05	30.12	13.896	
4	0.06667	40.01	18.46	

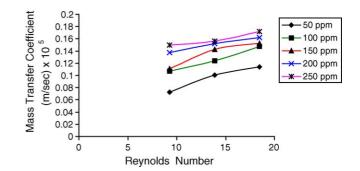


Fig. 2. Mass transfer coefficient of phenol vs. Reynolds number for different feed concentrations at feed flow rate of  $396 \text{ ml h}^{-1}$ .

Previously reported values of  $k_s$  for phenol biodegradation were in the range of  $0.176 \times 10^{-4}$  to  $7.43 \times 10^{-4}$  m s<sup>-1</sup> for differential fluidized bed biofilm reactor [5].

#### 4.1. Effect of Reynolds number on mass transfer coefficient

Reynolds number has been calculated for air based on the draft tube diameter. It is calculated using the relation  $V_g d_p \rho_g / \mu_g$ , based on the gas velocity in draft tube. The values of the Reynolds number have been given in Table 2. The effect of Reynolds number on mass transfer coefficient is shown in Figs. 2–5 for feed flow rates of  $0.11 \times 10^{-6}$ ,  $0.14 \times 10^{-6}$ ,

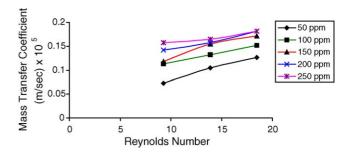


Fig. 3. Mass transfer coefficient of phenol vs. Reynolds number for different feed concentrations at feed flow rate of  $504 \text{ ml h}^{-1}$ .

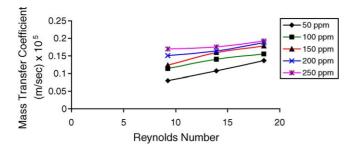


Fig. 4. Mass transfer coefficient of phenol vs. Reynolds number for different feed concentrations at feed flow rate of  $600 \text{ ml } \text{h}^{-1}$ .

 $0.166 \times 10^{-6}$  and  $0.177 \times 10^{-6}$  m<sup>3</sup> s<sup>-1</sup> (396, 504, 600 and 640 ml h<sup>-1</sup>) and feed concentrations of 0.05, 0.1, 0.15, 0.2 and 0.25 kg/m<sup>3</sup> (50, 100, 150, 200 and 250 ppm). In Fig. 2 mass transfer coefficient is found to increase with increase in Reynolds number. A similar trend is observed at all other feed flow rates, though the values of mass transfer coefficients are marginally larger at higher flow rates. Higher turbulence at higher flow rates could have contributed to this increase in mass transfer coefficient.

The values obtained in the present work are much smaller when compared to the values reported in literature [1,2,5]. This is because of the fact that the range of Reynolds number in the present study was from 9 to 20 whereas the values were about 1200 in case of Tang and Fan [1] and about 600 in the study of Livingston and Chase [2]. The Reynolds number varied between 120 and 150 in the studies reported by Beyenal and Tanyolac [5].

# 4.2. Effect of feed concentration on mass transfer coefficient

Variation of mass transfer coefficient with inlet feed concentration has been studied at feed flow rates of 396, 504, 600 and  $640 \text{ ml h}^{-1}$  for three different air flow rates of 2, 3 and 4 lpm. The results are presented in Figs. 6–9. From these figures it can be observed that mass transfer coefficient increases with increase in feed concentration.

For the biochemical reaction under study where the diffusion and chemical reaction are studied, both are significant to rate controlling. When Thiele modulus  $\phi_s < 0.2$  the rate of biochemical reaction is not controlled by diffusion. When  $\phi_s > 5$  the reaction is controlled by diffusion.  $\phi_s$  in the present study

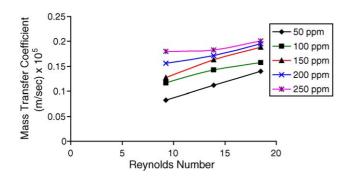


Fig. 5. Mass transfer coefficient of phenol vs. Reynolds number for different feed concentrations at feed flow rate of  $640 \text{ ml h}^{-1}$ .

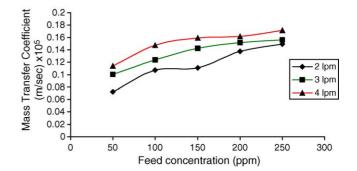


Fig. 6. Mass transfer coefficient of phenol vs. feed concentration for different air flow rates at feed flow rate of  $396 \text{ ml h}^{-1}$ .

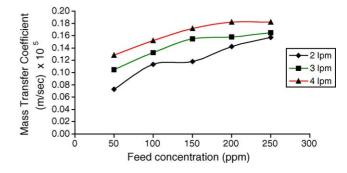


Fig. 7. Mass transfer coefficient of phenol vs. feed concentration for different air flow rates at feed flow rate of  $504 \text{ ml h}^{-1}$ .

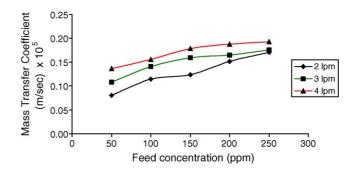


Fig. 8. Mass transfer coefficient of phenol vs. feed concentration for different air flow rates at feed flow rate of  $600 \text{ ml h}^{-1}$ .

varied between 1.0766 and 9.03. Both diffusion and chemical reaction are controlling. As the feed concentration increases  $\phi_s$  increases indicating the increasing dependence of rate on diffusion. The reaction rate becomes irrelevant as the  $\phi_s$  increases

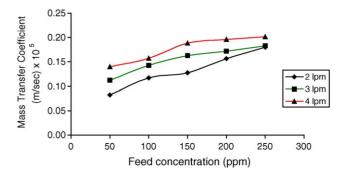


Fig. 9. Mass transfer coefficient of phenol vs. feed concentration for different air flow rates at feed flow rate of  $640 \text{ ml h}^{-1}$ .

Table 3 Sherwood number, Reynolds number and air/feed velocity ratios at various feed concentrations

Re	$V_{\rm g}/V_{\rm l}$	Sh for various feed concentrations					
		50 ppm	100 ppm	150 ppm	200 ppm	250 ppm	
9.264	303	2.913	4.297	4.449	5.513	5.998	
	238	2.929	4.55	4.734	5.705	6.315	
	201	3.229	4.586	4.955	6.058	6.828	
	188	3.3059	4.682	5.111	6.271	7.22	
13.896	454	4.024	4.979	5.725	6.094	6.29	
	357	4.193	5.299	6.207	6.323	6.608	
	301	4.317	5.633	6.395	6.604	7.045	
	281	4.493	5.733	6.54	6.8926	7.326	
18.46	603	4.566	5.902	6.387	6.491	6.889	
	474	5.079	6.1023	6.8806	7.298	7.298	
	400	5.47	6.227	7.145	7.535	7.727	
	374	5.617	6.319	7.559	7.852	8.072	
Schmidt	number	2645	3871	4364	4692	4818	

beyond 5. Therefore, the rate will increase as the feed concentration increases because the driving force required for diffusion, i.e. the concentration difference increases resulting in higher flux. The surface concentration of phenol on the bioparticle remained at very low level for the entire feed concentration range studied. Therefore as can be seen from Figs. 6–9 the mass transfer coefficient increases as the feed concentration increases.

#### 4.3. Dimensionless correlation

Large number of correlations are available in the literature for liquid phase mass transfer coefficients in bubble columns and columns with internal fittings, e.g. draft tubes, baffles, etc. [12,13]. But most of these relations pertain to chemical processes. Very few correlations are available in literature for fluidized bed bioreactors. Hence a correlation is developed between the dimensionless numbers Sherwood, Reynolds and Schmidt numbers, which show the effect of air and liquid flow rates and other liquid properties on mass transfer coefficient of phenol. To develop the correlation between Sherwood, Reynolds and Schmidt numbers, various liquid properties are found for the experimental conditions in the study. The dimensionless numbers obtained in the work have been mentioned in Table 3. At a given feed concentration Schmidt number was found to be a weak function of feed and air flow rates. Therefore, effect of feed and air flow rates on Schmidt number was neglected for a given feed concentration. Kinematic viscosity was determined using Redwood viscometer and diffusivity was calculated using the Wilke–Chang equation [14]. Fig. 10 shows the variation of Sherwood number with Schmidt number at different values of Reynolds number.

The dimensionless correlation has been obtained using regression on Sherwood number, Reynolds number, Schmidt number and ratio of air to feed velocity as:

$$Sh = 0.00559 Re^{0.6855} Sc^{0.8274} \left(\frac{V_{\rm g}}{V_{\rm l}}\right)^{-0.2955}$$

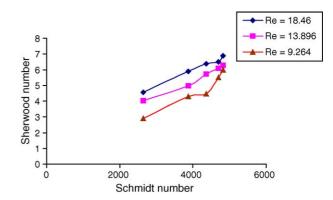


Fig. 10. Variation of Sherwood number with Schmidt number at a feed flow rate of  $390 \,\text{ml}\,\text{h}^{-1}$  at various Reynolds numbers based on gas velocity.

There have been not any correlations reported in literature for phenol biodegradation in fluidized bed bioreactors. Correlations were reported by Sheeja and Murugesan [8] for biodegradation of phenol in synthetic wastewater in packed bed up-flow reactors in terms of Colburn factor  $j_D$ :

$$j_{\rm D} = K R e^{n-1}$$

The values of K obtained were in the range of 1.34-1.51 depending on the size of beads used in the packed bed. n-1 was obtained as -0.28. If the above equation is rearranged to express in terms of Sherwood number,

$$Sh = KRe^{0.72}Sc^{2/3}$$

The Reynolds number was based on the liquid flow rate whereas in the present work it was based on the gas velocity. The effect of Schmidt number is different in the present study and from that given above, as the exponent 2/3 was fixed and not obtained from regression by Sheeja and Murugesan. Recently a similar correlation was reported [9] for treatment of phenolic effluents from petrochemical, leather and polymer industries.

Previously published correlations for mass transfer between liquid and solid in fluidized beds have the exponent for Reynolds and Schmidt numbers in the range of 0.5–0.67 and 0.333–0.436, respectively [15–17]. However, these correlations have not been for biochemical reactions. In biological processes the effect of physical properties is shown by the higher values of the Schmidt number and its exponent obtained in this work compared to that reported for chemical processes.

# 5. Conclusions

The mass transfer coefficient for phenol  $k_s$  increases with increase in feed concentration, air and feed flow rates. The first order rate expression can be used for modeling the phenol biodegradation taking place on bioparticle surface for the range of feed concentrations used in the study. A dimensionless correlation has been developed for mass transfer coefficient for phenol  $k_s$  in terms of dimensionless numbers Sherwood, Reynolds and Schmidt numbers and ratio of gas to liquid velocities. The effect of physical properties is more on the mass transfer coefficient in biological processes compared to chemical processes in fluidized beds.

#### References

- W.T. Tang, L.S. Fan, Steady state phenol degradation in a draft-tube fluidzed bed bioreactor, AIChE J. 33 (1987) 239–249.
- [2] A.G. Livingston, H.A. Chase, Modeling phenol degradation in a fluidized-bed Bioreactor, AIChE J. 35 (1989) 1980–1992.
- [3] L.S. Fan, R. Levya-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.
- [4] A.G. Livingston, Biodegradation of 3,4-dichloroaniline in a fluidized bed bioreactor and a steady state biofilm kinetic model, Biotechnol. Bioeng. 38 (1991) 260–272.
- [5] H. Beyenal, A. Tanyolac, The effect of biofilm characteristics on the external mass transfer coefficient in a differential fluidized bed biofilm reactor, Biochem. Eng. J. 1 (1998) 53–61.
- [6] A. Venu Vinod, G. Venkat Reddy, Simulation of biodegradation process of phenolic wastewater at higher concentrations in a fluidized-bed bioreactor, Biochem. Eng. J. 24 (2005) 1–10.
- [7] D.C. Arters, L.S. Fan, Soild liquid mass transfer in a gas-liquid-solid fluidized bed, Chem. Eng. Sci. 41 (1986) 107-115.

- [8] R.Y. Sheeja, T. Murugesan, Mass transfer studies on biodegradation of phenols in up-flow packed bed reactors, J. Hazard. Mater. 89 (2002) 287–301.
- [9] T. Murugesan, R.Y. Sheeja, A correlation for mass transfer coefficients during the biodegradation of phenolic effluents in a packed bed reactor, Sep. Purif. Technol. 42 (2005) 103–110.
- [10] N.H. Furman, Scott's Standard Methods of Chemical Analysis, vol. 2, fifth ed., D. Van Nostrand Co. Inc., New York, 1959.
- [11] W.K. Shieh, J.D. Keenan, Fluidized bed biofilm reactor for wastewater treatment, in: A. Fiechter (Ed.), Advances in Biochemical Engineering/Biotechnology, vol. 33, Springer, Berlin, 1986, pp. 132–168.
- [12] H.W. Blanch, D.S. Clark, Biochemical Engineering, Marcel Dekker Inc., New York, 1996.
- [13] R.E. Treybal, Mass Transfer Operations, third ed., McGraw-Hill, Singapore, 1980.
- [14] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, fourth ed., McGraw-Hill Book Company, New York, 1987.
- [15] T. Koloini, M. Sopcic, M. Zumer, Mass transfer in liquid fluidized beds at low Reynolds numbers, Chem. Eng. Sci. 32 (1977) 637–641.
- [16] P. Tournie, C. Laguerie, J.P. Couderc, Correlation for mass transfer between fluidized spheres and liquid, Chem. Eng. Sci. 34 (1979) 1247–1255.
- [17] K. Muroyama, T. Nakade, Y. Goto, T. Kato, Wall-to-liquid mass transfer in a gas-slurry transport bed, Chem. Eng. Sci. 56 (2001) 6099– 6106.