Research Article

Mass Transfer Studies on Adsorption of Phenol from Wastewater Using *Lantana camara,* Forest Waste

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Adsorption is one of the important treatment methods for the removal of pollutants from wastewater. The determination of rate controlling step in the process is important in the design of the process. Therefore, in the present work, mass transfer studies were done to evaluate the rate-limiting step in the adsorption of phenol from aqueous solution onto *Lantana camara*. Different mass transfer models were used to find the rate-limiting step and also to find the values of external mass transfer coefficient and diffusion coefficient. The Biot number was found to investigate the importance of external mass transfer to intraparticle diffusion. From the various models studied and the Biot numbers obtained, it was found that the adsorption on *Lantana camara* was controlled by film diffusion. The sensitivity analysis was performed to study the significance of the model parameters on the adsorption process.

1. Introduction

In the recent time, the increased industrial activities have escalated more environmental problems such as the contamination of water sources due to the accumulation of various toxic pollutants from the industrial wastewater. Phenol, one of the prominent pollutants in the wastewater, has been designated as priority pollutant by the environmental regulations [1]. Its permissible concentration should be less than 0.1 mg/L before it is released into the aquatic environment [1]. Phenol is introduced into the aquatic environment from the wastewater released from various industries such as pesticide, paper and pulp, resin, petrochemicals, fertilizers, and pharmaceutical industries and petroleum refineries [2]. It also causes harmful effects on the human health and aquatic life. Therefore, there is a need to treat phenol from wastewater before it is released into the environment.

Various treatment methods like biodegradation, biosorption, pervaporation, membrane separation process, extraction, adsorption on activated carbon, and advanced oxidation processes were used to treat phenol compounds from wastewater [3]. Adsorption using activated carbon is considered

to be an effective wastewater treatment. But because of the expensive nature of activated carbon, there is a growing interest in producing an adsorbent from low cost agricultural materials. Therefore, *Lantana camara*, an invasive poisonous forest weed found in the tropical moist deciduous forests, that is, eastern side of Western Ghats in Coorg region, Karnataka, India, was selected for adsorbent preparation [4]. Due to the infestation, the forest weed eliminates the native species and results in decreased biodiversity. It is considered as poisonous, as the weed harbors pests such as malarial mosquitoes and tsetse flies, resulting in serious health issues. Therefore, by using this weed for the adsorbent preparation, it can reduce the problem of disposing of the forest waste. In the previous work, the batch experiments were carried out to investigate adsorption isotherm, adsorption kinetics, and adsorption thermodynamics [5]. But the literature on the mass transfer studies on the adsorption of phenol from adsorbent is limited. Mass transfer studies are also required for finding the rate-limiting step.

Mass transfer finds extensive applications in chemical engineering separation processes, where material balance on components is performed. For separation processes,

thermodynamics determine the extent of separation, while mass transfer determines the rate at which the separation will occur [6].

Adsorption is a time-dependent process. In the removal of phenol from wastewater, it is required to know the rate of adsorption for design, operation control, and evaluation of adsorbent [7–9]. The transport of pollutant from the liquid phase to the solid phase is carried out by transfer of mass from one phase to another phase [10]. Therefore, to understand the suitability of the adsorbent for any adsorption process and efficiency of the process and for the design of wastewater treatment plants, it is required to know the steps involved in the adsorption of a pollutant from the aqueous solution [11].

It is studied that adsorption on an adsorbent from the aqueous phase involves three steps:

(i) Transport of the solute from bulk solution to the film surrounding the adsorbent (film diffusion).

(ii) Internal diffusion of solute from the film to the pores of the adsorbent.

(iii) Adsorption of the adsorbate on the external surface of the adsorbent through binding of the ions to the active sites [10, 12–15].

The slowest of these steps will control the process or will be the rate-limiting step. It will also determine the overall rate of the process. Therefore, the prediction of adsorption rate-limiting step is an important aspect for the study and design of adsorption process.

It is assumed that the third step is rapid when compared to the first two steps. This may be because of the following reasons. In a well agitated solid/liquid adsorber, mixing in the liquid is very rapid. Therefore, the concentration of adsorbate and concentration of the particles within the system are assumed to be uniform throughout [12, 16]. The step is also considered as equilibrium step, because the equilibrium between solute in solution and solute on adsorbent is established instantaneously. Thus, the amount of solute adsorbed on the pore surface is at equilibrium with the solute concentration in the solution [8, 17].

Therefore, in the adsorption process, there are mainly two mass transfer resistance types, external and internal diffusion [18]. However, the controlling step may exist between intraparticle and external transport mechanisms. The rate determining step depends on various factors like the particle size of the adsorbent, degree of mixing, and affinity of solute for adsorbent. It is studied that external transport is usually the rate-limiting step for a system having poor mixing, dilute solute concentration, small particle size of adsorbent, and high affinity of solute for adsorbent, whereas intraparticle step controls the process for a system having good mixing, high solute concentration, larger particle size of adsorbent, and low affinity of solute for adsorbent [19, 20].

In the current work, mass transfer studies were done to determine the rate-limiting step for the adsorption of phenol from aqueous solution on *Lantana camara*. The possibility of this step was investigated from the kinetic data by using various mass transfer models available from the literature. The rate-limiting step was also determined

Table 1: The characterisation of the adsorbent treated with HCl and KOH.

Parameter	Adsorbent treated with HCl	Adsorbent treated with KOH
Density, g/mL	0.2103	0.2248
Particle size, μm	11.59	11.68
Particle porosity	0.265	0.282
Surface area per unit volume of particle free slurry, m^{-1}	12559	12913.2

through dimensionless number that is Biot number [21, 22] and sensitivity analysis.

2. Materials and Methods

2.1. Adsorbent. The material *Lantana camara* was initially washed with distilled water to remove all the earthy matter. The materials were then dried in sunlight for 48 h, made into pieces, ground to fine powder, and sieved to particle sizes of less than 0.075 mm. To produce the chemically treated carbon and to improve the properties of the raw powder, various chemicals such as H_3PO_4, KNO_3, H_2SO_4, $ZnCl_2$, HCl, and KOH were treated with powder at 105°C as discussed in the previous work [5]. The characterisation of the carbon treated with the above chemicals was carried out. Various parameters such as particle size, surface area, pore volume, and percent removal of phenol were measured. From the preliminary results, the best two adsorbents treated with HCl and KOH were used for batch studies as described in the previous work [5]. The mass transfer studies were carried out with both adsorbents. The properties of both adsorbents required for mass transfer studies are shown in Table 1.

2.2. Adsorbate. Phenol has a chemical formula C_6H_5OH with a molecular weight of 94 g/mol. Phenol of analytical grade (Merck India Ltd.) was used for the preparation of stock solution of concentration 1000 mg/L. The experimental solutions of concentrations 25, 50, 100, 150, 200, and 250 mg/L were prepared by diluting the stock solution to the required proportions. The other chemicals, potassium hydroxide (Merck India Ltd., AR grade), potassium nitrate (Merck India Ltd., AR grade), zinc chloride (Merck India Ltd., AR grade), hydrochloric acid (SD Fine Chemicals, India, AR grade), sulphuric acid (SD Fine Chemicals, India, AR grade), and orthophosphoric acid (SD Fine Chemicals, India, AR grade), were used for the chemical treatment of carbon.

2.3. Adsorption Experiments. The batch experiments were conducted with adsorbent treated with HCl and KOH. The adsorbent was treated with 200 mL solution of 25, 50, 100, 150, 200, and 250 mg/L concentrated phenol solution placed in 250 mL standard flask. 0.75 g and 1 g of the adsorbent treated with HCl and KOH, respectively, were added to the flask and placed in a shaker at 298 K, with rotation speed of 140 rpm. The flask containing adsorbent treated with HCl and KOH was agitated for 510 min and 570 min, respectively, until the

equilibrium was reached. The aqueous samples were collected at regular intervals of time. The concentration of phenol adsorbed was measured using UV-vis spectrophotometer.

2.4. Theoretical Investigation.

For any adsorption process, it is important to know the extent of transfer of pollutant species from bulk to the surface of the solid adsorbent particles and at the interface of solid adsorbent particles or at the interface of liquid and solid particles. The slowest of these steps will be the controlling process. Therefore, in order to find the rate-limiting step, various mass transfer models were examined and also some dimensionless number and sensitivity analysis were studied.

2.4.1. External Diffusion Model.

When the transport of the solute molecules from the liquid phase to the solid phase boundary plays an important role in adsorption, then the liquid film diffusion model can be applied. The external diffusion model assumes that the concentration at the adsorbent surface tends to zero or the intraparticle resistance is negligible [8, 23] and the intraparticle diffusion can be neglected at early times of contact [8, 23, 24]. This model is derived on the application of Fickien's laws, expressing the concentration of the solute in the solution, as a function of the difference in the concentrations of the solute in the solution and at the particle surface [25].

The change of solute concentration with respect to time can be written as follows:

$$\frac{dC/C_o}{dt} = -k_f A, \tag{1}$$

where C is the bulk liquid phase concentration of solute at any time t, C_o is the initial concentration of phenol, k_f is the external mass transfer coefficient, and A is the surface area of adsorbent per unit volume of particle free slurry (m^{-1}) and is given by

$$A = \frac{6M}{Vd_p\rho\left(1 - \varepsilon_p\right)}, \tag{2}$$

where V is the volume of solution (L), M is the adsorbent mass (g), ε_p is bed porosity, and ρ is bulk density (g/cm^3) [12, 16].

The external mass transfer coefficient k_f can be calculated from the slope of the dimensionless curve, C/C_o, versus time t.

2.4.2. Furusawa and Smith Model.

The effect of external mass transfer resistance on adsorption rate was analysed using the Furusawa and Smith model [26–30]. The mass transfer coefficient, β_L (m s^{-1}), of phenol at the adsorbent-solution interface was determined by using

$$\begin{aligned}\ln\left(\frac{C_t}{C_o} - \frac{1}{1 + mk_L}\right) &= \ln\left(\frac{mk_L}{1 + mk_L}\right) \\ &\quad - \left(\frac{1 + mk_L}{mk_L}\right)\beta_L At,\end{aligned} \tag{3}$$

where k_L is a constant (L/g) and m and A are the mass and outer surface of the adsorbent particle per unit volume of particle free slurry (g/L and m^{-1}), respectively. A linear plot of $\ln(C_t/C_o - 1/(1 + mk_L))$ versus t was plotted and the coefficient β_L was found. The value of k_L was taken from the previous batch studies.

2.4.3. Furusawa and Smith Model (Modified) [31].

The proposed modified equation for external mass transfer is given by

$$\left(\frac{1}{1 + 1/mk_L}\right)\ln\left(\frac{C_t}{C_o} - \frac{1}{mk_L}\left(1 - \frac{C_t}{C_o}\right)\right) = -kAt. \tag{4}$$

The external mass transfer coefficient k was calculated from the linear plot of the above equation. In (3), the intercept obtained $\ln(mk_L/(1 + mk_L))$ has to be adjusted to zero. But here the intercept will be zero.

2.4.4. Film Diffusion Model.

Using Fick's equation, the diffusion process was studied on the exterior and interior surface of the adsorbent [32–34]. The equation at initial period of adsorption is given by

$$\frac{q_t}{q_e} = 6\left(\frac{D_1}{\pi a^2}\right)^{1/2} t^{1/2}. \tag{5}$$

The plot of q_t/q_e versus $t^{1/2}$ represents mainly three stages of adsorption. The first linear portion related to the film diffusion, the second linear portion represented the intraparticle diffusion, and the last linear portion indicates adsorption-desorption equilibrium [33]. From these regions, the rate-limiting step can be calculated.

2.4.5. Particle Diffusion Model.

Due to the porous nature of the adsorbent, intraparticle mass diffusion can be the rate-limiting step [33, 35, 36]. The relationship between the adsorption capacities at any time and at equilibrium is given by

$$\begin{aligned}\ln\left[\frac{1}{1 - F^2(t)}\right] &= \frac{\pi^2}{a^2}D_e t \\ F(t) &= \frac{q_t}{q_e},\end{aligned} \tag{6}$$

where q_t and q_e are amount of uptake at time t and at equilibrium, respectively; a is the particle radius. The diffusion coefficient D_e is calculated by using the values obtained from the straight line plot of $-\ln(1 - F^2(t))$ versus t.

2.4.6. Mass Diffusivity.

The values of diffusion coefficient mainly depend on the surface properties of adsorbents. The diffusion coefficients for the intraparticle transport of phenol within the pores of adsorbent particles have been investigated at different concentrations using the following expression:

$$D_m = \frac{0.03a^2}{t^{1/2}}. \tag{7}$$

The mass diffusivity (D_m) is inversely proportional to the half-reaction time $t^{1/2}$ [28]. Half-adsorption time, $t^{1/2}$, is defined as the time required for the adsorption to take up half as much what the adsorbent can take at its equilibrium value [37]. This time is also often used as a measure of the adsorption rate

$$t^{1/2} = \frac{1}{k_2 q_e},$$ (8)

where k_2 and q_e are the second-order rate constant and equilibrium adsorption capacity (taken from the previous batch studies [5]) and a is the particle radius. It is assumed that the solid phase consists of spherical particles with an average radius between the radii corresponding to upper- and lower-size fractions [28, 38].

2.4.7. The Representation of Experimental Parameters (k_f and D_e) in terms of Dimensionless Group. The experimental parameters can also be represented in terms of dimensionless groups in order to study the mass transfer behaviour. The parameters were expressed in terms of Biot number to examine the rate-limiting step. An expression for Biot number (Bi) was derived in terms of concentration, to show the effect of concentration on the adsorption process. Biot number relates the external mass transfer resistance with the internal mass transfer resistance as follows [39]. It is the ratio of the rate of transport across the liquid layer to the rate of intraparticle mass transfer [40]. It can be used as a key factor for finding the rate-limiting step.

It is given by

$$\text{Bi} = \frac{k_f d}{D_e}.$$ (9)

The adsorption process is mainly controlled by internal diffusion mechanism if Bi is greater than 100 and the adsorption process is controlled by film transfer if Bi is less than 100 [21].

2.4.8. Transport Number. The transport number is also used as criteria to know the mode of diffusion [2, 15]. It is given by

$$\frac{q_t}{q_e} = K_m t^n,$$ (10)

where K_m is the adsorbent-adsorbate interaction coefficient and n is the transport number. A straight plot of $\log(q_t/q_e)$ versus $\log t$ was made and the constants K_m and n were found. The values of n show the type of transport mechanism. A value of $n = 1$ indicates the non-Fickian mechanism and $n = 0.5$ represents the Fickian mechanism (surface mechanism). The non-Fickian mechanism is applied when there is swelling or change in the structure [41]. The constant K_m depends on the characteristics of the adsorbents.

2.4.9. Sensitivity Analysis. Sensitivity analysis was carried out to evaluate the significance of the mass transfer parameters on the adsorption process and also to find the rate controlling step. The parameter was changed about its base value while the other values were being kept constant [42]. The parameters selected were k_f and D_e and their effect on the concentration decay curve was investigated. The values of both k_f and D_e were varied from 0.5 to 2 times the base values while other parameters were kept constant and the sensitivity of the parameters was analysed. Finally, to study the effect of mass transfer coefficient in detail on the adsorption process, k_f value was varied in the range $k_f/4$, $k_f/2$, k_f, $2k_f$, and $4k_f$ and the nature of concentration decay curve obtained was analysed.

3. Results and Discussion

3.1. External Diffusion Model. It was observed that the mass transfer coefficient decreases with increase in phenol initial concentration and is shown in Table 2. The probable reason is that, by increasing the concentration, the driving force increases. Since the number of active sites on the adsorbent surface is fixed, by increasing the concentration, the mass transfer decreases. Therefore, with increasing concentration, the mass transfer coefficient decreases [18].

Another reason for this behaviour is that, from the adsorption equilibrium theory, the external mass transfer is dependent on the slope of the operating lines on equilibrium isotherms. Therefore, the higher the value of C_o, the lower the slope of the operating lines. Thus, mass transfer coefficient is related to the slope of the curves. Therefore, the mass transfer coefficient decreases with increase in concentration [16]. The external mass transfer is also the controlling factor when linearity of the model is obtained [43, 44]. Similar results have been reported by other researchers in [7, 12, 16, 23].

3.2. Furusawa and Smith Model. The analysis of the data from Table 3 shows that the mass transfer coefficient obtained decreases with increased concentration of phenol. The results indicate that the values of regression coefficient (R^2 values) obtained are well above 0.95 showing that external mass transfer can be the slowest step [27, 28]. The value of β_L indicates the velocity of pollutant to move from liquid phase to the surface of the adsorbent to remove pollutant from wastewater. Therefore, the above model can be validated for the system.

3.3. Furusawa and Smith Model (Modified). Plotting the model is easier because the model intercept is equal to zero. From the values of the regression coefficient obtained as shown in Table 4, the model can be applied for the system. This signifies that surface mass transfer will dominate the process. These findings are the same as other research results [31].

3.4. Film Diffusion Model. The plot of q_t/q_e versus $t^{1/2}$ was made and it represented three stages of adsorption. From Figures 1(a), 1(b), 1(c), 1(d), 1(e), 1(f), 2(a), 2(b), 2(c), 2(d), 2(e), and 2(f), the time taken for film diffusion, intraparticle diffusion, and adsorption process was found. Then, the ratio of time taken for film diffusion to the time taken for intraparticle diffusion was found and is shown in Tables 5 and 6. If the above ratio is more than 1, it shows that film diffusion is dominating the process. If the ratio is less than 1, it indicates

TABLE 2: Mass transfer coefficients from the external diffusion model for the adsorption of phenol.

C_o, mg/L	Adsorbent treated with HCl		Adsorbent treated with KOH	
	k_f, m/s	R^2	k_f, m/s	R^2
25	2.11×10^{-9}	0.9422	1.55×10^{-9}	0.9843
50	2.070×10^{-9}	0.9572	1.539×10^{-9}	0.9779
100	2.0569×10^{-9}	0.9413	1.5186×10^{-9}	0.9785
150	2.037×10^{-9}	0.9281	1.4977×10^{-9}	0.9729
200	2.0304×10^{-9}	0.9276	1.4924×10^{-9}	0.9745
250	2.0171×10^{-9}	0.9191	1.4872×10^{-9}	0.9774

TABLE 3: Mass transfer coefficients from the Furusawa and Smith model for the adsorption of phenol.

C_o, mg/L	Adsorbent treated with HCl		Adsorbent treated with KOH	
	β_L, m/s	R^2	β_L, m/s	R^2
25	8.5665×10^{-9}	0.9717	6.25×10^{-9}	0.9948
50	7.9075×10^{-9}	0.9828	5.73×10^{-9}	0.9925
100	7.512×10^{-9}	0.966	5.4166×10^{-9}	0.9904
150	7.1168×10^{-9}	0.9525	5.0015×10^{-9}	0.99
200	6.4578×10^{-9}	0.9534	4.79315×10^{-9}	0.9904
250	6.32×10^{-9}	0.9545	4.68×10^{-9}	0.9891

TABLE 4: Mass transfer coefficients from the Furusawa and Smith model (modified) for the adsorption of phenol.

C_o, mg/L	Adsorbent treated with HCl		Adsorbent treated with KOH	
	k, m/s	R^2	k, m/s	R^2
25	9.2894×10^{-9}	0.9419	6.598×10^{-9}	0.9841
50	8.62×10^{-9}	0.9568	6.179×10^{-9}	0.9776
100	8.3605×10^{-9}	0.941	5.55×10^{-9}	0.9773
150	7.9624×10^{-9}	0.9278	5.44×10^{-9}	0.9726
200	7.43×10^{-9}	0.9272	5.2367×10^{-9}	0.9743
250	7.298×10^{-9}	0.9186	5.1320×10^{-9}	0.9751

TABLE 5: The time taken by the adsorbent treated with HCl for the three different stages of adsorption.

HCl treated adsorbent, concentration	Time taken for film diffusion, min	Time taken for intraparticle diffusion, min	Time taken for adsorption, min	Ratio of time taken for film diffusion to that for intraparticle diffusion
25 mg/L	174.4	39.7	9	4.39
50 mg/L	110.25	64	49	1.722
100 mg/L	196	36	4	5.44
150 mg/L	182.25	42.25	6.25	4.31
200 mg/L	144	30.25	25	4.76
250 mg/L	156.25	56.25	6.25	2.77

TABLE 6: The time taken by the adsorbent treated with KOH for the three different stages of adsorption.

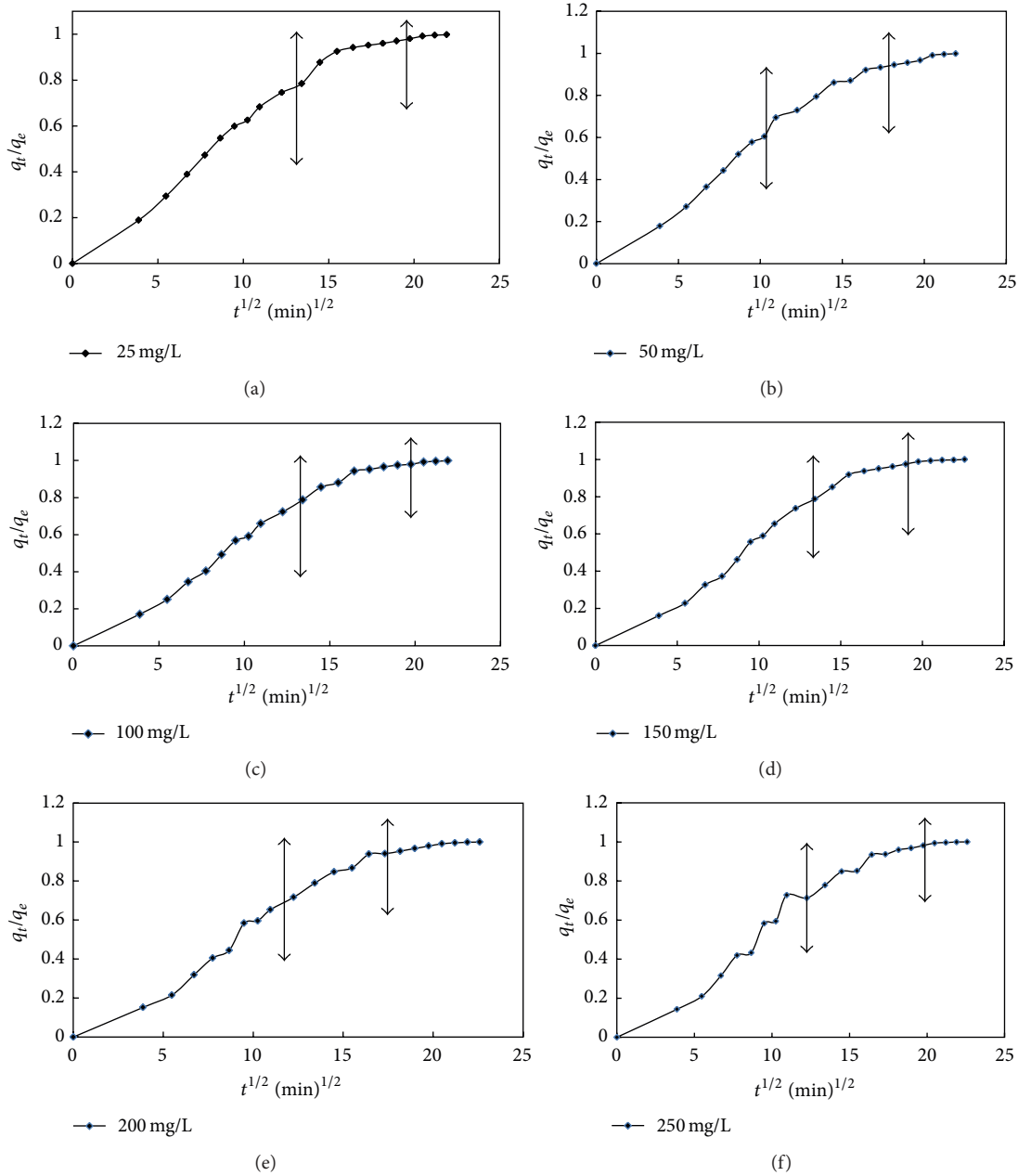| KOH treated adsorbent	Time taken for film diffusion, min	Time taken for intraparticle diffusion, min	Time taken for adsorption, min	Ratio of time taken for film diffusion to that for intraparticle diffusion
25 mg/L	104.04	92.16	16	1.128
50 mg/L	156.25	56.25	14.44	2.77
100 mg/L	163.84	59.84	10.89	2.73
150 mg/L	169	42.25	23.04	4
200 mg/L	144	44.89	26.01	3.2078
250 mg/L	146.41	60.84	15.21	2.4064

FIGURE 1: The plot of q_t/q_e versus $t^{1/2}$ showing all three regions for adsorbent treated with HCl for the adsorption of phenol.

that the process is controlled by intraparticle diffusion. From the results, it was found that the ratio is more than 1, showing that film diffusion is the slowest step [33].

3.5. Particle Diffusion Model. From the values of the correlation coefficient obtained as shown in Table 7, it was found that the model could not be validated for the system [35, 45, 46]. The calculated R^2 values show agreement of experimental points with the model proposed. The values of the calculated diffusion coefficients do not change with phenol concentration, which shows that they are independent

of the initial concentration of solution [46]. From the values of D_e obtained (10^{-9} to 10^{-17} m^2/s), it can be suggested that it is applied for chemisorption system [33, 45]. A similar trend has been reported in [27].

3.6. Mass Diffusivity. The diffusion coefficients are calculated by taking various factors like concentration, dosage, pH, and temperature into consideration. The values obtained were in the range of 1.282×10^{-16} to 2.85×10^{-16} m^2/s and 1.3989×10^{-16} to 2.004×10^{-16} m^2/s for adsorbent treated with HCl and KOH, respectively, and are shown in Table 8.
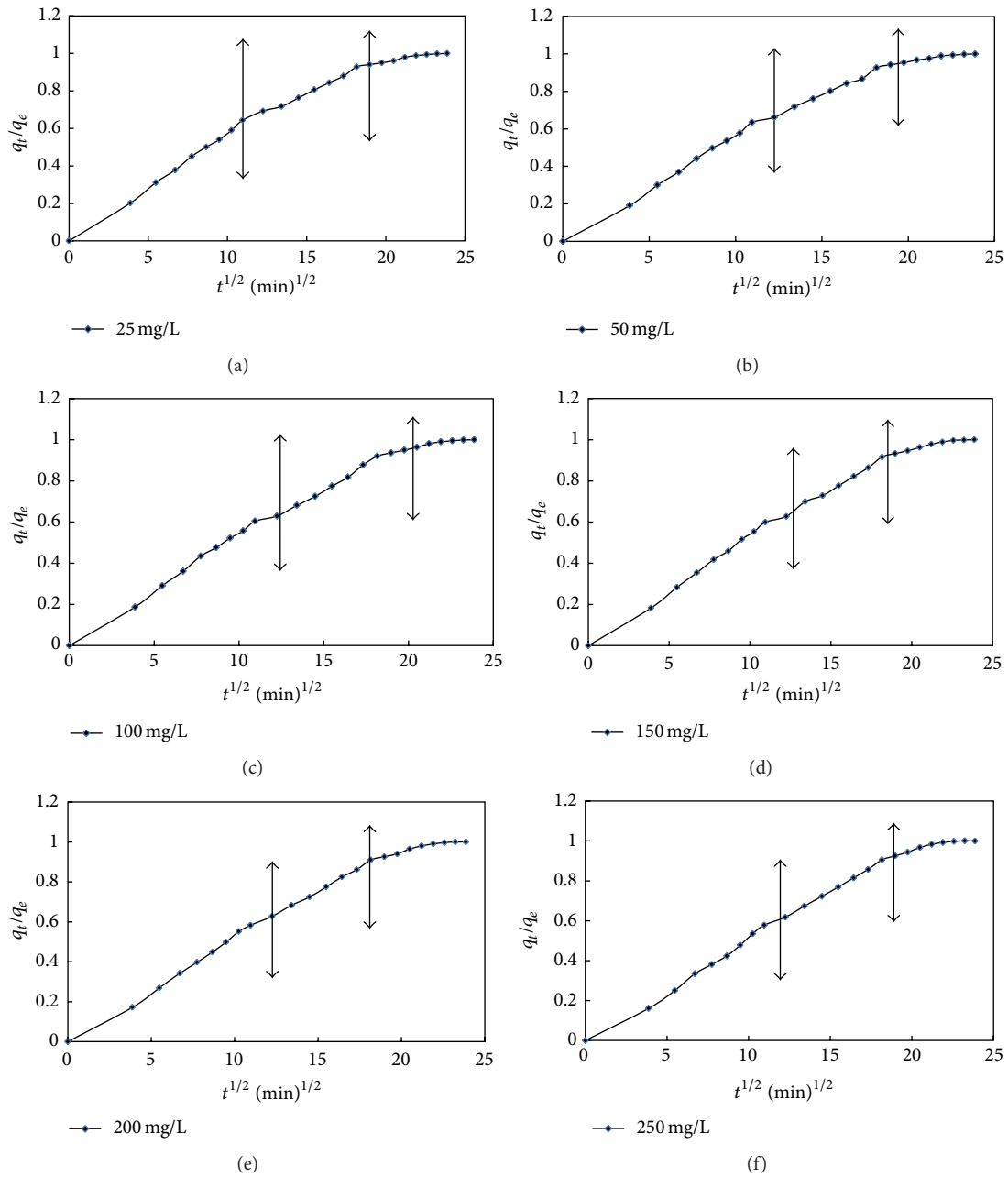
FIGURE 2: The plot of q_t/q_e versus $t^{1/2}$ showing all three regions for adsorbent treated with KOH for the adsorption of phenol.

TABLE 7: The values of diffusion coefficients from the particle diffusion model at different concentrations.

C_o, mg/L	Adsorbent treated with HCl		Adsorbent treated with KOH	
	D_e, m²/s	R^2	D_e, m²/s	R^2
25	5.0471×10^{-16}	0.9211	3.7433×10^{-16}	0.904
50	4.99×10^{-16}	0.877	3.7555×10^{-16}	0.8997
100	5.0187×10^{-16}	0.8868	3.7435×10^{-16}	0.8718
150	4.9904×10^{-16}	0.9114	3.7435×10^{-16}	0.8438
200	4.9904×10^{-16}	0.8669	3.7550×10^{-16}	0.8352
250	5.0471×10^{-16}	0.8339	3.9163×10^{-16}	0.8063

TABLE 8: The values of diffusion coefficient for both adsorbents at different concentrations.

C_o, mg/L	Adsorbent treated with HCl		Adsorbent treated with KOH	
	$t^{1/2}$, s	D_m, m^2/s	$t^{1/2}$, s	D_m, m^2/s
25	3533.19	2.85×10^{-16}	5105.47	2.004×10^{-16}
50	5309.88	1.8375×10^{-16}	5531.36	1.8494×10^{-16}
100	6844.20	1.4719×10^{-16}	5489.67	1.86×10^{-16}
150	7853.91	1.282×10^{-16}	5690.28	1.7977×10^{-16}
200	7086.54	1.4216×10^{-16}	6421.25	1.593×10^{-16}
250	6304.90	1.5979×10^{-16}	7312.40	1.3989×10^{-16}

TABLE 9: The values of Biot number for both adsorbents at different initial concentrations.

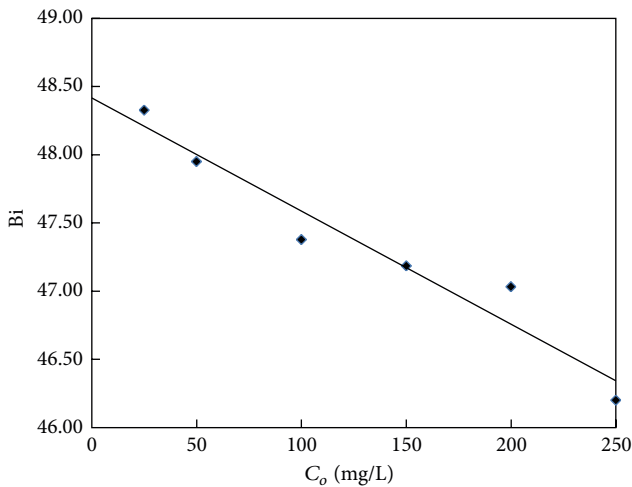| C_o, mg/L	Adsorbent treated with HCl		Bi	Adsorbent treated with KOH		Bi
	k_f, m/s	D_e, m^2/s		k_f, m/s	D_e, m^2/s	
25	2.11×10^{-9}	5.0471×10^{-16}	48.3275	1.55×10^{-9}	3.7433×10^{-16}	48.36
50	2.070×10^{-9}	4.99×10^{-16}	47.9501	1.539×10^{-9}	3.7555×10^{-16}	47.87
100	2.0569×10^{-9}	5.0187×10^{-16}	47.3774	1.5186×10^{-9}	3.7435×10^{-16}	47.38
150	2.037×10^{-9}	4.9904×10^{-16}	47.1857	1.4977×10^{-9}	3.7435×10^{-16}	46.73
200	2.0304×10^{-9}	4.9904×10^{-16}	47.0328	1.4924×10^{-9}	3.7550×10^{-16}	46.42
250	2.0171×10^{-9}	5.0471×10^{-16}	46.1997	1.4872×10^{-9}	3.9163×10^{-16}	44.35

FIGURE 3: The effect of initial concentration on the Biot number for adsorbent treated with HCl.
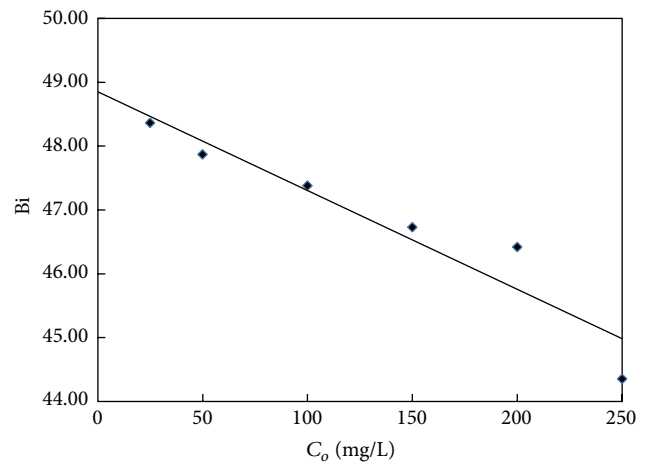

FIGURE 4: The effect of initial concentration on the Biot number for adsorbent treated with KOH.

D_m values obtained in our study were compared with the values available from the literature. Similar results have been reported by other researchers [11, 47].

3.7. The Representation of Experimental Parameters in terms of Biot Number. The calculated external mass transfer coefficients and diffusion coefficients were expressed in the form of Biot number and are shown in Table 9. The dimensionless numbers obtained are less than 100. This indicates that the adsorption of phenol onto the adsorbent is controlled by external film mass transfer. Similar observations have been made by authors [21].

The effect of phenol initial concentration on dimensionless mass transfer number is shown in Figures 3 and 4. From the linearity of the curve as shown in Figures 3 and 4, (11) and (12) were obtained for adsorbent treated with HCl and adsorbent treated with KOH, respectively. The expression shows the relation between initial concentration and the Biot number. It was also found that the mass transfer decreases with increasing phenol concentration. The results were similar to those discussed in the film diffusion model. The regression coefficients were found to be 0.9433 and 0.9068 for adsorbent treated with HCl and adsorbent treated with KOH, respectively. Similar expressions were obtained by the authors [12, 48]:

$$\text{Bi} = 48.416 \left(C_o \right)^{-0.0083}, \tag{11}$$

$$\text{Bi} = 48.851 \left(C_o \right)^{-0.0155}. \tag{12}$$

TABLE 10: The transport number and the model constant for both adsorbents at different initial concentrations.

C_o, mg/L	Adsorbent treated with HCl		Adsorbent treated with KOH	
	n	k_m	n	k_m
25	0.4514	0.0704	0.4208	0.0774
50	0.4717	0.0618	0.4338	0.07164
100	0.5003	0.05262	0.4442	0.0665
150	0.5274	0.04516	0.4538	0.06284
200	0.5339	0.04334	0.4718	0.05641
250	0.5417	0.04162	0.4924	0.04985
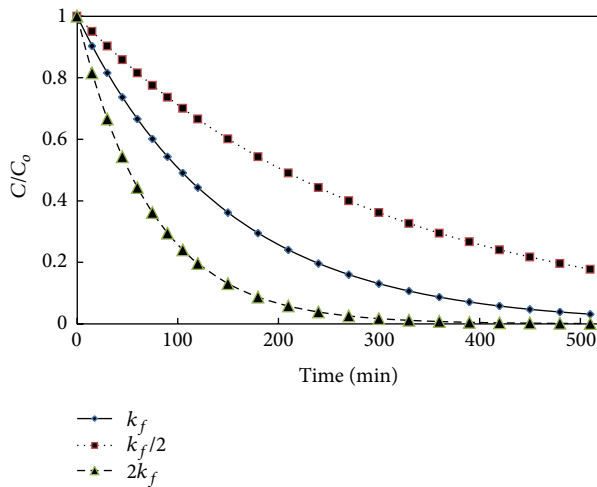
FIGURE 5: The plot of sensitivity analysis for showing the effect of k_f on the adsorption process for the adsorbent treated with HCl.
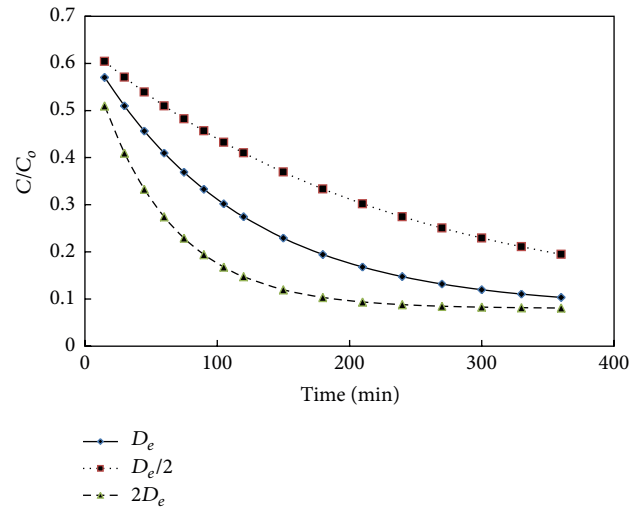
FIGURE 6: The plot of sensitivity analysis for showing the effect of D_e on the adsorption process for the adsorbent treated with HCl.

3.8. Transport Number. The values of k_m and n were calculated and are shown in Table 10. It was found that the transport number, n, was found to be less than 0.5, thus showing that the adsorption follows Fickian diffusion mechanism, where phenols interact on the surface of the adsorbents. These results are similar to those reported by authors [2, 15].

3.9. Sensitivity Analysis. The values of both k_f and D_e for the adsorbent treated with HCl were varied from 0.5 to 2 times the base values while other experimental conditions were kept constant. It was observed that the concentration curve was very sensitive to the external mass transfer coefficient. The spreading of the concentration curves was more as shown in Figure 5. All the curves covered larger concentration region.

But varying the value of D_e within the selected range has a little effect on the concentration curve. As it can be seen from Figure 6, for various values of D_e concentration curve was covered to lesser extent. This shows that the external mass transfer has more influence on the mass transfer of phenol from the aqueous solution. This also signifies that the external mass transfer resistance is more important than the internal mass transfer resistance. A similar trend has been reported in [49, 50].

To study the effect of mass transfer coefficient of the adsorption process in detail, k_f value for the adsorbent
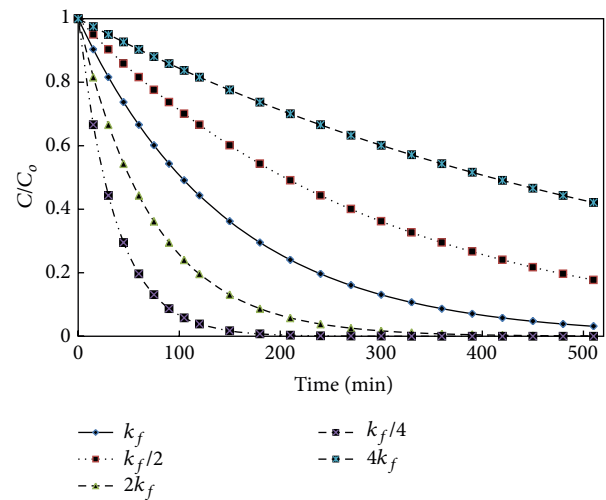

FIGURE 7: The effect of mass transfer coefficient on the adsorption process for the adsorbent treated with HCl.

treated with HCl was varied in the range $k_f/4$, $k_f/2$, k_f, $2k_f$, and $4k_f$ and was shown in Figure 7. It was found that when k_f value increases, more mass transfer takes place and it takes less time for the total adsorption process. This is because of

the reason that the larger the value of k_f, the smaller the film resistance, thereby leading to more mass transfer. This can be observed in the concentration decay curves. Similar results have been reported by other researchers [51, 52].

4. Conclusion

The current study shows that *Lantana camara* can be used as a potential adsorbent for the removal of phenol from aqueous solution. The mass transfer studies were carried out from the data obtained from the batch kinetic experiments. The rate-limiting step was found using various mass transfer models. The values of external mass transfer coefficient were obtained in the range of 1.4872×10^{-9} to 9.2894×10^{-9} m/s and the intraparticle diffusion coefficient ranged from 1.3989×10^{-16} to 5.0471×10^{-16} m^2/s. The analysis of different mass transfer models shows the external mass transfer as the slowest step in the sorption process. The Biot number obtained in the range of less than 100 indicates that the process was controlled by film diffusion. An expression was derived which shows the correlation between the Biot number and the initial concentration of phenol. From the sensitivity analysis, it was found that the adsorption process is more dependent on k_f than D_e.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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