Hindawi Publishing Corporation
International Journal of Chemical Engineering
Volume 2016, Article ID 7086761, 11 pages
http://dx.doi.org/10.1155/2016/7086761

Research Article

Simultaneous Adsorption of Cr(VI) and Phenol from Binary Mixture Using Iron Incorporated Rice Husk: Insight to Multicomponent Equilibrium Isotherm

Ankur Gupta and Chandrajit Balomajumder

Department of Chemical engineering, Indian Institute of Technology Roorkee, Roorkee 247667, India

Correspondence should be addressed to Ankur Gupta; guptaankur599@gmail.com

Received 1 December 2015; Revised 4 February 2016; Accepted 8 February 2016

Academic Editor: Janez Levec

Fe modified rice husk was prepared as a low cost biosorbent for the removal of Cr(VI) and phenol both singly and in combination from single and binary simulated synthetic waste water. Rice husk was modified by treating with $FeSO_4{\cdot}7H_2O$. The results showed that impregnation of iron onto the surface of rice husk improved the adsorption capability of both Cr(VI) and phenol. The effects of process parameters for multicomponent system such as pH, adsorbent dose, and contact time onto the percentage removal of both Cr(VI) and phenol were investigated. The experimental data for the adsorption of both Cr(VI) and phenol onto the surface of Fe modified rice husk applied to various kinetic and adsorption isotherm models. Multicomponent isotherm models such as Nonmodified Langmuir, Modified Langmuir, Extended Langmuir, Extended Freundlich, Competitive Nonmodified Redlich Peterson, Competitive Modified Redlich Peterson were applied. The results show that Extended Freundlich model best described the experimental data for both Cr(VI) and phenol from binary solution. Pseudo second-order model agreed well with Cr(VI) while pseudo first-order model agreed well with phenol. Maximum adsorption capacity in synthetic binary solution of Cr(VI) and phenol was found to be 36.3817 mg g^{-1} for Cr(VI) and 6.569 mg g^{-1} for phenol, respectively.

1. Introduction

Heavy metals are often present with phenolic compounds in the environment which have adverse effects on living species including man [1]. Precipitation/coagulation [2], chemical oxidation [3], biodegradation [4], adsorption [5], ion exchange [6], membrane processing [7], electrolytic methods [8], and so forth are some important methods which have been used to remove the heavy metal ion and phenolic contents together from the effluents of various industries such as leather tanning, electroplating, and alloying [5]. Cr(VI) and its copollutants such as phenol, naphthalene, and trichloroethylene released from these industries contaminate ground water aquifers, lake, river sediments, and soil [9]. Much research has been carried out on the uptake of single pollutant; nevertheless due to the fact that organic pollutants also exist with metallic species, in the recent year simultaneous removal of phenol and Cr(VI) has gained a great attention in waste water treatment processes [1]. Biosorption is proved to be most promising technologies for the simultaneous removal of organic compound and heavy metal ions from waste water and an alternative to conventional or traditional methods such as precipitation, ion exchange, and catalytic reaction [10]. Nanobiocatalyst is also fabricated by the researcher for the degradation of toxic pollutant [11]. Mixed culture of bacterium is also used for the degradation of organic dye [12–14]. Fluidized bed reactor was also used for the treatment of industrial waste water [15]. To optimize the cost of the process the use of low cost biosorbent is an efficient method for the removal of toxic pollutant [16]. In literature lots of biosorbent were used for the removal of Cr(VI) [17] such as, rice husk ash, activated alumina [18], wood apple shell [19], neem saw dust [20], pine needle powder [21], activated carbon from olive bagasse [22], and egg shell membrane [23]. The biosorbent used for the removal of phenol are bentonite [24] and polymerized saw dust [25]. Modification of biosorbent by impregnation of metal ions and acid treatment enhances the percentage removal of pollutants [26–28]. Chromium is found in the environment predominantly in two forms Cr(III) and Cr(VI) while Cr(VI) is most mutagenic and carcinogenic to the living organism [29]. Chromium sulphate [Cr(III)] is used as tanning agent which is converted to Cr(VI) causing severe contamination of ground water. Phenol is also highly toxic and recalcitrant organic compound used as biocide in leather tanning process [30]. According to WHO the maximum contaminant level of chromium in the drinking water is 0.05 mg L^{-1} [31]. According to the US environmental protection agency permissible limit of phenol for discharge in waste water is 0.005 mg L^{-1} [32]. The aim of this work is (i) to study the effect of process parameters such as pH, contact time, and adsorbent dose on the percentage removal of Cr(VI) and phenol from binary simulated synthetic solution and (ii) to determine the suitability of various single and multicomponent equilibrium isotherm models, and (iii) to determine the kinetics of adsorption of Cr(VI) and phenol onto the surface of Fe treated rice husk.

2. Materials and Methods

2.1. Surface Modification of Rice Husk. 2 g of rice husk was added to 8 mL of 2 M $FeSO_4{\cdot}7H_2O$ solution in 500 mL conical flak and then kept on stirring plate at 105°C. 0.1 M of NaOH was added drop wise to the solution by the help of burette fitted to conical flask to increase the pH 4-5 so that iron is precipitated. This process was carried out continuously 3-4 h. Upon cooling the rice husk was covered with a thick layer of orange colour iron oxide. Then rice husk was washed with distilled water to remove extra quantity of iron precipitate which was not impregnated on the surface of rice husk. Finally this Fe treated rice husk was dried in an oven at 50°C for 2 h and then sieved to obtain homogeneous particle size [33].

2.2. Batch Experiments. Batch adsorption studies were carried out in 250 mL flat bottom flask with working volume of 50 mL in incubator shaker at 120 rpm and 30°C. Binary solution of Cr(VI) and phenol was prepared by mixing them in 2 : 1 ratio as they are generally present in this ratio in industrial waste water such as such as tannery, textile, electroplating, and alloying. Initial concentration of Cr(VI) and phenol in binary solution was chosen as 100 mg L^{-1} and 50 mg L^{-1}, respectively. The effect of various parameters such as pH, contact time, adsorbent dose, and initial concentration of Cr(VI) and phenol was determined. The optimum value of process parameters such as pH, contact time, adsorbent dose, and initial concentration was determined for the maximum percentage removal of Cr(VI) and phenol. The pH was varied from 2 to 9, adsorbent dose 0.2 to 1.6 g, and contact time 0.5 to 14 h. Similar experiments were also carried out for single component for the same range of parameters to find the multicomponent parameters. The pH of binary solution was maintained by 0.1 N HNO_3 and 0.1 N NaOH. Samples were agitated in incubator shaker under controlled temperature at a constant speed of 120 rpm at 30 ± 1°C. After certain time interval samples were withdrawn from shaker and filtered using Whatman filter paper Cat. number 1001 125. Thereafter concentration of Cr(VI) and phenol in filtrate was measured using UV-visible spectrophotometer by diphenyl carbazide method at 540 nm for Cr(VI) and 4-amino antipyrine method at 570 nm for phenol. There was no oxidation reaction in the experimental system as when the binary solution of phenol and Cr(VI) was prepared their initial concentration was investigated at different interval of time, which was constant which proved that phenol was not oxidized to CO_2 and H_2O. When the Fe treated rice husk was added the concentration of both Cr(VI) and phenol started to decrease which confirmed the simultaneous adsorption of Cr(VI) and phenol.

The percentage removal was calculated as

$$\frac{C_i - C_t}{C_i} \times 100. \tag{1}$$

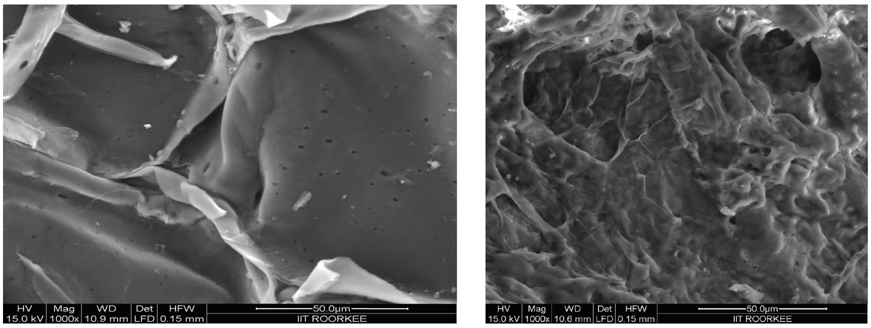
The adsorption capacity q_e (mg/g) was calculated as follows:

$$q_e = \frac{C_i - C_t}{C_i} \times 100. \tag{2}$$

3. Characterization of Fe Treated Rice Husk

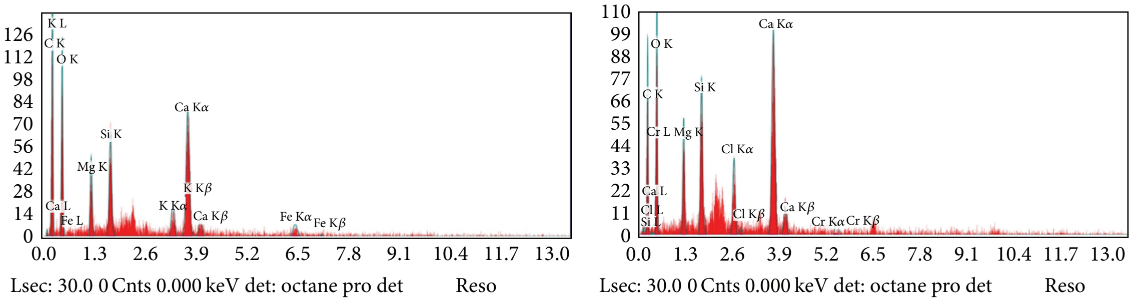
3.1. SEM (Scanning Electron Micrograph) and EDX Analysis of Biosorbent. The surface texture and composition of Fe treated rice husk were obtained by SEM and EDX, respectively (Quanta 200F, FEI, Netherlands). It is clear from the SEM Figure 1(a) before adsorption of Cr(VI) and phenol that the surface was homogeneous and porous but after simultaneous biosorption of Cr(VI) and phenol surface was rough and lesser porous than before adsorption Figure 1(b) [34, 35]. As in Figure 1(a) large numbers of small pores are clearly visible while in Figure 1(b) after adsorption these pores were not present which was rougher and bulky than before adsorption. EDX was carried out to give the elemental composition of the samples. EDX analysis of Fe treated rice husk before adsorption is shown in Figure 2(a) showing the peaks mainly for elements C, O, and Si and also smaller peaks for Fe, Mg, K, and Ca. The peak of Fe in EDX spectra shows that iron was impregnated on the surface of rice husk. After simultaneous adsorption of Cr(VI) and phenol the elemental compositions in weight % of peak of C, N, O, and Ca obtained from EDX analysis were different from before adsorption shown in Figure 2(b) which shows simultaneous adsorption of phenol and Cr(VI). In the EDX spectra the adsorption of phenol was confirmed by changes in the percentage of carbon and oxygen on the surface of Fe treated rice husk after adsorption. The peak of carbon and oxygen before adsorption was different from after adsorption while the adsorption of Cr(VI) was confirmed by the peak of Cr in EDX spectrum after adsorption.

3.2. FTIR of Biosorbent before and after Adsorption. FTIR (NICOLET, 6700, USA) spectrum of Fe treated rice husk before and after adsorption is shown in Figures 3(a) and 3(b),



(a) (b)

Figure 1: (a) SEM image of Fe treated rice husk before adsorption. (b) SEM image of Fe treated rice husk after simultaneous adsorption of Cr(VI) and phenol.



(a) (b)

Figure 2: (a) EDX analysis of Fe treated rice husk before adsorption. (b) EDX analysis of Fe treated rice husk after simultaneous adsorption of Cr(VI) and phenol.

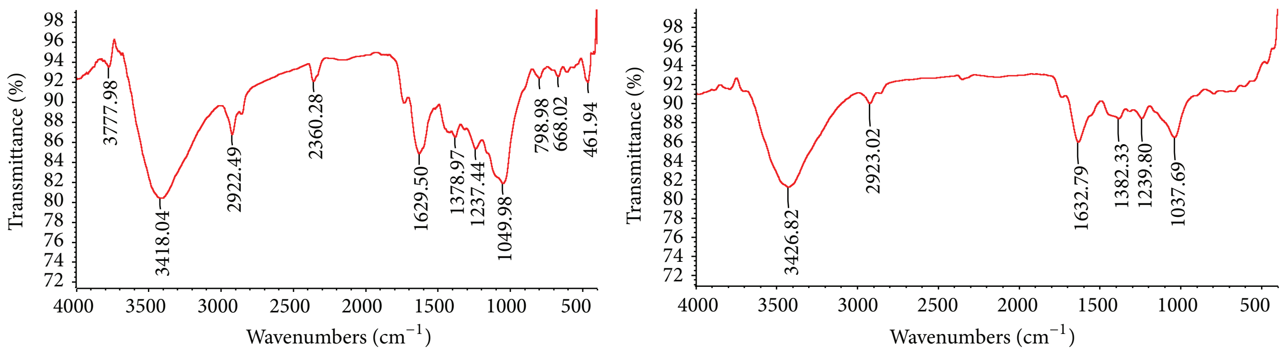
respectively. Strong band at 3777.28 and 34180.4 cm^{-1} shows vibrations of N-H and O-H functional groups. The bands at 2922.49–2360.28 cm^{-1} were assigned to the C-H stretching mode, which represents the aliphatic nature of the adsorbent. The adsorption bands at around 1629.50–1378.97 cm^{-1} were characteristics of C=C in aromatics rings. Peaks at 1237.44–1049.88 cm^{-1} attributed to C-O group on the surface of biosorbent [5, 36, 37]. Furthermore peaks at 798.88–461.94 cm^{-1} indicated the presence of silica $\mathrm{SiO_2}$. From the FTIR spectrum before and after simultaneous removal of phenol and Cr(VI) it is clear that there is decrease in peak in wavelength ranges 2360.28 cm^{-1} and 798.88–461.94 cm^{-1} which indicates simultaneous adsorption of Cr(VI) and phenol.

4. Results and Discussion

4.1. Process Parameter Optimization

4.1.1. Effect of pH. The changes in percentage removal of Cr(VI) and phenol by adsorption on Fe treated rice husk due to change in pH are shown in Figure 4. pH reflects the nature of biosorption mechanism on the surface of biosorbent. Physciochemical interaction of pollutants in solution is related to pH [1, 5]. pH affects the property of functional groups such as carboxylate, phosphate, and amino groups present on the surface of biosorbent which is responsible for the adsorption of pollutant [38]. Simultaneous removal of phenol and Cr(VI) depends on their chemistry of adsorption on the surface of biosorbent. The same pH binding profile for binary solution of phenol and Cr(VI) could be due to the behaviour of chemical interaction of each component with biosorbent. Maximum percentage removal of both components was obtained at pH 5 as shown in Figure 4. At low pH large hydrogen ions compete with metal ions at binding site resulting in low uptake; therefore optimum pH for maximum percentage removal of both components was usually between 5 and 9. It could be due to fact that at low pH value Cr(VI) was present in the form of $\mathrm{Cr_2O_7}^{2-}$ and $\mathrm{HCrO_4}^{-}$ but at higher pH value $\mathrm{CrO_4}^{2-}$ ions prevailed in the solution; uptake of these metal ions depends upon the affinity with biosorbent [1]. In contrast to Cr(VI) adsorption, phenol adsorption was due to van der Waals forces and π-π interaction between phenyl ring and biosorbent [39].

4.1.2. Effect of Quantity of Fe Treated Rice Husk. Fe treated rice husk was used as biosorbent for the dual biosorption of phenol and Cr(VI) from binary mixture of them. The optimum quantity of Fe treated rice husk for the maximum percentage removal of both phenol and Cr(VI) simultaneously was 24 $\mathrm{g\,L^{-1}}$ as shown in Figure 5. The simultaneous removal of both phenol and Cr(VI) increases with increase



(a)

(b)

Figure 3: (a) FTIR spectra of Fe treated rice husk before adsorption. (b) FTIR spectra of Fe treated rice husk after simultaneous adsorption of Cr(VI) and phenol.

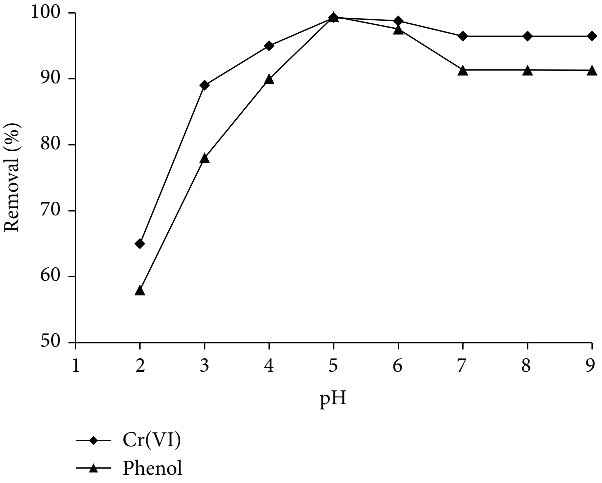


Figure 4: Effect of varying pH on adsorption of Cr(VI) and Phenol.

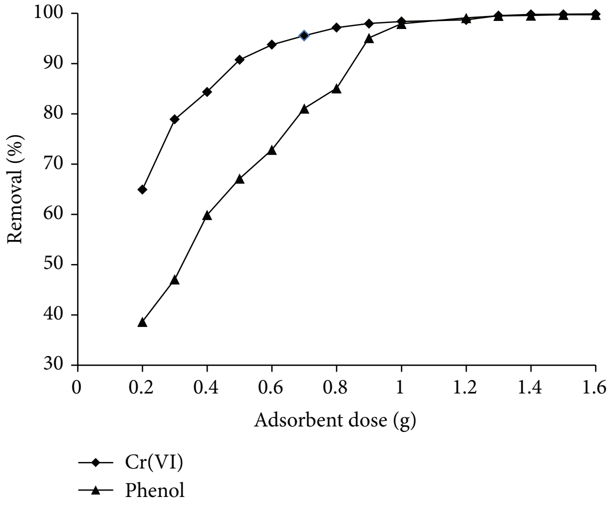


Figure 5: Effect of quantity of Fe treated rice husk on adsorption of Cr(VI) and phenol.

in quantity of biosorbent and then becomes constant. It could be due to fact that, with the increase in quantity of biosorbent, surface area as well as number of possible active sites increases [40]. After reaching the optimum adsorbent dose, the percentage removal becomes constant as there is no effect on the percentage removal with the increase in quantity of Fe treated rice husk. It could be due to the fact that the concentration gradient between the adsorbent surface and solution becomes zero; therefore overlapping of adsorbent particles occurs after reaching optimum adsorbent quantity [41, 42]. Quantity of Fe treated rice husk was varied from 0.2 g to 1.6 g in 50 mL binary solution of phenol and Cr(VI) but after 1.2 g percentage removal of phenol and hexavalent chromium becomes constant; therefore 24 g L^{-1} was considered as optimum biomass dose. Further equilibrium and kinetic studies were carried out at this optimum dose.

4.1.3. Effect of Contact Time. Contact time is important parameter to find the equilibrium condition. At equilibrium there was no change in concentration of adsorbate on the surface of adsorbent as well as in solution. The time required to reach equilibrium condition for phenol was less than that of Cr(VI). It could be due to lower concentration of phenol in binary mixture. Equilibrium time for Cr(VI) and phenol was found to 12 h and 9 h, respectively. Figure 6 shows that initially both Cr(VI) and phenol were adsorbed onto the surface of biosorbent very rapidly after that it is adsorbed gradually and then becomes constant. It could be due to fact that initially there was high concentration gradient between the bulk liquid and adsorbent surface after concentration gradient decreases [43, 44].

4.2. Multicomponent Isotherm Modelling. Heavy metals are generally present with organic compound; therefore presence of more than one component causes interference and competition for adsorption. Adsorption isotherm of multicomponent solution leads to more complex mathematical formulation of the equilibrium [45]. Many multicomponent isotherm models have been proposed in literature. These models are derived from single component models which are modified and nonmodified. Multicomponet isotherms

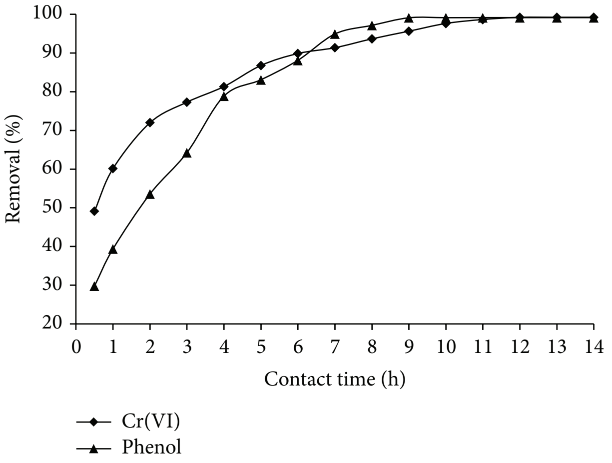


Figure 6: Effect of contact time on adsorption of Cr(VI) and phenol.

models are used to calculate the value of one component i adsorbed per unit weight of adsorbent ($q_{e,i}$) in presence of another component j at equilibrium. If nonmodified model fails to predict the adsorption capacity of one component i in the presence of another component j, in that case a value of correction factor is added to the nonmodified model to predict the adsorption capacity. The value of correction factor depends upon the characteristic and concentration of all other component in multicomponent solutions. Various mono- and multicomponent isotherm models are given as follows [1, 2, 46].

Langmuir model:

$$q_e = Q_o \frac{K_L C_e}{1 + K_L C_e}. \tag{3}$$

Freundlich model:

$$q_e = K_F C_e^{1/n}. \tag{4}$$

Redlich Peterson model:

$$q_e = \frac{K_{\mathrm{RP}} C_e}{1 + a_{\mathrm{RP}} C_e^{\beta}}. \tag{5}$$

Competitive Nonmodified Redlich Peterson model:

$$q_{e_i} = \frac{K_{\mathrm{RP}_i} C_{e_i}}{1 + \sum_{j=1}^{N} a_{\mathrm{RP}_j} C_{e_j}^{\beta_j}}. \tag{6}$$

Competitive Modified Redlich Peterson model:

$$q_{e_i} = \frac{K_{\mathrm{RP}_i} \left(C_{e_i}/n_i\right)}{1 + \sum_{j=1}^{N} a_{\mathrm{RP}_j} \left[C_{e_j}/n_j\right]^{\beta_j}}. \tag{7}$$

Nonmodified Competitive Langmuir model:

$$q_{e,i} = \frac{Q_{o,i} b_i C_{e,i}}{\left(1 + \sum_{j=1}^{N} b_j C_{e,j}\right)}. \tag{8}$$

Table 1: Parameters from single component modelling for adsorption of phenol and Cr(VI).

Adsorption isotherm model	Parameters	Cr(VI)	Phenol
Langmuir	Q_o	7.5596	4.2302
	K_L	0.7587	1.1068
	MPSD	17.85	24.33
Freundlich	K_F	1.93	3.669
	n	4.68	5.80
	MPSD	12.69	6.56
Redlich Peterson	K_{RP}	8429.73	43551.33
	a_{RP}	2291.86	22539.05
	β	0.894	0.787
	MPSD	6.56	12.69

Modified Competitive Langmuir model:

$$q_{e,i} = \frac{\left(Q_{o,i} b_i C_{e,i}/n_j\right)}{\left(1 + \sum_{j=1}^{N} b_j \left(C_{e,j}/n_j\right)\right)}. \tag{9}$$

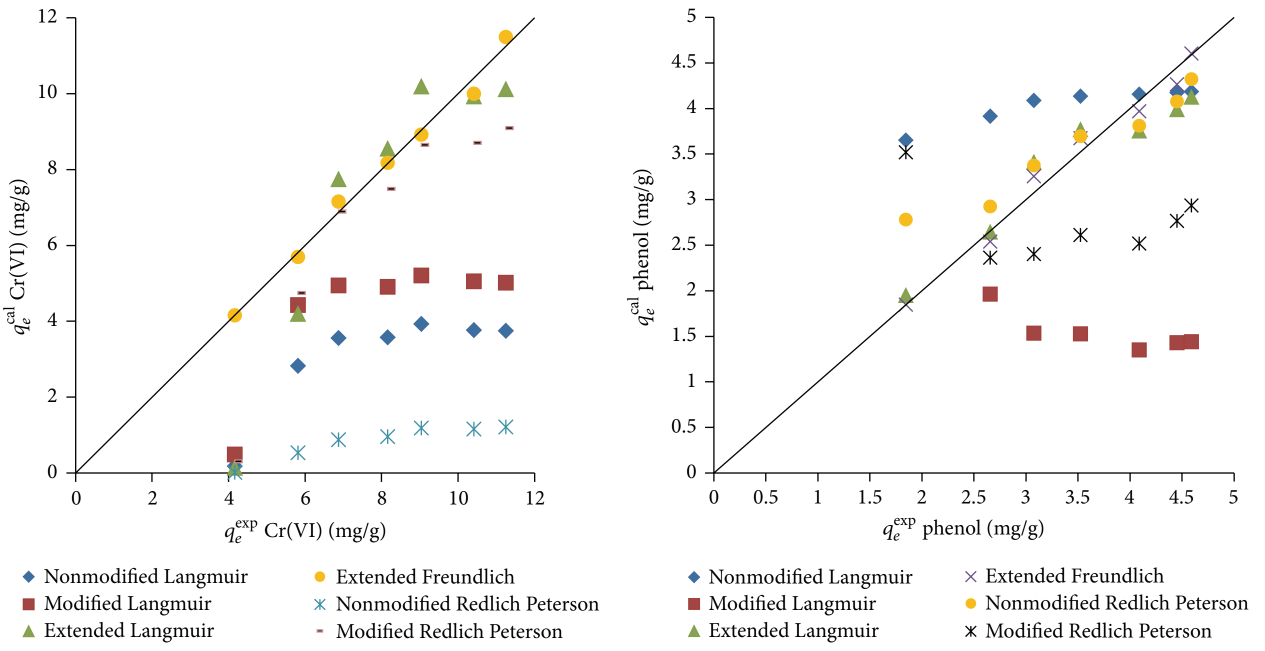
Extended Langmuir model:

$$q_{e,i} = \frac{Q_{o,i} b_i C_{e,i}}{\left(1 + \sum_{j=1}^{N} b_j C_{e,j}\right)}. \tag{10}$$

Extended Freundlich model:

$$\begin{aligned} q_{e,i} &= \frac{\left(K_{F,i} C_{e,i}^{1/(n_i + x_i)}\right)}{\left(C_{e,i}^{x_i} + y_i C_{e,j}{}^{Z_i}\right)} \\ q_{e,j} &= \frac{\left(K_{F,j} C_{e,j}^{1/(n_j + x_j)}\right)}{\left(C_{e,j}^{x_j} + y_j C_{e,i}{}^{Z_j}\right)}. \end{aligned} \tag{11}$$

4.2.1. Estimation of Parameters of Single Component Isotherm Model. The adsorptive equilibrium data for the adsorption of Cr(VI) and phenol on Fe treated rice husk was analysed using Microsoft Excel 2010. Single component modelling was carried out to determine best fit equilibrium model and for the estimation of parameters of multicomponent models. Table 1 summarizes the parameters obtained from single component model. Langmuir constant K_L measures the interaction between adsorbate and adsorbent. Langmuir constant K_L obtained for phenol was more than that of Cr(VI) which indicates the more stable phenol : carbon interaction than Cr(VI) : carbon interaction at the adsorbent surface [42]. Biosorption capacity for Cr(VI) 7.5596 mg g^{-1} was more than that of phenol 4.2301 mg g^{-1} by reason of higher concentration of Cr(VI) in binary solution. Freundlich constant n obtained for both Cr(VI) and phenol is greater than 1 and lies in the range of 2–10 which shows favourable adsorption. Redlich Peterson exponent β lies in the range of 0-1 suggesting good adsorption. The parameters of Langmuir isotherm are used to derive $R_L = 1/(1 + K_L C_i)$; the separation factor which explains the feasibility of adsorption process



(a) (b)

Figure 7: (a) Comparison of experimental and calculated value of q_e for Cr(VI) in binary mixture. (b) Comparison of experimental and calculated value of q_e for phenol in binary mixture.

[47] was less than 1. Depending upon the results listed in Table 1 best isotherm models fitted for Cr(VI) are in following order: Redlich Peterson > Freundlich > Langmuir, while that of phenol is Freundlich > Redlich Peterson > Langmuir.

4.2.2. Estimation of Parameters of Multicomponent Isotherm Model. The binary biosorption of phenol and Cr(VI) fitted to Nonmodified Langmuir, Modified Langmuir, Extended Langmuir, Extended Freundlich, Nonmodified Competitive Redlich Peterson model, and Modified Redlich Peterson model. The values of parameters of theses binary biosorption models were given in Table 2. The experimental and calculated values of binary biosorption of phenol and Cr(VI) were compared shown in Figures 7(a) and 7(b), respectively. It is cleared that Extended Freundlich was agreed well to experimental data for binary biosorption of Cr(VI) and phenol since most of the data point fall around 45° line [45] which is also confirmed by their lower MPSD values given in Table 1 in comparison to other multicomponent isotherms. Figures 8(a) and 8(b) compared the uptake ($\mathrm{mg\,g^{-1}}$) of Cr(VI) and phenol, respectively, with concentration which shows that Extended Langmuir, Extended Freundlich, and Nonmodified Redlich Peterson for Cr(VI) agreed well with experimental specific uptake while Extended Freundlich, Extended Langmuir, and Modified Redlich Peterson agreed well with phenol which is confirmed by lower MPSD values as shown in Table 2. Nonmodified Langmuir and Modified Langmuir shows a very poor fit to the experimental data for both Cr(VI) and phenol with very high MPSD values.

Table 2: Parameters of multicomponent isotherms for adsorption of phenol and Cr(VI).

Isotherm model	Parameter	Cr(VI)	Phenol
Nonmodified Langmuir	MPSD	85.1483	57.7399
Modified Langmuir	n_j	−0.6851	−1.3429
	MPSD	67.5289	99.6646
Extended Langmuir	$Q_{o,i}$	36.3817	6.5689
	b_i	0.02268	0.0742
	MPSD	46.0621	9.7955
Extended Freundlich	x_i	0.32182	−0.0922
	y_i	−0.03329	3.4655
	z_i	0.9131	−0.0516
	MPSD	2.9079	4.4603
Nonmodified Redlich Peterson	MPSD	119.3248	27.1295
Modified Redlich Peterson	K_{RP}	8429.7329	43551.3300
	a_{RP}	2291.8563	22539.0503
	β	0.8282	0.7866
	n_j	0.0024	0.2620
	MPSD	49.1062	58.5988

4.3. Kinetic Modelling. Kinetic modelling was carried out to know the nature of adsorption such as physisorption and chemisorption’s [48]. Various kinetic models are available in literature [49]. Kinetic models such as pseudo first-order

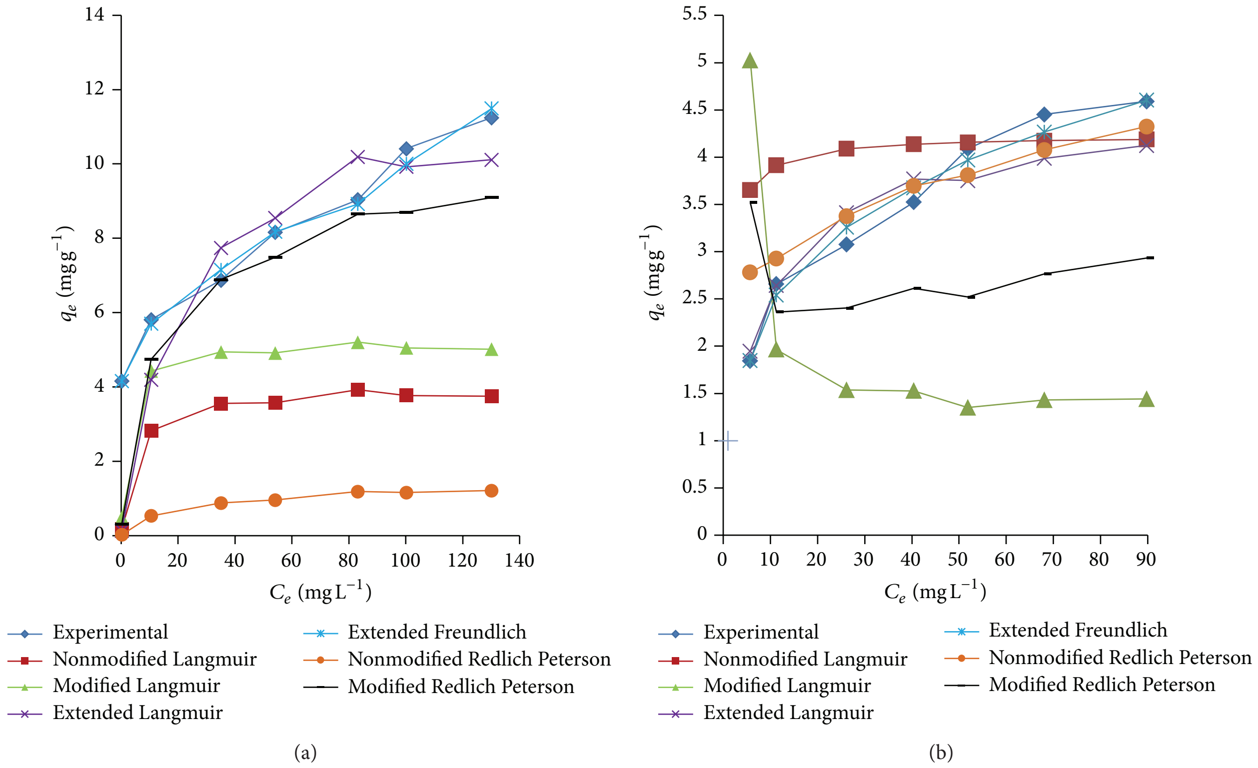


FIGURE 8: (a) Comparison of multicomponent isotherm for Cr(VI). (b) Comparison of multicomponent isotherm for phenol.

and pseudo second-order models and intraparticle diffusion model have been applied in the present study [50, 51].

Pseudo first-order model:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t. \tag{12}$$

Pseudo second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}. \tag{13}$$

Intraparticle diffusion model:

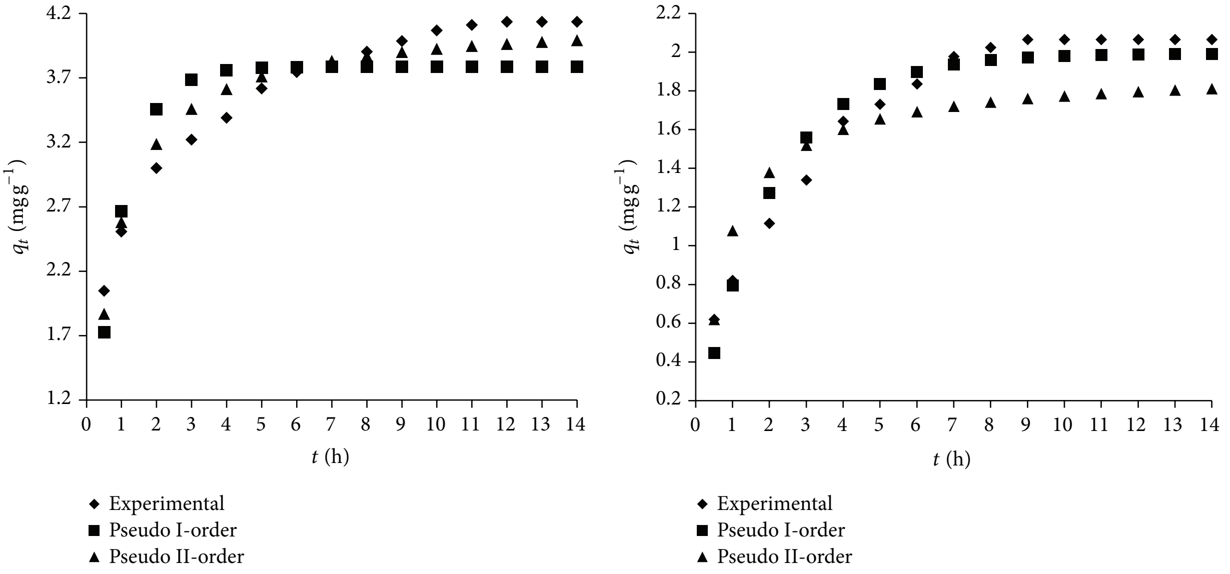
$$q_t = k_{\text{id}} t^{1/2} + I. \tag{14}$$

Experimental data for the binary biosorption of Cr(VI) and phenol on the surface of Fe treated rice husk agreed well with both pseudo first-order and pseudo second-order kinetic model and results were shown in Tables 3 and 4, respectively. For Cr(VI) pseudo second-order model was best fitted to experimental data in comparison to pseudo first-order model while for phenol pseudo first-order model best described the experimental data which is confirmed by lower ARE values. A comparative plot of experimental and calculated value of adsorption capacity q_t (mg g^{-1}) varied with time was plotted for both Cr(VI) and phenol as shown in Figures 9(a) and 9(b), respectively. From the figures it was cleared that experimental adsorption capacity was in good agreement with pseudo second-order model for Cr(VI) while pseudo first-order model for phenol.

TABLE 3: Parameters of kinetic modelling for adsorption of Cr(VI).

Kinetic parameters	Cr(VI)
Pseudo first-order model	
k_1	1.2168
Q_o	3.7859
ARE	2.3310
Pseudo second-order model	
k_2	0.3909
q_e^{cal}	4.1667
ARE	1.1662
Intraparticle diffusion model	
K_{id}	0.650
R^2	0.929

To determine the nature of diffusion intraparticle diffusion model [52] was also applied for the binary biosorption of Cr(VI) and phenol. According to intraparticle diffusion model a plot of q_t (mg L^{-1}) versus $t^{0.5}$ was drawn in Figure 10 [53]. Applicability of intraparticle diffusion model as a rate controlling step depends upon that the plot passes through the origin [54] but here plot for both phenol and Cr(VI) does not passes through the origin which states that here intraparticle diffusion is not a rate controlling step.



(a) (b)

Figure 9: (a) Comparative plot of experimental and calculated value of q_t by pseudo first-order and pseudo second-order kinetic model for Cr(VI). (b) Comparative plot of experimental and calculated value of q_t by pseudo firs-order and pseudo second-order kinetic model for phenol.

Table 4: Parameters of kinetic modeling for adsorption of phenol.

Kinetic parameters	Cr(VI)
Pseudo first-order model	
k_1	0.5079
Q_o	1.9932
ARE	2.5272
Pseudo second-order model	
k_2	0.6778
q_e^{cal}	1.9108
ARE	3.8065
Intraparticle diffusion model	
K_{id}	0.492
R^2	0.901

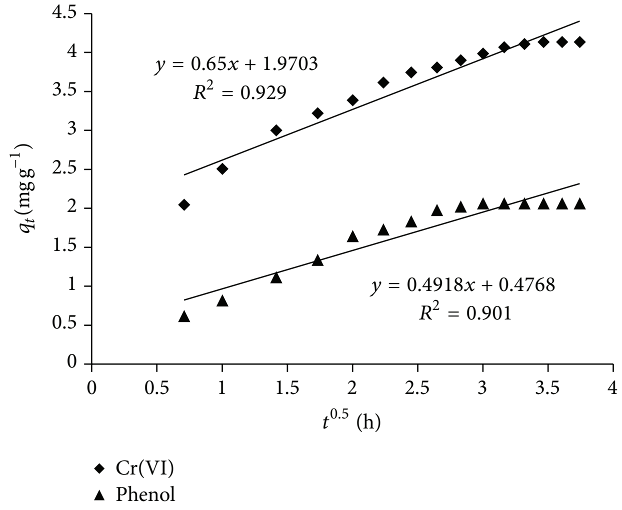


Figure 10: Intraparticle diffusion plot for simultaneous adsorption of Cr(VI) and phenol.

4.4. Validation of Model. MPSD Marquardt's percent standard deviation is applied for the validation of equilibrium data as given by following equation [55, 56]:

$$\text{MPSD} = 100 \times \sqrt{\frac{1}{N-P} \sum_{i=1}^{n} \left(\frac{q_{e,i}^{\text{exp}} - q_{e,i}^{\text{cal}}}{q_{e,i}^{\text{exp}}} \right)^2}. \tag{15}$$

More accurate estimation of q_e value depends upon MPSD value. The MPSD value should be smaller for correct estimation of q_e. Average Relative Error (ARE) between the experimental and calculated values was calculated for the validation of kinetic model. The equation for calculating ARE is given by the following equation [42, 43]:

$$\text{ARE}\ (\%) = \sqrt{\sum_{i=1}^{N} \left(\frac{q_{e,i}^{\text{exp}} - q_{e,i}^{\text{cal}}}{q_{e,i}^{\text{exp}}} \right)^2} \times \frac{100}{N}. \tag{16}$$

For the accurate estimation of q_t value ARE should be smaller.

5. Conclusion

Industrial effluents such as tannery, textile, electroplating, alloying contain Cr(VI) and phenol as major pollutants. Hence in this paper adsorption system for the simultaneous removal of Cr(VI) and phenol by Fe treated rice husk was carried out. Monocomponent model such as Langmuir, Freundlich, and Redlich Peterson and multicomponent model such as Nonmodified Langmuir, Competitive Modified Langmuir, Extended Langmuir, Extended Freundlich, Competitive Nonmodified Redlich Peterson, and Competitive Modified Redlich Peterson isotherms models were applied to predict the equilibrium uptake of phenol and Cr(VI) both singly and in combination. Adsorption capacity for Cr(VI) and phenol for multicomponent system is found to be more in comparison to single component model. It could be due to fact that phenol acts as electron donor which enhances the Cr(VI) adsorption. It is concluded that the entire equilibrium model fitted well with the experimental results in the studied concentration range but Extended Freundlich for both phenol and Cr(VI) for multicomponent system was agreed better with the experimental results. For monocomponent adsorption Redlich Peterson for Cr(VI) and Freundlich for phenol best described the experimental data. For multicomponent system kinetic of adsorption of Cr(VI) onto the surface of Fe treated rice husk agreed well with pseudo second-order model while for the adsorption of phenol pseudo first-order model predicts well the experimental data.

Nomenclature

q: Specific uptake capacity of adsorbent (mg g^{-1} of adsorbent)
C_i: Initial pollutant concentration (mg L^{-1})
C_t: Pollutant concentration at time t (mg L^{-1})
C_e: Equilibrium concentration (mg L^{-1})
V: Volume of solution L
W: Mass of adsorbent used (g)
q_e: Specific uptake of adsorbent at equilibrium (mg g^{-1} of adsorbent)
MPSD: Marquardt's percent standard deviation
ARE: Average Relative Error
$q_{e,i}^{\text{exp}}$: Experimental specific uptake (mg g^{-1})
$q_{e,i}^{\text{cal}}$: Calculated specific uptake (mg g^{-1})
N: Number of observations in the experimental isotherm
P: Number of parameters in the regression model
R_L: Separation factor
K_L: Langmuir constant (L g^{-1})
K_F: Constant in Freundlich model (mg g^{-1})/(mg L^{-1})$^{1/n}$
n: Constant in Freundlich model
K_{RP}: Redlich Peterson isotherm constant (L g^{-1})
a_{RP}: Redlich Peterson isotherm constant (L mg^{-1})$^{\beta}$
β: Redlich Peterson isotherm exponent
Q_o: Adsorption capacity of one adsorbate when present alone
$Q_{o,i}$: Constant in Modified Langmuir model for ith component (mg g^{-1})
$C_{e,i}$: Concentration of ith component in the binary mixture at equilibrium (mg L^{-1})
$q_{e,i}$: Amount of ith component adsorbed per gram of adsorbent at equilibrium (mg g^{-1})
$K_{F,i}$: Constant in Extended Freundlich constant for ith component (mg g^{-1})/(mg L^{-1})$^{1/n}$
x_i, y_i, z_i: Constant in Extended Freundlich model for the ith component
n_i: Correction factor for ith component in Modified Langmuir and Modified Redlich Peterson model
k_1: Rate constant in pseudo first-order model (h^{-1})
k_2: Rate constant of pseudo second-order kinetic model (mg g^{-1} h^{-1})
k_{id}: Intraparticle diffusion constant (mg g^{-1} h$^{-0.5}$).

Conflict of Interests

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

Acknowledgments

The author gratefully acknowledges financial support provided by the MHRD Assistantship by Government of India and Chemical Engineering Department, IIT Roorkee, for the facility provided for conducting research work.

References

[1] Z. Aksu and D. Akpinar, "Competitive biosorption of phenol and chromium(VI) from binary mixtures onto dried anaerobic activated sludge," *Biochemical Engineering Journal*, vol. 7, no. 3, pp. 183–193, 2001.

[2] S. Golbaz, A. J. Jafari, M. Rafiee, and R. R. Kalantary, "Separate and simultaneous removal of phenol, chromium, and cyanide from aqueous solution by coagulation/precipitation: mechanisms and theory," *Chemical Engineering Journal*, vol. 253, pp. 251–257, 2014.

[3] I. M. Dittert, H. de Lima Brandão, F. Pina et al., "Integrated reduction/oxidation reactions and sorption processes for Cr(VI) removal from aqueous solutions using *Laminaria digitata* macro-algae," *Chemical Engineering Journal*, vol. 237, pp. 443–454, 2014.

[4] C. I. Nair, K. Jayachandran, and S. Shashidhar, "Biodegradation of phenol," *African Journal of Biotechnology*, vol. 7, no. 25, pp. 4951–4958, 2008.

[5] A. Gładysz-Płaska, M. Majdan, S. Pikus, and D. Sternik, "Simultaneous adsorption of chromium(VI) and phenol on natural red clay modified by HDTMA," *Chemical Engineering Journal*, vol. 179, pp. 140–150, 2012.

[6] S. A. Cavaco, S. Fernandes, M. M. Quina, and L. M. Ferreira, "Removal of chromium from electroplating industry effluents by ion exchange resins," *Journal of Hazardous Materials*, vol. 144, no. 3, pp. 634–638, 2007.

[7] L. Lin, X. Xu, C. Papelis, T. Y. Cath, and P. Xu, “Sorption of metals and metalloids from reverse osmosis concentrate on drinking water treatment solids,” *Separation and Purification Technology*, vol. 134, pp. 37–45, 2014.

[8] S. S. Hamdan and M. H. El-Naas, “Characterization of the removal of Chromium(VI) from groundwater by electrocoagulation,” *Journal of Industrial and Engineering Chemistry*, vol. 20, no. 5, pp. 2775–2781, 2014.

[9] Y.-H. Lin, C.-L. Wu, C.-H. Hsu, and H.-L. Li, “Biodegradation of phenol with chromium(VI) reduction in an anaerobic fixed-biofilm process—kinetic model and reactor performance,” *Journal of Hazardous Materials*, vol. 172, no. 2-3, pp. 1394–1401, 2009.

[10] C. Quintelas, E. Sousa, F. Silva, S. Neto, and T. Tavares, “Competitive biosorption of ortho-cresol, phenol, chlorophenol and chromium(VI) from aqueous solution by a bacterial biofilm supported on granular activated carbon,” *Process Biochemistry*, vol. 41, no. 9, pp. 2087–2091, 2006.

[11] M. Seenuvasan, K. S. Kumar, M. A. Kumar, J. Iyyappan, and J. R. G. Suganthi, “Response surface estimation and canonical quantification for the pectin degrading Fe_3O_4-SiO_2-nanobiocatalyst fabrication,” *International Journal of ChemTech Research*, vol. 6, no. 7, pp. 3618–3627, 2014.

[12] M. A. Kumar, V. V. Kumar, R. Ponnusamy et al., “Concomitant mineralization and detoxification of acid red 88 by an indigenous acclimated mixed culture,” *Environmental Progress & Sustainable Energy*, vol. 34, no. 5, pp. 1455–1466, 2015.

[13] M. A. Kumar, A. Vijayalakshmi, E. Ann Raeboline Lincy et al., “Biotransformation of reactive black HEBL into 3 nitroso-3-azabicyclo (3.2.2) nonane by an acclimated mixed culture,” *International Journal of ChemTech Research*, vol. 6, no. 9, pp. 4172–4179, 2014.

[14] M. A. Kumar, V. V. Kumar, M. P. Premkumar et al., “Chemometric formulation of bacterial consortium-AVS for improved decolorization of resonance-stabilized and heteropolyaromatic dyes,” *Bioresource Technology*, vol. 123, pp. 344–351, 2012.

[15] S. Karthikeyan, M. A. Kumar, P. Maharaja, T. Partheeban, J. Sridevi, and G. Sekaran, “Process optimization for the treatment of pharmaceutical wastewater catalyzed by poly sulpha sponge,” *Journal of the Taiwan Institute of Chemical Engineers*, vol. 45, no. 4, pp. 1739–1747, 2014.

[16] T. Vidhyadevi, A. Murugesan, S. S. Kalaivani et al., “Optimization of the process parameters for the removal of reactive yellow dye by the low cost *Setaria verticillata* carbon using response surface methodology: thermodynamic, kinetic, and equilibrium studies,” *Environmental Progress & Sustainable Energy*, vol. 33, no. 3, pp. 855–865, 2014.

[17] S. E. Bailey, T. J. Olin, R. M. Bricka, and D. D. Adrian, “A review of potentially low-cost sorbents for heavy metals,” *Water Research*, vol. 33, no. 11, pp. 2469–2479, 1999.

[18] A. K. Bhattacharya, T. K. Naiya, S. N. Mandal, and S. K. Das, “Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents,” *Chemical Engineering Journal*, vol. 137, no. 3, pp. 529–541, 2008.

[19] A. S. Sartape, P. D. Raut, and S. S. Kolekar, “Efficient adsorption of chromium(VI) ions from aqueous solution onto a low-cost adsorbent developed from *Limonia acidissima* (wood apple) shell,” *Adsorption Science and Technology*, vol. 28, no. 6, pp. 547–560, 2010.

[20] V. Vinodhini and N. Das, “Packed bed column studies on Cr (VI) removal from tannery wastewater by neem sawdust,” *Desalination*, vol. 264, no. 1-2, pp. 9–14, 2010.

[21] M. R. Hadjmohammadi, M. Salary, and P. Biparva, “Removal of Cr(VI) from aqueous solution using pine needles powder as a biosorbent,” *Journal of Applied Sciences in Environmental Sanitation*, vol. 6, no. 1, pp. 1–13, 2010.

[22] H. Demiral, I. Demiral, F. Tümsek, and B. Karabacakoğlu, “Adsorption of chromium(VI) from aqueous solution by activated carbon derived from olive bagasse and applicability of different adsorption models,” *Chemical Engineering Journal*, vol. 144, no. 2, pp. 188–196, 2008.

[23] H. Daraei, A. Mittal, J. Mittal, and H. Kamali, “Optimization of Cr(VI) removal onto biosorbent eggshell membrane: experimental & theoretical approaches,” *Desalination and Water Treatment*, vol. 52, no. 7–9, pp. 1307–1315, 2014.

[24] D. Hank, Z. Azi, S. Ait Hocine, O. Chaalal, and A. Hellal, “Optimization of phenol adsorption onto bentonite by factorial design methodology,” *Journal of Industrial and Engineering Chemistry*, vol. 20, no. 4, pp. 2256–2263, 2014.

[25] D. N. Jadhav and A. K. Vanjara, “Removal of phenol from waste water using sawdust polymerized sawdust and sawdust carbon II,” *Indian Journal of Chemical Technology*, vol. 11, pp. 35–41, 2004.

[26] S. Kuo and R. Bembenek, “Sorption and desorption of chromate by wood shavings impregnated with iron or aluminum oxide,” *Bioresource Technology*, vol. 99, no. 13, pp. 5617–5625, 2008.

[27] R. Fonseca-Correa, L. Giraldo, and J. C. Moreno-Piraján, “Trivalent chromium removal from aqueous solution with physically and chemically modified corncob waste,” *Journal of Analytical and Applied Pyrolysis*, vol. 101, pp. 132–141, 2013.

[28] M. Owlad, M. K. Aroua, and W. M. A. Wan Daud, “Hexavalent chromium adsorption on impregnated palm shell activated carbon with polyethyleneimine,” *Bioresource Technology*, vol. 101, no. 14, pp. 5098–5103, 2010.

[29] F. N. Acar and E. Malkoc, “The removal of Chromium(VI) from aqueous solutions by *Fagus orientalis* L.,” *Bioresource Technology*, vol. 94, no. 1, pp. 13–15, 2004.

[30] S. Srivastava, A. H. Ahmad, and I. S. Thakur, “Removal of chromium and pentachlorophenol from tannery effluents,” *Bioresource Technology*, vol. 98, no. 5, pp. 1128–1132, 2007.

[31] M. Bansal, D. Singh, and V. K. Garg, “A comparative study for the removal of hexavalent chromium from aqueous solution by agriculture wastes’ carbons,” *Journal of Hazardous Materials*, vol. 171, no. 1-3, pp. 83–92, 2009.

[32] A. Banerjee and A. K. Ghoshal, “Phenol degradation performance by isolated *Bacillus cereus* immobilized in alginate,” *International Biodeterioration and Biodegradation*, vol. 65, no. 7, pp. 1052–1060, 2011.

[33] S. Nethaji, A. Sivasamy, and A. B. Mandal, “Preparation and characterization of corn cob activated carbon coated with nano-sized magnetite particles for the removal of Cr(VI),” *Bioresource Technology*, vol. 134, pp. 94–100, 2013.

[34] Z. A. AL-Othman, R. Ali, and M. Naushad, “Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: adsorption kinetics, equilibrium and thermodynamic studies,” *Chemical Engineering Journal*, vol. 184, pp. 238–247, 2012.

[35] A. S. K. Kumar, T. Gupta, S. S. Kakan et al., “Effective adsorption of hexavalent chromium through a three center (3c) co-operative interaction with an ionic liquid and biopolymer,” *Journal of Hazardous Materials*, vol. 239-240, pp. 213–224, 2012.

[36] N. A. Oladoja, I. A. Ololade, O. A. Alimi, T. A. Akinnifesi, and G. A. Olaremu, “Iron incorporated rice husk silica as a sorbent for

hexavalent chromium attenuation in aqueous system," *Chemical Engineering Research and Design*, vol. 91, no. 12, pp. 2691–2702, 2013.

[37] G. Qu, D. Liang, D. Qu et al., "Simultaneous removal of cadmium ions and phenol from water solution by pulsed corona discharge plasma combined with activated carbon," *Chemical Engineering Journal*, vol. 228, pp. 28–35, 2013.

[38] L. Yun-Guo, F. Bao-Ying, F. Ting, Z. Hai-Zhou, and L. Xin, "Tolerance and removal of chromium(VI) by *Bacillus* sp. strain YB-1 isolated from electroplating sludge," *Transactions of Nonferrous Metals Society of China*, vol. 18, no. 2, pp. 480–487, 2008.

[39] N. Chaudhary and C. Balomajumder, "Optimization study of adsorption parameters for removal of phenol on aluminum impregnated fly ash using response surface methodology," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 45, no. 3, pp. 852–859, 2014.

[40] V. K. Garg, R. Gupta, R. Kumar, and R. K. Gupta, "Adsorption of Chromium from aqueous solution on treated sawdust," *Bioresource Technology*, vol. 92, no. 1, pp. 79–81, 2004.

[41] H. B. Senturk, D. Ozdes, A. Gundogdu, C. Duran, and M. Soylak, "Removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite: equilibrium, kinetic and thermodynamic study," *Journal of Hazardous Materials*, vol. 172, no. 1, pp. 353–362, 2009.

[42] B. Agarwal, C. Balomajumder, and P. K. Thakur, "Simultaneous co-adsorptive removal of phenol and cyanide from binary solution using granular activated carbon," *Chemical Engineering Journal*, vol. 228, pp. 655–664, 2013.

[43] R. R. Dash, C. Balomajumder, and A. Kumar, "Treatment of metal cyanide bearing wastewater by simultaneous adsorption and biodegradation (SAB)," *Journal of Hazardous Materials*, vol. 152, no. 1, pp. 387–396, 2008.

[44] V. Mishra, C. Balomajumder, and V. K. Agarwal, "Design and optimization of simultaneous biosorption and bioaccumulation (SBB) system: a potential method for removal of Zn(II) ion from liquid phase," *Desalination and Water Treatment*, vol. 51, no. 16–18, pp. 3179–3188, 2013.

[45] S. Kumar, M. Zafar, J. K. Prajapati, S. Kumar, and S. Kannepalli, "Modeling studies on simultaneous adsorption of phenol and resorcinol onto granular activated carbon from simulated aqueous solution," *Journal of Hazardous Materials*, vol. 185, no. 1, pp. 287–294, 2011.

[46] A. Leitao and R. Serrao, "Adsorption of phenolic compounds from water on activated carbon: prediction of multicomponent equilibrium isotherms using single-component data," *Adsorption*, vol. 11, no. 2, pp. 167–179, 2005.

[47] K. R. Hall, L. C. Eagleton, A. Acrivos, and T. Vermeulen, "Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions," *Industrial and Engineering Chemistry Fundamentals*, vol. 5, no. 2, pp. 212–223, 1966.

[48] A. Marsal, F. Maldonado, S. Cuadros, M. Elena Bautista, and A. M. Manich, "Adsorption isotherm, thermodynamic and kinetics studies of polyphenols onto tannery shavings," *Chemical Engineering Journal*, vol. 183, pp. 21–29, 2012.

[49] N. Gupta, C. Balomajumder, and V. K. Agarwal, "Adsorption of cyanide ion on pressmud surface: a modeling approach," *Chemical Engineering Journal*, vol. 191, pp. 548–556, 2012.

[50] Y. S. Ho and G. McKay, "Pseudo-second order model for sorption processes," *Process Biochemistry*, vol. 34, no. 5, pp. 451–465, 1999.

[51] S. Lagergren, "About the theory of so called adsorption of soluble substances," *Kungliga Svenska Vetenskapsakademiens Handlingar*, vol. 24, no. 4, pp. 1–39, 1898.

[52] W. J. Weber and J. C. Morris, "Kinetics of adsorption in column of fluidized media," *Journal of the Water Pollution Control Federation*, vol. 37, pp. 425–443, 1965.

[53] M. N. Sepehr, A. Amrane, K. A. Karimaian, M. Zarrabi, and H. R. Ghaffari, "Potential of waste pumice and surface modified pumice for hexavalent chromium removal: characterization, equilibrium, thermodynamic and kinetic study," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 45, no. 2, pp. 635–647, 2014.

[54] N. Talreja, D. Kumar, and N. Verma, "Removal of hexavalent chromium from water using Fe-grown carbon nanofibers containing porous carbon microbeads," *Journal of Water Process Engineering*, vol. 3, pp. 34–45, 2014.

[55] E. Repo, R. Petrus, M. Sillanpää, and J. K. Warchoł, "Equilibrium studies on the adsorption of Co(II) and Ni(II) by modified silica gels: one-component and binary systems," *Chemical Engineering Journal*, vol. 172, no. 1, pp. 376–385, 2011.

[56] M. Hadi, M. R. Samarghandi, and G. McKay, "Equilibrium two-parameter isotherms of acid dyes sorption by activated carbons: study of residual errors," *Chemical Engineering Journal*, vol. 160, no. 2, pp. 408–416, 2010.