



Adsorption of phenol and *p*-chlorophenol from their single and bisolute aqueous solutions on Amberlite XAD-16 resin

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Abstract

Removal of phenol and *p*-chlorophenol from synthetic single and bisolute aqueous solutions at 303.15 K through adsorption on Amberlite XAD-16 resin under batch equilibrium and dynamic column experimental conditions was investigated. The equilibrium adsorption data from single component solutions were fitted to Langmuir and Freundlich adsorption isotherm models to evaluate the model parameters and the parameters in turn were used to predict the extent of adsorption from bisolute aqueous solutions using Ideal Solution Adsorption (IAS) model. The effect of pH on removal of phenol and *p*-chlorophenol from single and bisolute systems was studied. The breakthrough capacity and total capacity of the resin for the adsorbates at different concentrations were evaluated through column adsorption studies. Attempts were made to regenerate the resin by solvent washing using methanol as an eluent. The limited number of adsorption–desorption cycles indicated that the adsorption capacity of the resin remained unchanged.

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1. Introduction

Phenols are pollutants of great concern because they are toxic and are known or suspected to be carcinogenic when present at elevated levels in the environment. They occur in wastewater of a number of industries, such as high temperature coal conversion, petroleum refining, resin and plastics. At present several methods, such as microbial degradation, adsorption, chemical oxidation, incineration, solvent extraction, reverse osmosis and irradiation, are being used for removing phenols from wastewater. A variety of adsorbents

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used for removal of phenols from single solute aqueous solutions include activated carbon [1], bentonite and perlite [2], rubber seed coat [3], hydrotalcite and its calcined product [4], acid-activated bituminous shale [5], zirconium(IV) arsenate–vanadate ion-exchanger [6], cross-linked polyvinylpyrrolidone [7], activated natural zeolites [8], water-insoluble cationic starch [9] and polymeric XAD-4 resins [10,11]. A significant aspect of the resin adsorption is that the bonding forces between the adsorbent and the adsorbate are usually weaker than those encountered in activated carbon adsorption. Regeneration of the resin can be accomplished by simple, non-destructive means, such as solvent washing, thus providing the potential for solute recovery. A search of the literature indicates that a number of attempts are made to study the competitive adsorption of phenols on activated carbon [12–16]. Though a large body of data are available on the adsorption of phenols on polymeric resins from single solute aqueous solutions, but a very few attempts have been made to characterize the adsorption of phenols from their bisolute aqueous solutions. The objective of the present study is to examine the use of Amberlite XAD-16 resin, a polystyrene–divinyl benzene copolymer, as an adsorbent for the removal of phenol and *p*-chlorophenol from single and bisolute aqueous solutions under equilibrium and dynamic column experimental conditions. Effect of pH on the extent of adsorption is studied. In addition, equilibrium adsorption data from bisolute aqueous solutions are evaluated using the parameters obtained from single solute adsorption data on the basis of Ideal Solution Adsorption (IAS) model. The loaded adsorbent with the phenols is regenerated with solvent washing technique using methanol as an eluent.

2. Experimental

2.1. Materials

Macro reticular resin Amberlite XAD-16, a cross-linked styrene–divinylbenzene polymer, is obtained from Sigma Chemicals, USA. The resin is purified by the procedure described earlier [17]. The characteristics of the resin are as follows: surface area 800 m²/g, average pore diameter 100 Å, wet density 1.02 g/cm³, mesh size 20–60 and moisture content 62%. Phenol (Ranbaxy, India, AR grade), *p*-chlorophenol (Riedel, Germany, AR grade) and methanol (SD Fine Chemicals, India, AR grade) are purified by fractional distillation in vacuum. Deionized double distilled water is used throughout this investigation.

2.2. Method

A known concentration of single or bisolute aqueous solutions of phenol and *p*-chlorophenol are prepared by dissolving required amounts of the solutes. The equilibrium adsorption data are obtained by contacting a known weight of resin (about 0.3 g) with 100 ml of aqueous solution of phenols at different initial concentrations in 125 ml stoppered Erlenmeyer flasks. The flasks are shaken for 6 h in a shaker-thermostatic bath at 303 K. The time required to reach equilibrium is ascertained by the fact that the concentration of the adsorbate remains constant. The samples are filtered through Whatman No. 5 filter paper to eliminate any fine particles. Then the concentrations of phenol and *p*-chlorophenol from single solute

Table 1
Molar extinction coefficients (ϵ) of phenol and *p*-chlorophenol (*p*-CP) and standard deviation (σ)

Adsorbate	Wavelength			
	210 nm		223 nm	
	ϵ	σ	ϵ	σ
Phenol	6.3507	0.0010	2.7241	0.0010
<i>p</i> -CP	4.0334	0.0006	8.0224	0.0011

solutions are determined by measuring absorbance using Shimadzu UV-240 spectrophotometer at 210 and 223 nm, respectively, and solving Beer–Lambert equation. 210 and 223 nm are the wavelengths of maximum absorption (λ_{\max}) for phenol and *p*-chlorophenol, respectively. At λ_{\max} the two peaks are well resolved. In case of bisolute systems, the absorbance of the solution is measured at both the wavelengths and the concentrations are obtained by solving the following equations:

$$A_{210} = \epsilon_{1(210)}lC_1 + \epsilon_{2(210)}lC_2 \quad (1)$$

$$A_{223} = \epsilon_{1(223)}lC_1 + \epsilon_{2(223)}lC_2 \quad (2)$$

where A_{210} and A_{223} are the absorbance at 210 and 223 nm, respectively, and are measured experimentally for the bisolute solutions. $\epsilon_{1(210)}$, $\epsilon_{1(223)}$, $\epsilon_{2(210)}$ and $\epsilon_{2(223)}$ are the molar extinction coefficients of phenol (1) and *p*-chlorophenol (2) at 210 and 223 nm, respectively, and are computed from single solute absorbance. The values of molar extinction coefficients are given Table 1. The path length is l . C_1 and C_2 , the concentrations of phenol and *p*-chlorophenol in mmol/l, are determined by solving Eqs. (1) and (2). The reproducibility is checked by comparing the measured concentrations with the actual values. The amount of solute i adsorbed per unit mass of adsorbent (q_i) is calculated from mass balance using the equation,

$$q_i = \frac{(C_{0,i} - C_{e,i})V}{m} \quad (3)$$

where $C_{0,i}$ and $C_{e,i}$ are initial and equilibrium concentrations of component i , respectively, m is the mass of adsorbent and V is the volume of the solution in liters. The pH of the solution is adjusted using 1 M solutions of sulfuric acid and sodium hydroxide and measured with Elico model L1-120 digital pH meter.

Dynamic adsorption studies are carried out in a column made up of stainless steel tube of 0.8 cm i.d. and 10 cm length. The column is filled with XAD-16 resin without air gaps. Glass wool is placed at the bottom and top of the column. Prior to adsorption studies the column is washed with methanol followed by water to clean the surface and pores of the resin beads. The influent aqueous solution containing known concentration of single or bisolute adsorbate is allowed to flow through the column bed in down flow mode at a constant flow rate, 6 bed volumes per hour (bed volume = 5 cm³), i.e. at a flow rate of 30 ml/h. The effluent solution is collected at different intervals and the concentration is determined spectrophotometrically. Dynamic column adsorption characteristics of phenol

at concentrations of 10.63 and 21.25 mmol/l in the absence of chlorophenol and in the presence of chlorophenol at concentrations of 7.78 and 15.56 mmol/l are studied. Similarly, chlorophenol adsorption is studied at concentrations of 7.78 and 15.56 mmol/l in the absence of phenol and in the presence of phenol at concentrations of 10.63 and 21.25 mmol/l.

Desorption of the adsorbate from the loaded resin is carried out by solvent elution method using methanol as an eluent. The eluent is allowed to flow through the loaded bed in down flow mode at 6 bed volumes per hour and the effluent along with solutes is collected at different time intervals at the bottom of the column. The concentrations of the solutes are determined by evaporating methanol, diluting to appropriate concentration and measuring the absorbance. After regeneration the adsorption bed is washed with water to remove methanol and water is drained from the column. The column is used in subsequent adsorption–desorption experimental cycles.

3. Results and discussion

3.1. Equilibrium adsorption data

Removal of phenol in the presence of various concentrations of *p*-chlorophenol and of *p*-chlorophenol in the presence of different concentrations of phenol on XAD-16 resin is shown in Figs. 1 and 2, respectively, by plotting initial concentration against the amount adsorbed per unit weight of the resin. The plots indicate that the extent of adsorption of

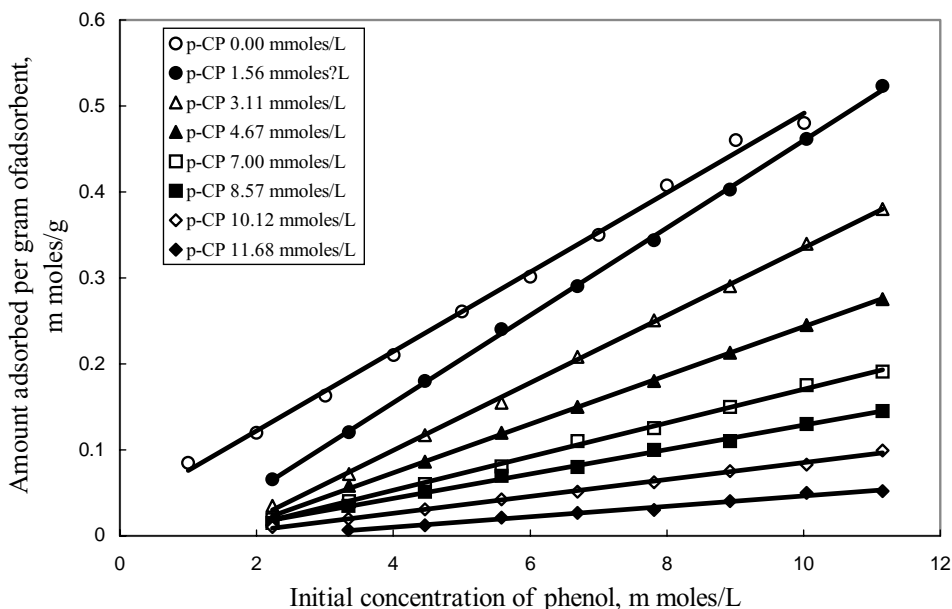


Fig. 1. Effect of initial concentration on the adsorption of phenol on XAD-16 resin in presence of *p*-chlorophenol (*p*-CP).

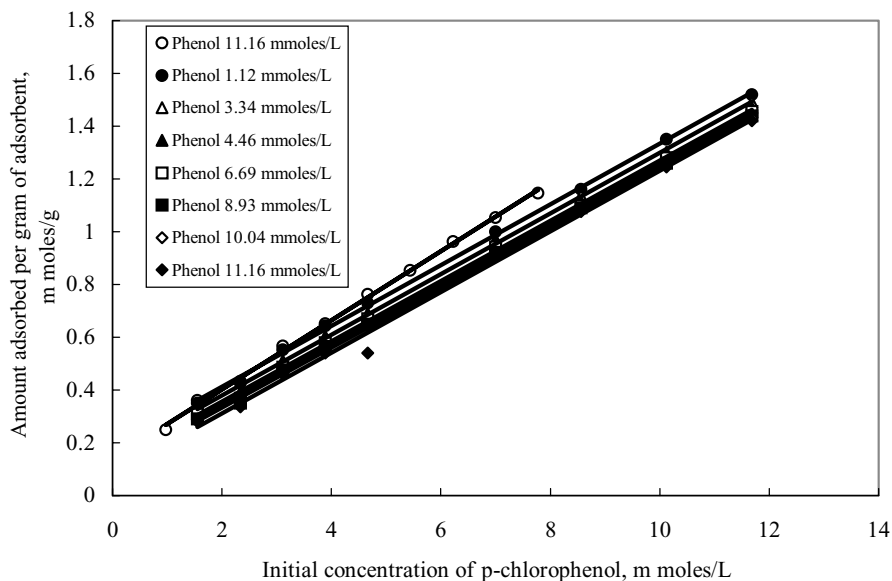


Fig. 2. Effect of initial concentration on adsorption of *p*-chlorophenol on XAD-16 resin in presence of phenol.

phenol and *p*-chlorophenol increases with the increase of initial concentration from single as well as bisolute aqueous solutions. All the adsorption isotherms are linear with in the concentration range studied. Further, the plots indicate that the slope of linear isotherms of phenol/*p*-chlorophenol decreases in the bisolute systems as the concentration of *p*-chlorophenol/phenol increases. From this observation it may be concluded that the extent of adsorption of phenol/*p*-chlorophenol decreases as the concentration of the other component increases. However, this effect is more pronounced in phenol adsorption compared to that of *p*-chlorophenol. *p*-Chlorophenol is more favorably adsorbed on XAD-16 resin among phenol and *p*-chlorophenol, which may be attributed to its relatively low solubility in water. Whenever a component is relatively less soluble in water due to difference in hydrophobicity, it has a tendency to 'salting out' from aqueous phase resulting in more favorable adsorption.

3.2. Adsorption isotherms

Batch equilibrium adsorption data of phenol and *p*-chlorophenol from single solute aqueous solutions are fitted to Langmuir and Freundlich adsorption isotherm equations,

$$q_i = \frac{Q_i^0 b_i C_{e,i}}{(1 + b_i C_{e,i})} \quad (4)$$

$$q_i = k_i C_{e,i}^n \quad (5)$$

where Q_i^0 and b_i are Langmuir parameters and k_i and n are Freundlich parameters of component i . The values of the parameters are evaluated from the single component adsorption

Table 2

Parameters of Langmuir and Freundlich isotherms for adsorption of phenol and *p*-chlorophenol (*p*-CP) on XAD-16 resin

Parameters	Langmuir model		Parameters	Freundlich model	
	Phenol	<i>p</i> -CP		Phenol	<i>p</i> -CP
Q^0	1.5029	2.2702	k	0.0748	0.4071
b	0.0511	0.2150	n	0.8720	0.7089
R^2	0.9977	0.9934	R^2	0.9962	0.9977

data following least square fitting procedure and the values are given in Table 2 along with the regression coefficients. Langmuir and Freundlich plots are shown in Figs. 3 and 4, respectively. Q_i^0 gives the maximum monolayer adsorption capacity of the resin in mmol/g of adsorbent. The results in Table 2 indicate that the resin shows more adsorption capacity towards *p*-chlorophenol than phenol. The parameters of the isotherms are in turn used to evaluate the extent of adsorption from bisolute aqueous solution using Eq. (6), formulated basing on Langmuir multi-solute adsorption model,

$$q_i = \frac{Q_i^0 b_i C_{e,i}}{1 + \sum b_i C_{e,i}} \quad (6)$$

The following equation similar to Freundlich empirical equation, developed on the basis of IAS model, is used to predict the bisolute adsorption,

$$C_{e,i} = \frac{q_i}{q_t} \left\{ \frac{1}{k_i (\sum n_i/n_j q_j)} \right\}_i^{1/n} \quad (7)$$

where $q_t = (q_1 + q_2)$. Amount adsorbed per unit weight of adsorbent, calculated using Eqs. (6) and (7), along with the experimental results are shown in Figs. 5 and 6 for phenol

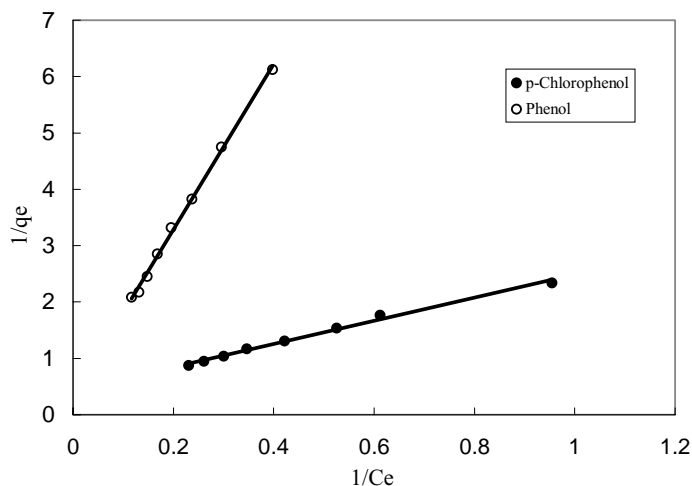


Fig. 3. Langmuir isotherms for adsorption of phenol and *p*-chlorophenol on Amberlite XAD-16 resin.

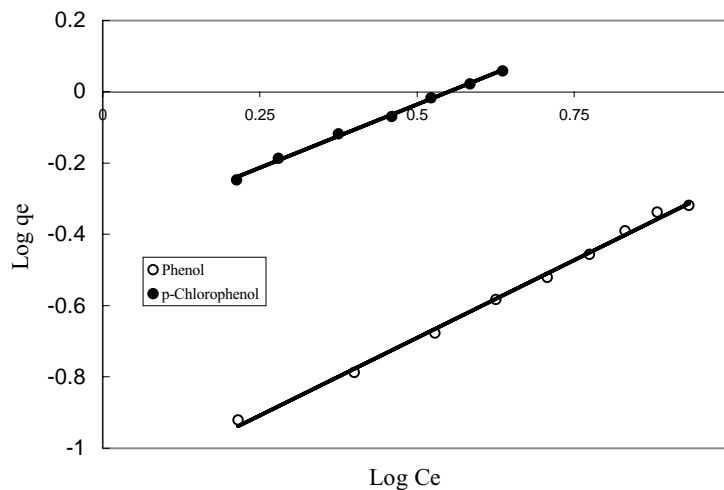


Fig. 4. Freundlich isotherms for adsorption of phenol and *p*-chlorophenol on Amberlite XAD-16 resin.

and *p*-chlorophenol, respectively, at one composition as a representative of whole set of data. A comparison of the predicted values with the experimental results indicates that both Eqs. (6) and (7) are capable of representing the adsorption behavior from bisolute aqueous solutions and hence using these equations extent of adsorption from bisolute aqueous

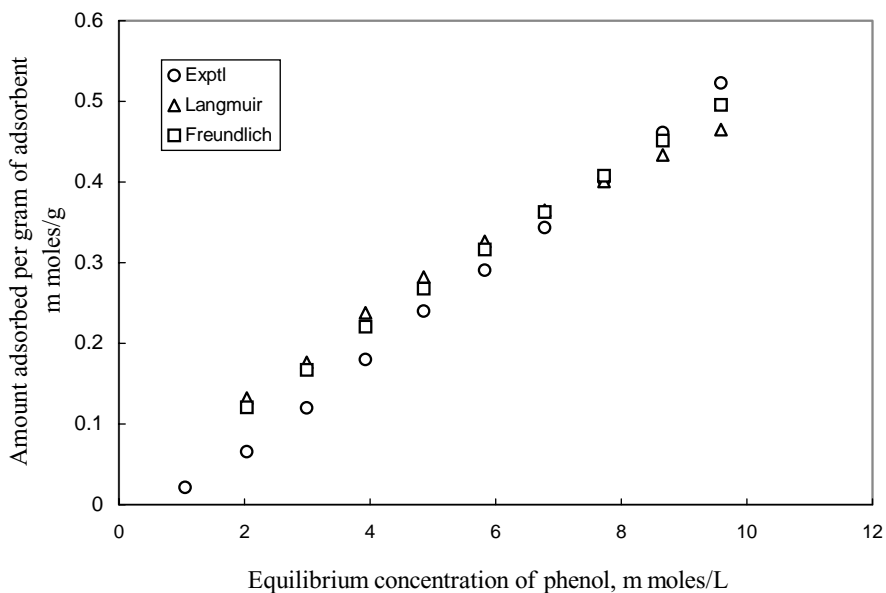


Fig. 5. Comparison of experimental data with Langmuir and Freundlich adsorption isotherms for phenol on XAD-16 in presence of *p*-CP (0.9756 mmol/l).

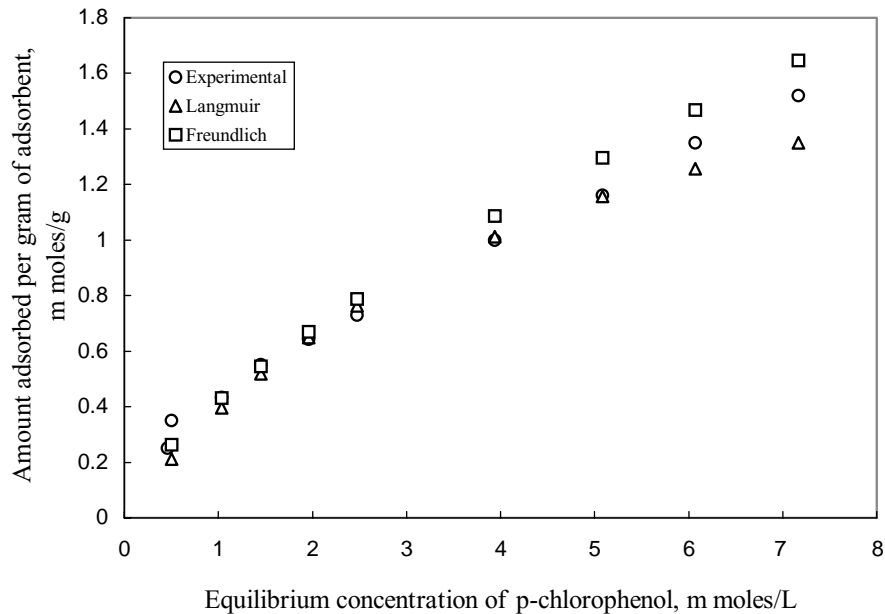


Fig. 6. Comparison of experimental data with Langmuir and Freundlich adsorption isotherms for adsorption of *p*-chlorophenol on XAD-16 in presence of phenol (1.1158 mmol/l).

solutions could be predicted from the parameters obtained from single solute adsorption data.

3.3. Effect of pH

Several experiments are conducted to study the effect of pH on adsorption of phenol and *p*-chlorophenol from aqueous solutions individually and combined and the results are included in Figs. 7 and 8 for phenol and *p*-chlorophenol, respectively. The effect of solution pH on the removal of phenols from aqueous solution could be explained by considering the presence of ionic and molecular forms of phenols in aqueous solution. Phenols act as weak acids in aqueous solution and the dissociation of hydrogen ion from phenols strongly depends on the pH of the solution. In acidic solutions the molecular form dominates and in alkaline medium the anionic form is the predominant species. Experimental results show that the phenol and *p*-chlorophenol are removed effectively by XAD-16 resin at around pH 6 and reduce on either side of pH 6 in single as well as bisolute solutions. Both phenol and chlorophenol exist predominantly as neutral molecules at pH 6. Therefore, the interaction between the resin and phenols is considered mainly as non-polar and the forces responsible for adsorption are physical van der Waals forces. This behavior provides potential for recovery of the adsorbate as well as regeneration of adsorbent by simple non-destructive methods, such as solvent washing.

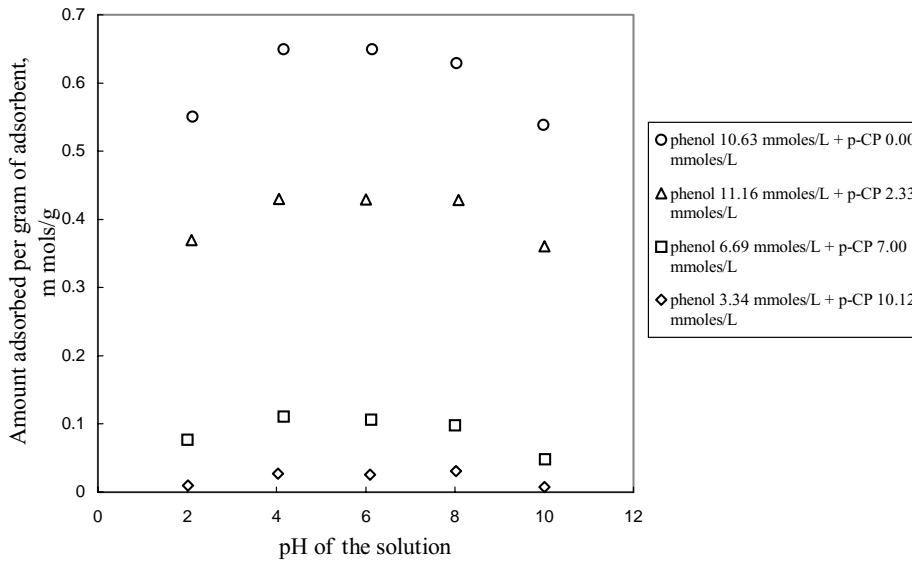


Fig. 7. Effect of pH on adsorption of phenol on Amberlite XAD-16 resin in presence of *p*-chlorophenol (*p*-CP).

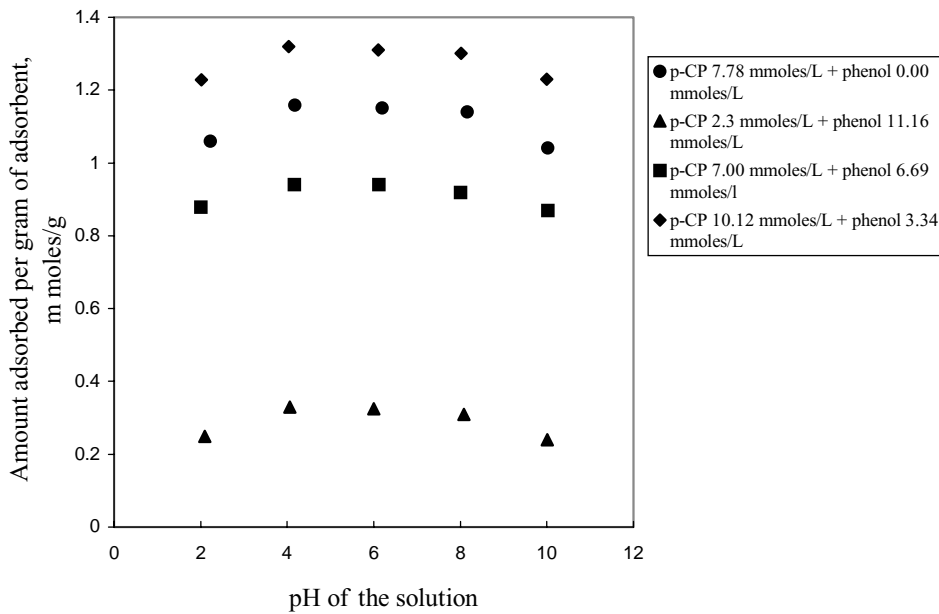


Fig. 8. Effect pH on adsorption of *p*-chlorophenol (*p*-CP) on Amberlite XAD-16 resin in presence of phenol.

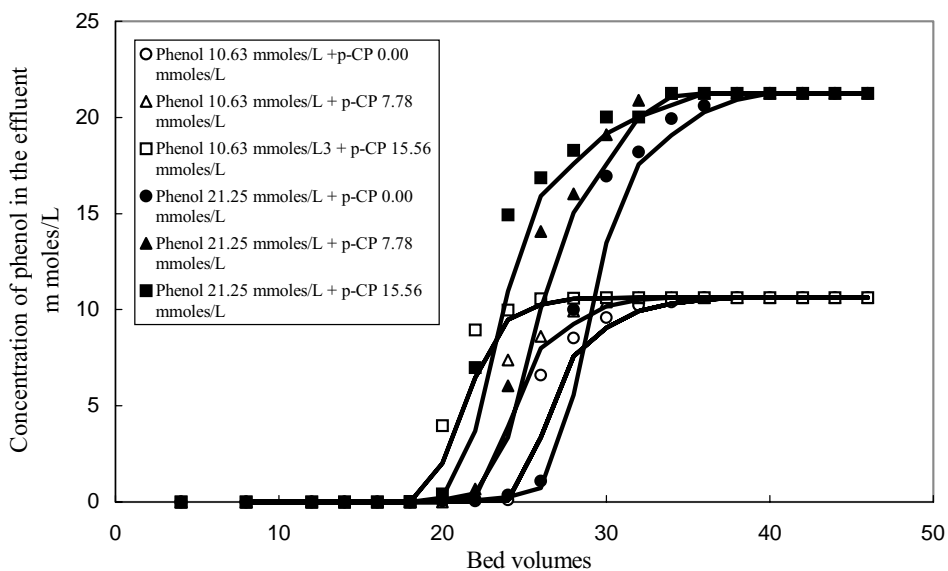


Fig. 9. Breakthrough curves for phenol in the presence of *p*-chlorophenol (*p*-CP) on Amberlite XAD-16 resin at 303.15 K.

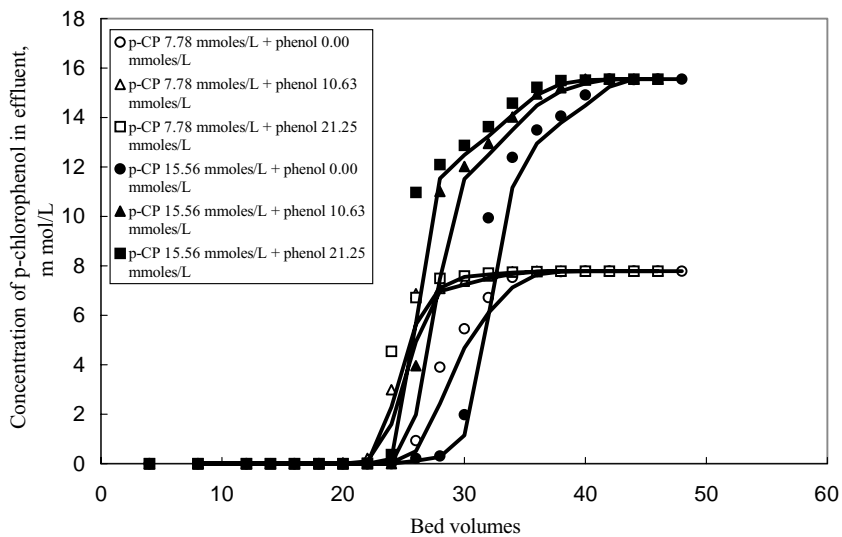


Fig. 10. Breakthrough curves for *p*-chlorophenol (*p*-CP) in presence of phenol on Amberlite XAD-16 resin at 303.15 K.

3.4. Column adsorption data

The results of dynamic flow experiments are used to obtain the breakthrough curves for phenol and *p*-chlorophenol adsorption from single and bisolute aqueous solutions by plotting bed volume versus effluent concentration. The curves are given in Figs. 9 and 10 for phenol and *p*-chlorophenol, respectively, in the presence of different concentrations of the other component. An examination of the curves indicates that no leakage of solute is observed up to certain bed volumes depending on the nature and concentration of the adsorbate and the presence of the second component. Later the concentration of the adsorbate in the effluent increases sharply and finally reaches the influent concentration. The breakthrough capacity, which is the amount adsorbed before the appearance of adsorbates in the effluent, and the total capacity, which is the amount adsorbed until the effluent concentration of the adsorbate is equal to the influent solution concentration, are computed from the breakthrough curves. The values are included in Table 3. The data indicate that breakthrough capacity and total capacity of the resin for phenol as well as *p*-chlorophenol increase with increase in the influent solution concentration from both single and bisolute aqueous solutions. However, the presence of second component decreases both the capacities. This may be attributed to the fact that both the components are competing for the same adsorption sites on the resin.

3.5. Regeneration of the loaded adsorption bed

When the bed gets exhausted or the effluent coming out of the column reaches the influent solution concentration, the regeneration of the adsorption bed to recover the adsorbed material becomes quite essential. The regeneration could be accomplished by a variety of techniques, such as thermal desorption, steam washing, solvent extraction, etc. Each method has inherent advantages and limitations. In this study several solvents are tried to regenerate the adsorption bed. Methanol is found to be effective in desorbing and recovering phenols almost quantitatively from the adsorption bed. The column is regenerated with methanol, as eluent after the column was fully loaded with phenols by passing the eluent at a fixed flow

Table 3
Breakthrough capacity and total capacity of XAD-16 resin for phenol and *p*-chlorophenol (*p*-CP) adsorption

Influent solution concentration (mmol/l)		Breakthrough capacity (mmol/g)		Total adsorption capacity (mmol/g)	
Phenol	<i>p</i> -CP	Phenol	<i>p</i> -CP	Phenol	<i>p</i> -CP
10.63	0.00	1.0062	0.00	1.1027	0.00
10.63	7.78	0.8257	0.6788	1.0140	0.7672
10.63	15.56	0.7410	1.5820	0.8308	1.7068
21.25	0.00	2.0356	0.00	2.3934	0.00
21.25	7.78	1.8242	0.6755	2.1466	0.7494
21.25	15.56	1.6571	1.4632	1.9244	1.5961
0.00	7.78	0.00	0.7403	0.00	0.8805
0.00	15.56	0.00	1.5929	0.00	1.9432

Table 4

Summary of the results of desorption of phenol and *p*-chlorophenol (*p*-CP) from loaded resins with single and bisolute solutions

Influent solution concentration (mmol/l)		Amount of solute adsorbed (mmol)		Amount of solute desorbed (mmol)		Percentage of desorption	
Phenol	<i>p</i> -CP	Phenol	<i>p</i> -CP	Phenol	<i>p</i> -CP	Phenol	<i>p</i> -CP
10.63	0.00	1.388	0.00	1.353	0.00	97.48	0.00
10.63	7.78	1.2970	0.9819	1.2676	0.9623	97.68	98.00
10.63	15.56	1.0714	2.2011	1.0405	2.1786	97.12	98.98
21.25	0.00	3.009	0.00	2.9778	0.00	98.62	0.00
21.25	7.78	2.7600	0.9637	2.7313	0.9422	98.96	97.77
21.25	15.56	2.4748	2.0542	2.4496	2.0272	98.98	98.68
0.00	7.78	0.00	1.1272	0.00	1.1100	0.00	98.47
0.00	15.56	0.00	2.4888	0.00	2.4788	0.00	99.57

rate. The regenerated column was used in the second cycle for adsorption of phenols and the adsorption–desorption process is repeated for several cycles. Summary of the results of desorption of phenol and *p*-chlorophenol from loaded resins with single and bisolute solutions are included in Table 4. The desorption curves for phenol and *p*-chlorophenol from single and bisolute aqueous solutions are given in Figs. 11 and 12, respectively. Better than 97% recovery of the adsorbates is attained. The limited number of adsorption–desorption cycles indicates that the XAD-16 resin could be used in cycles for the removal of phenols from wastewater.

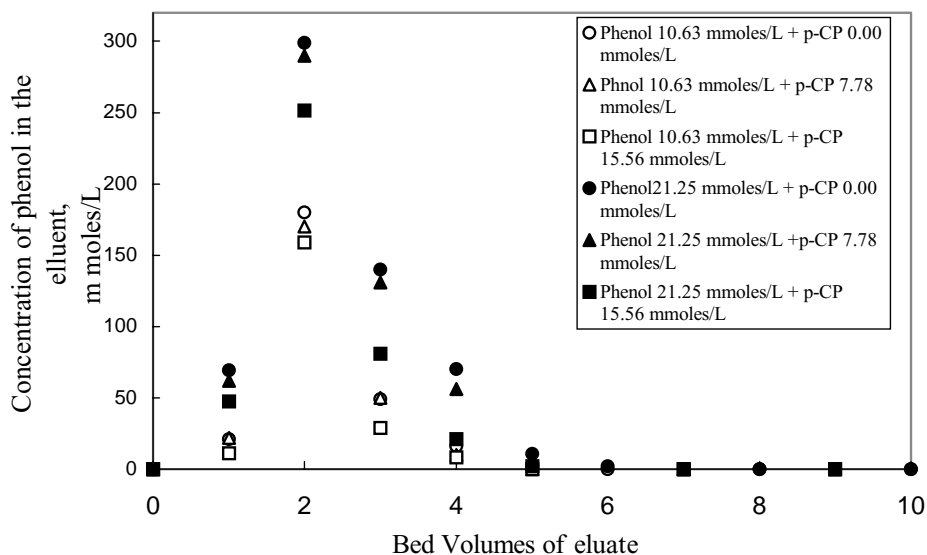


Fig. 11. Desorption of phenol from Amberlite XAD-16 resin loaded with phenol and *p*-chlorophenol (*p*-CP).

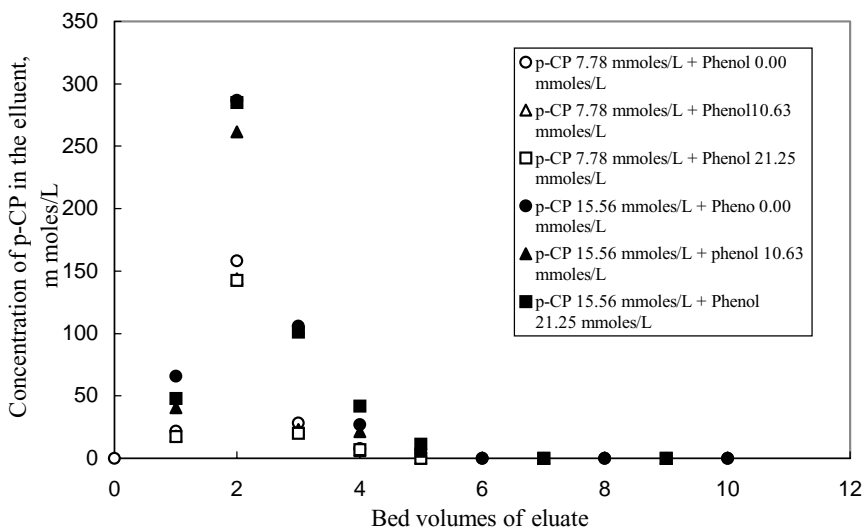


Fig. 12. Desorption of *p*-chlorophenol (*p*-CP) from Amberlite XAD-16 resin loaded with phenol and *p*-chlorophenol.

4. Conclusion

The removal of phenol and chlorophenol from single and bisolute aqueous solutions through adsorption on XAD-16 resin is found to be feasible around pH 6, but decreases significantly on either side of this pH. Langmuir and Freundlich adsorption models represent the experimental data adequately with the regression coefficient values better than 0.99. The parameters of the models could be used to predict the adsorption behavior of phenols from the bisolute aqueous solutions using IAS model. Experimental data indicate that XAD-16 resin shows more adsorption capacity for chlorophenol ($Q^0 = 2.27$ mmol/g) than phenol ($Q^0 = 1.50$ mmol/g), which may be explained on the basis of difference in solubility and hydrophobicity of phenol and *p*-chlorophenol in water. Further, results from the limited number of column adsorption–desorption cycle indicate that the adsorption capacity of the resin remains unchanged and the resin could be used to remove phenols from wastewater in cycles.

References

- [1] F. Caturla, J.M. Martin-Martinez, M. Molina-Sabio, F. Rodriguez-Reinoso, R. Torregrosa, J. Colloid Interface Sci. 124 (1988) 528.
- [2] B. Koumanova, P. Peeva-Antova, J. Hazard. Mater. A90 (2002) 229.
- [3] S. Rengaraj, S. Moon, R. Sivabalan, B. Arabindoo, V. Murugesan, J. Hazard. Mater. B89 (2002) 185.
- [4] M.A. Ulibarri, I. Pavlovic, M.C. Hermosin, J. Cornejo, Appl. Clay Sci. 10 (1995) 131.
- [5] T. Esmat, A. Resat, U. Catay, Water Res. 32 (1998) 2315.
- [6] K.S. Kader Abdul, J. Uthayavani, E. Subramanian, Indian J. Environ. Prot. 18 (1998) 181.

- [7] S.Z. Qureshi, M.A. Khan, N. Rahman, *Water Treat.* 9 (1994) 27.
- [8] I.M. Bendiyasa, S. Syamsiah, S. Indriani, Adsorption science and technology, in: *Proceedings of the Second Pacific Basin Conference on Adsorption Science and Technology, Brisbane, Australia, 14–18 May 2000*, p. 593.
- [9] C. Wu-Chung, F. Tzu-Ping, *J. Polym. Res.* 4 (1997) 47.
- [10] Y. Ku, K.-C. Lee, *J. Hazard. Mater.* 80 (2000) 59.
- [11] T. Devarajulu, K. Rambabu, A. Krishnaiah, D.-S. Viswanath, *Bull. Pure Appl. Sci.* 14 (1999) 21.
- [12] F. Mijangos, A. Navarro, M. Martin, *Spec. Publ.: R. Soc. Chem.* 196 (1997) 332.
- [13] A. Seidel, G. Reschke, S. Friedrich, D. Gelbin, *Adsorpt. Sci. Technol.* 3 (1986) 189.
- [14] G.A. Sorial, M.T. Suidan, R.D. Vidic, S.W. Maloney, *J. Environ. Eng. (N.Y.)* 119 (1993) 1026.
- [15] G.A. Sorial, M.T. Suidan, R.D. Vidic, S.W. Maloney, *J. Environ. Eng. (N.Y.)* 119 (1993) 1044.
- [16] W. Rong-Chi, Y. Jung-Jeng, *J. Chin. Inst. Chem. Eng.* 28 (1997) 185.
- [17] T. Devarajulu, G. Vanisree, A. Krishnaiah, *Indian J. Environ. Health* 41 (1999) 98.