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# Adsorptive Separation and Recovery of Chlorinated Phenols

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**Abstract:** Adsorption as a process for the removal and recovery of chlorinated phenols (dichlorophenols, trichlorophenol, and 2,4-dichlorophenoxyaxceticacid) from aqueous solutions has been studied. Equilibrium adsorption studies of these compounds were carried out individually using three different commercially available polymeric resins; Amberlite XAD-4, Amberlite XAD-7, and INDION 1014 MN-2 (IMN-2) having a different surface area and polarity to compare their equilibrium loading capacities. As IMN-2 gave the highest capacity, it was used for further investigation involving column breakthrough studies. A combined approach of solubility and steric hindrance is used to compare the adsorption capacity of isomers. The effect of presence of salts (NaCl and $Na_2SO_4$) on the adsorption capacity of 2,3-DCP and 2,4-DCP (only on IMN-2) was also studied. A Langmuir adsorption isotherm was found to correlate the equilibrium data. Column studies were also carried out to investigate the breakthrough behavior at a flow rate of 0.16 bed volume/min. LUB values were calculated to find out the column efficiency. 15-30 bed volumes of methanol accomplished the regeneration of the loaded bed.

**Keywords:** Adsorption, chlorophenols, equilibrium, Freundlich isotherm, Langmuir isotherm, LUB

## INTRODUCTION

Chlorinated phenols are industrially important as intermediates in chemical synthesis and for their antimicrobial properties. These chlorophenols are

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versatile intermediates in chemical synthesis because both the hydroxyl group and the aromatic ring can react by electrophilic as well as nucleophilic substitutions. Some chlorophenols are produced in chlorination of pulp during the bleaching operation in paper industries (1). These compounds also represent a particular class of toxic chemicals that are used in herbicides, fungicides, insecticides, and algaecides (Table 1). Although these chlorophenols have low solubility in water, they are frequent pollutants in effluents of industries either producing or using them. The presence of chlorophenols affects not only aquatic life but also plants and humans (2). Thus, the presence of these toxic chlorinated phenolic compounds in effluent discharged is of increasing concern, due to the mounting evidence of adverse ecologic and public health impacts. As a direct consequence, more stringent water regulations have been introduced to limit such contamination of wastewater. Degradation processes for many chlorophenols are available (3–4), but they have limitations, such as they are applicable for very low concentrations of these pollutants and are also very slow. The results (3–4) are not directly applicable for actual onsite situations where higher concentrations of these pollutants are involved.

An alternative non-destructive approach for the removal of organic compounds from aqueous medium is adsorption. Adsorption has emerged as a separation and recovery method, which is independent of the concentration of the solute to be adsorbed. It was successfully used to adsorb chlorophenols on activated carbon (5–6) and on organoclays (7). Recent use of synthetic adsorbents (8–9) for the removal of other organic impurities shows successful regeneration of adsorbents facilitating their reuse. These studies show that adsorption has also the ability to increase very low feed solute concentration; to concentrations ranging several 100 to 1000 folds (9), thereby reducing the treatment load on further processing. Availability of synthetic adsorbents with a wide range of properties, ease of operation, and better economic aspects has made adsorption a widely accepted process. With this background the present study was concerned with the removal of chlorophenols using synthetic resins.

This investigation dealt with adsorption of 2,3-dichlorophenol (2,3-DCP), 2,4-dichlorophenol (2,4-DCP), 2,5-dichlorophenol (2,5-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), and 2,4-dichlorophenoxyacidic acid (2,4-D). These compounds have separated from their aqueous solutions on commercially available polymeric adsorption resins of different properties. The effect of the presence of salts (NaCl and $Na_2SO_4$) on adsorption of 2,3-DCP and 2,4-DCP was also investigated. The main objective of this work was to check for the feasibility of removal and recovery of chlorinated phenols from aqueous streams by adsorption on synthetic resins. In designing of the adsorption system, the data needed for scale up of the adsorber are

(i) equilibrium adsorption isotherms and
(ii) dynamic column breakthrough data under the similar conditions.

## Theory

Adsorption is the accumulation of atoms or molecules (adsorbate) on a solid surface (adsorbent) from the carrier medium. This is a spontaneous process, accompanied by a decrease in the free energy of the system. The adsorption process is always exothermic regardless of the type of forces involved (10). Desorption is defined as the reverse of adsorption, wherein the adsorbed molecules are removed from the surface of the adsorbent. Generally adsorption-desorption can be written as:

$$\text{Adsorbent} + \text{Adsorbate} \underset{\text{Desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \text{Solute adsorbed on adsorbent}$$

## Adsorption Equilibria

The equilibrium adsorption capacity is used for comparison between adsorbents. An adsorption isotherm is a relation between the amount of solute adsorbed by an adsorbent and the corresponding equilibrium fluid concentration at constant temperature. There are many adsorption isotherms developed out of which two widely used isotherms for representing the equilibrium data are the Freundlich and the Langmuir isotherm (11).

The loading of an adsorbent can be calculated by a simple mass balance of solute, which is given as

$$\mathrm{q} = \frac{(\mathrm{C_o} - \mathrm{C}) \cdot \mathrm{V}}{\mathrm{m}} \tag{1}$$

Freundlich and Langmuir isotherms are given by equations (2) and (3), respectively.

$$\mathrm{q} = \mathrm{k}\,\mathrm{C}_{\mathrm{eq}}^{1/n} \tag{2}$$

$$\frac{\mathrm{q}}{\mathrm{q_{max}}} = \frac{\mathrm{KC_{eq}}}{1 + \mathrm{KC_{eq}}} \tag{3}$$

In equation (2), k and n are constants depending on the nature of solid and solute and on the temperature with k being related to the maximum binding capacity and n related to the affinity or binding strength (11). An adsorbent yielding high values of k and n is considered to be ideal. In equation (3) K is the equilibrium adsorption constant, which also depends on the nature of the solid and the solute.

The extent of interaction between the solute and the bulk adsorbent phase can be obtained by calculating $\mathrm{F_p}$, the fraction of pore volume filled as a function of fluid phase concentration of the solute using equation (4) as per Gusler et al. (12),

$$\mathrm{F_P} = \frac{[\mathrm{C_0V} - \mathrm{C(V} - \mathrm{mV_P} \times 10^{-3})] \times 10^{-3}}{\mathrm{V_P}\rho \mathrm{m}} \tag{4}$$

The fraction of pore volume filled gives the indication of absorption of solute into the polymer matrix. Here $F_p < 1$, indicates that the solute is present as free dissolved solute in the carrier solvent (water in this case). It also indicates that the solute is not in the *absorbed* state but is only *adsorbed* on the polymer matrix surface. Alternatively, there is no penetration of the solute into the polymer matrix. However, when $F_p$ obtained from equation (4), is greater than 1, the only explanation is that besides adsorption, the *absorption* of the solute by the polymer matrix is also contributing to the removal of the solute from the fluid phase (Gussler et al., 12).

## Effect of the Presence of Salt

In the case of adsorption of organic solutes from aqueous solutions in the presence of salt on synthetic hydrophobic polymeric resins, the adsorption capacity of the resin increases due to the salting-out effect. The solubility of neutral organic compounds generally shows an inverse dependence on the ionic strength (13). As reported by Deosarkar and Pangarkar (8) water in the presence of dissolved ions is more ordered and compressible and the cavity volume available to accommodate neutral organic solutes is reduced. Hence the organic solute can easily accumulate on the resin surface, thereby increasing the overall loading. The increased capacity is in proportion to the ionic strength of the solution (14). In the study of Rexwinkel et al. (14) with solutes having a high vapor pressure at room temperature, they were distributed among two phases i.e. the liquid in bulk phase and the gas inside the pores of the adsorbent. In the present case the solutes have high boiling points. Further the pores are filled with water, hence the distribution of the solute is between two phases i.e. the solid phase of the adsorbent and the bulk liquid phase. The following equation can correlate this relation (8):

$$m_s^{salt} = \frac{q}{C_e} = m_s^0 10^{sI} \tag{5}$$

$m_s^0$ for particular solutes can be calculated from their individual isotherm data at $s = 0$ and $m_s^{salt}$ from the data in presence of salt.

## Length of Unused Bed (LUB)

Operations in fixed bed columns have been widely described elsewhere (Treybal, 15, Collins, 16, and Lukchis (17)). The operation in fixed bed columns leads to the breakthrough curves (obtained by plotting time of operation (t) against concentration of the outgoing fluid ($C/C_0$ or C)). For design and scale-up purpose, the principle data needed is the length of unused bed (LUB) (11, 15). The term length of used bed ($L_b$) represents the part of the column in which the adsorbent is completely saturated by the adsorbate. While the length of the unused bed represents the length of the mass-transfer zone, which is the part of the column where the adsorbent is not completely used and is still available for adsorption. The scale-up principle is based on the fact that the length of the unused bed or unused adsorbents is independent of the total bed length (16). LUB is a good parameter for performance evaluation in a fixed bed.

LUB can be calculated by the approach given by Collins (16) as

$$\mathrm{LUB} = \left(1 - \frac{t_b}{t^*}\right) \times L_b \tag{6}$$

where $t_b$ is breakpoint time and $t^*$ can be obtained by drawing a vertical line on the breakthrough a time when the adsorbed quantity of a solute equals its unadsorbed quantity in the effluent. Also the LUB does not change with the length of the bed used (16). The value of $t^*$ can also be approximately calculated as given below (11, 16):

$$t^* = \frac{1}{2}(t_e - t_b) \tag{7}$$

Here $t^*$ can also be calculated as time at which $C/C_0$ equals 0.5 on the breakthrough curve (18).

## EXPERIMENTAL

### Materials

For single solute adsorption studies, solutions were prepared using pure samples of the solutes. Distilled water was used for the preparation of aqueous solutions. Rohm and Haas Co., USA supplied the polymeric adsorbents, Amberlite XAD-4, and Amberlite XAD-7, while Ion Exchange India Ltd supplied INDION 1014 MN-2 (IMN2). The physical properties of the adsorbents are reported elsewhere (8). Chlorophenols solutes obtained from M/s. Aarti Chemical Ltd, India were of high purity (>99.5%). A.R. grade sodium chloride (Merck India Ltd, India) and sodium sulphate (s. d. Fine Chem. Ltd., India) were used to study the effect of the presence of salt on adsorption.

### Adsorbent Preparation

Conditioning of the adsorbent was done by washing it with methanol and then drying in water bath at 80°C at 100 mm Hg absolute pressure. This was done to remove any impurities present in the adsorbent. These vacuum dried adsorbents were stored in sealed flasks to prevent ingress of moisture.

## Equilibrium Adsorption Studies

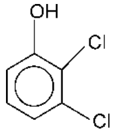
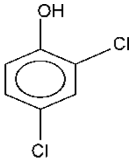
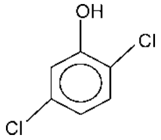
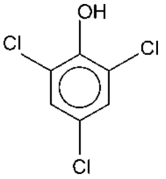
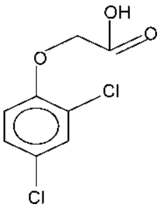
For individual equilibrium adsorption studied, solutions of solute concentration 1000 ppm each for 2,3-DCP, 2,4-DCP, 2,5-DCP, 2,4,6-TCP, and 2,4-D were prepared using distilled water. These values of initial concentration for equilibrium studies are much less than their actual solubility (Table 1). The purpose of studying is to decide the adsorbent giving maximum loading per unit weight of the adsorbent. Similarly for 2,4,6-TCP and 2,4-D initial concentration taken were 600 and 800 ppm respectively. Fixed amounts of these aqueous solutions ($50 \times 10^{-3}$ liters) were taken in conical stoppered flasks and different weights of the adsorbents were added. These flasks were sealed and kept for mechanical shaking at temperature $29 \pm 2°C$, rotating at 180 rpm, for more than 24 hrs assuring that equilibrium was attained. This was checked by analyzing aliquots, which showed that there was no change in the liquid phase concentrations beyond 16 hours. The aqueous solutions were analyzed for their equilibrium concentrations by UV spectrophotometer. In a similar manner, the effect of the presence of salts ($Na_2SO_4$ and NaCl) on adsorption of 2,3-DCP and 2,4-DCP only on IMN-2 was also studied at salt concentrations of 2, 5 and 10 wt.%. Approximately 40% of total experiments were randomly rechecked. The reproducibility was found to be within $\pm 5\%$.

## Dynamic Column Breakthrough Studies

A glass column of 1200 mm height and 15.6 mm I. D. was used for the column exhaustion studied. The column was packed upto 400 mm by preparing slurry of the adsorbent with water. To avoid channeling, this slurry was poured in the column, which was filled with distilled water. The concentration of the solute in solution (in distilled water) used for breakthrough study was in the range of 70-90% of its solubility. This solution was then passed downflow through the column. The continuous flow rate for the breakthrough runs was adjusted to 0.16 bed volumes per minute (12 ml/min) using a peristaltic pump. Outlets aliquots were collected periodically and analyzed till the time the outlet aliquot concentration was the same as the inlet feed solution concentration. For desorption/regeneration, the cheaper and easily available solvent methanol was used as the eluant. The flow rate of methanol was maintained at 0.08 bed volume/minute (6 ml/min). Similarly here also the outlet aliquots were collected periodically and analyzed for the solute content. The disorption was done till the time pure methanol came out of the column. The analysis of all the samples was done using Chemito 2100 UV Spectrophotometer at corresponding wavelength giving maximum absorbance.

The loading capacity, q (mmol/g) was determined from a solute mass balance equation (1), knowing the initial and final bulk concentrations. The equilibrium adsorption data for adsorption were fitted to the Freundlich and

***Table 1.*** Properties of compounds used

| Compound | Molecular weight,[a] g/mol | Structure | Melting point,[a] (°C) | Boiling point,[a] (°C) | Solubility, ppm[b] | LD 50 oral mouse, mg/kg[c] |
|---|---|---|---|---|---|---|
| 2,3-DCP | 163 |  | 57 | 206 | 4206.5 | 2376 |
| 2,4-DCP | 163 |  | 45 | 210 | 4681.2 | 580 |
| 2,5-DCP | 163 |  | 59 | 225 | 2665.2 | 946 |
| 2,4,6-TCP | 197.45 |  | 69.5 | 246 | 822.8 | 820 |
| 2,4-D | 221.04 |  | 141 | — | 744.5 | 375 |

| Compound | Threshold concentration[d] | Uses[d] | Toxic effect[d] |
|---|---|---|---|
| 2,3-DCP | 0.04 μg/l | Intermediate | Skin irritant |
| 2,4-DCP | 0.02 mg/l | Organic synthesis | Skin irritant, toxic to aquatic organisms |
| 2,5-DCP | — | Sex pheromone of lone star tick | Skin irritant |

(*continued*)

*Table 1.* Continued

| Compound | Threshold concentration$^d$ | Uses$^d$ | Toxic effect$^d$ |
|---|---|---|---|
| 2,4,6-TCP | 0.021 mg/l | Selective weed killer, in manufacture of wood and glue preservative | Eye and skin irritant, Hematological effect |
| 2,4-D | — | Weedicide, fungicide | Skin and eye irritant, causes dermatitis, liver and kidney damage |

[a] See Ref. [21].
[b] Measured.
[c] See Ref. [22].
[d] Ref. [23].

Langmuir isotherms, equations (2) and (3). Different adsorption isotherms have been used to characterize physicalsolute adsorption (Treybal, 15). The two main types widely used are (1) Freundlich and (2) Langmuir isotherms. The second has a relatively sound theoretical basis whereas the former is mainly empirical but is easier to use. In the following the data fits are given for the above types.

## RESULTS AND DISCUSSION

The purpose of the equilibrium adsorption study is to find the best resin, which gives the highest adsorbing capacity. For dichlorophenols, the adsorption equilibrium data could be satisfactorily fitted to Freundlich and Langmuir isotherms. The same behavior was also reported for 2,4-DCP on coconut coir (18) and also by Gustafson et al. (19) on styrene-divinylbenzene copolymer.

### Freundlich Isotherms

For Freundlich isotherm, the results were plotted as adsorbed phase concentration (mmol/g) against equilibrium concentration in solution (mmol/l). For all equilibrium studies the data were correlated using Freundlich equation, equation (2). Representative results (for 2,3-DCP) are shown in Fig. 1. For the other solutes the Freundlich constants given in Table 2 allow a comparison of adsorbents. All adsorbents show favorable isotherms. It was also observed that the loading was inversely proportional to the

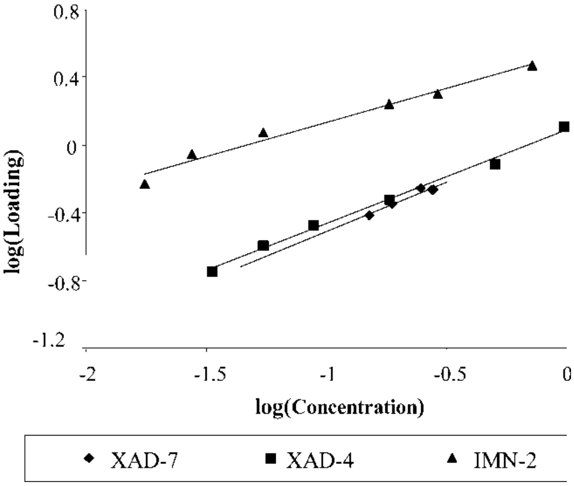


*Figure 1.* Equilibrium adsorption of 2,3-DCP (Freundlich curves). Sample volume = 50 ml, initial 2,3-DCP concentration = 1000 ppm (6.135 mmol/l), time of equilibration = 24 hrs, temperature = 29 ± 2°C, speed of shaker = 180 rpm.

aqueous solubility of the compound 2,4,6-TCP, which has less solubility and is adsorbed more than other dichlorophenols (Table 4).

The order of the adsorption capacity is IMN-2 > XAD-4 > XAD-7 (Table 2). From these data it is evident that all, INDION 1014 MN2 (IMN-2) gives highest capacity. The k values for IMN-2 range from 2-5 times of k values obtained for XAD-4 and XAD-7. This can be attributed to its high surface area (1000 $m^2/g$ as against 450, 750 for XAD-7, XAD-4, respectively) and hydrophobicity among the resins considered. Also as per the manufacturer, a certain undisclosed surface treatment is given to INDION 1014 MN-2, which may be responsible for higher values of the adsorption capacity. Chlorophenols are weak acids and hence it is possible that the surface treatment employed for INDION 1014 MN-2, specifically

*Table 2.* Freundlich parameters for single solute equilibrium adsorption studies

| | XAD-7 | | | XAD-4 | | | IMN-2 | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | k[a] | n | $R^2$ | k[a] | n | $R^2$ | k[a] | N | $R^2$ |
| 2,3-DCP | 1.1723 | 1.722 | 0.95 | 1.2728 | 1.7126 | 0.99 | 3.4507 | 2.2286 | 0.98 |
| 2,4-DCP | 1.0108 | 2.3696 | 0.99 | 1.058 | 2.0206 | 0.99 | 2.7712 | 3.033 | 0.92 |
| 2,5-DCP | 1.5619 | 1.645 | 0.99 | 2.035 | 1.0913 | 0.91 | 4.3 | 2.2983 | 0.97 |
| 2,4,6-TCP | 2.3901 | 1.1594 | 0.99 | 8.342 | 0.9106 | 0.88 | 13.509 | 1.427 | 0.94 |
| 2,4-D | 0.6016 | 1.0768 | 0.99 | 1.048 | 1.0697 | 0.99 | 3.4121 | 1.2923 | 0.97 |

[a] Units mmol/g.

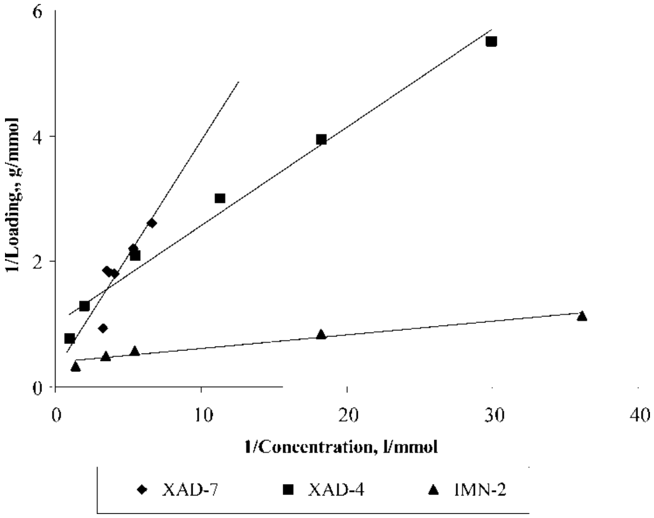


*Figure 2.* Equilibrium adsorption of 2,3-DCP (Langmuir curves). Sample volume = 50 ml, initial 2,3-DCP concentration = 1000 ppm (6.135 mmol/l), time of equilibration = 24 hrs, Temperature = 29 ± 2°C, speed of shaker = 180 rpm.

increases the adsorption of hydrophobic acidic solutes (9). Similar superior results showing high adsorption capacity of IMN-2 for other compounds are also reported by Deosarkar and Pangarkar (8).

The low equilibrium capacity shown by XAD-7 can be attributed to its intermediate polar nature. Though in some cases XAD-7 shows comparable capacity with XAD-4, still IMN-2 shows the best performance. With these results only IMN-2 was considered for further studies.

## Langmuir Isotherms

The equilibrium data were correlated using the Langmuir isotherm, equation (3). It was found that all compounds except 2,4,6-TCP do follow the Langmuir

*Table 3.* Langmuir parameters for single solute equilibrium adsorption studies

| | XAD-7 | | | XAD-4 | | | IMN-2 | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | $q_{max}$[a] | b | $R^2$ | $q_{max}$[a] | b | $R^2$ | $q_{max}$[a] | b | $R^2$ |
| 2,3-DCP | 0.841 | 7.994 | 0.99 | 1.166 | 3.259 | 0.97 | 2.344 | 20.91 | 0.99 |
| 2,4-DCP | 1.064 | 5.051 | 0.99 | 1.347 | 2.828 | 0.98 | 3.389 | 7.007 | 0.97 |
| 2,5-DCP | 0.859 | 9.191 | 0.99 | 3.287 | 0.951 | 0.97 | 5.288 | 7.083 | 0.97 |
| 2,4-D | 1.3885 | 3.885 | 0.99 | 2.061 | 0.6026 | 0.92 | 5.379 | 1.44 | 0.99 |

[a] Units mmol/g.

isotherm. This may be due to repulsion amongst 2,4,6-TCP adsorbed molecules (11). Representative results for 2,3-DCP are shown in Fig. 2 and the Langmuir constants for all solutes are tabulated in Table 3. The low concentrations of chlorophenols used for equilibrium studies allow fitting of the data linearity by the Langmuir adsorption isotherm. IMN-2 has the maximum loading capacity ($q_{max}$) amongst all the resins studied. The value $q_{max}$ for IMN-2 is found to be 2-6 times that of $q_{max}$ value for XAD-7 and XAD-4.

## Adsorption Results of 2,4,6-TCP

A compound that has low solubility in water generally has a higher affinity for non-polar solid surfaces than for water and will therefore have a tendency to concentrate on such surfaces. As observed by Gustafson et al. (19), in homologous series, the degree of adsorption increases via hydrophobic bonding as the molecular weight of the adsorbate increases. In case of chlorophenol, 2,4,6-TCP, which has less solubility, is adsorbed more than other dichlorophenols (Table 3). 2,4,6-TCP was comparatively highly adsorbed on every resin studied. The adsorption capacity observed is: 2,4,6-trichlorophenol > dichlorophenols, which also agrees with the findings of Shirgaonkar et al., (6) who used powdered activated carbon adsorbent Filtrasorb-400 for adsorbing a number of phenol derivatives. XAD-7, XAD-4, and IMN-2 show nearly linear behavior during adsorption of 2,4,6-TCP. Thus, it can be concluded that with an increasing number of the chlorine substituent for homologous series of organic molecules, as the size increases the solubility generally decreases resulting in increase in the extent of adsorption.

## Adsorption Results for 2,4-D

In case of adsorption of 2,4-D, more numbers of functional groups are attached to 2,4-D molecule resulting in increased size. Therefore, higher adsorption is expected than 2,4-DCP. However, 2,4-D shows the lowest adsorption on XAD-7, which is of intermediate polarity (Table 2). This can be explained by the lower surface area of XAD-7 (than other resins studied).

In case of XAD-4, loading of 2,4-D is higher than that of loading on XAD-7 but lower than IMN-2. In this case loading is nearly equal to that of 2,4-DCP. However, on IMN-2, loading is double of that of 2,4-DCP, indicating that the hydrophobic effect dominates over steric hindrance in the case of 2,4-D.

## Effect of Salt

The effect of the presence of salt on the adsorption of 2,3-DCP and 2,4-DCP was studied with concentrations of NaCl and $Na_2SO_4$ at 2, 5 and 10% (w/w).

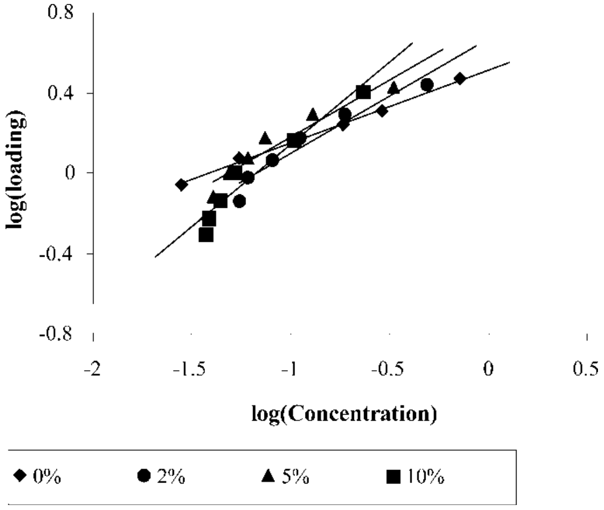


***Figure 3.*** Effect of presence of salt (NaCl) on adsorption of 2,3-DCP on IMN2 (Freundlich curves). Sample volume = 50 ml, initial 2,3-DCP concentration = 1000 ppm (6.135 mmol/l), time of equilibration = 24 hrs, temperature = 29 ± 2°C, speed of shaker = 180 rpm.

This study was carried out only for IMN-2. The results are shown in Fig. 3 for 2,3-DCP. The data for Freundlich parameter k and n are reported in Table 4. It was observed that there is an increase in the equilibrium capacity of the adsorbent in the presence of salt (8–12, 14). It can be seen that at lower concentration of solute (below 0.05 mmol/l), the effect of the presence of salt is not significant, whereas at higher solute concentration, adsorption increases significantly with increase in the amount of salt.

***Table 4.*** Effect of presence salt on adsorption on IMN-2

| | | NaCl | | | $Na_2SO_4$ | | |
|---|---|---|---|---|---|---|---|
| Compound | Salt% | k | n | $R^2$ | k | n | $R^2$ |
| 2,3-DCP | 0 | 3.45 | 2.23 | 0.98 | 3.45 | 2.23 | 0.98 |
| | 2 | 4.62 | 1.76 | 0.94 | 3.60 | 2.62 | 0.98 |
| | 5 | 5.61 | 1.77 | 0.92 | 3.80 | 2.69 | 0.98 |
| | 10 | 9.14 | 1.22 | 0.95 | 8.54 | 2.35 | 0.95 |
| 2,4-DCP | 0 | 2.77 | 3.03 | 0.92 | 2.77 | 3.03 | 0.92 |
| | 2 | 3.41 | 2.87 | 0.97 | 3.21 | 3.09 | 0.99 |
| | 5 | 4.09 | 2.68 | 0.98 | 5.27 | 2.10 | 0.98 |
| | 10 | 5.07 | 2.45 | 0.96 | 7.15 | 1.87 | 0.99 |

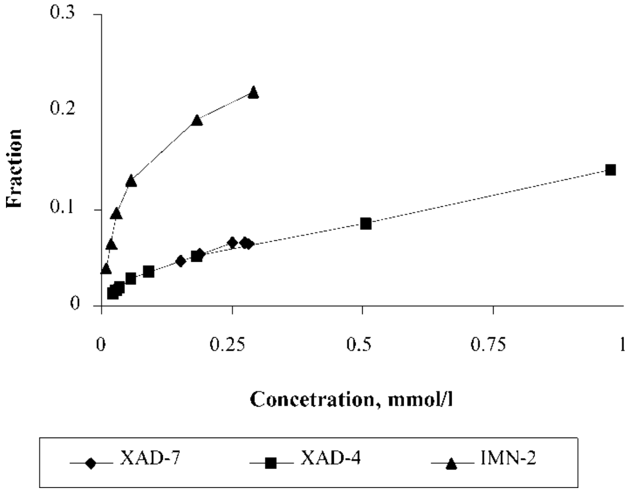


*Figure 4.* Fraction of pore volume filled for 2,3-DCP. Sample volume = 50 ml, initial 2,3-DCP concentration = 1000 ppm (6.135 mmol/l), time of equilibration = 24 hrs, temperature = 29 ± 2 °C, speed of shaker = 180 rpm.

## Fraction of Pore Volume

Single solute data were also represented in terms of the fraction of pore volume filled at equilibrium. These calculations were made using equation (4). Representative results for 2,3-DCP are shown in Fig. 4. It can be observed that the maximum value of the fraction of pore volume filled by the solutes does not exceed 0.5. This fact indicates that there is no matrix penetration by all the solutes and also that the solute are present as surface adsorbed molecules (Table 5).

*Table 5.* Conditions during operation, breakpoint (at 10 ppm) and saturation point loadings

| Compound | Initial Concentration, (ppm) | Weight of the resin, (g) | Breakpoint Loading, (mg/g resin) | Saturation loading, (mg/g resin) |
|---|---|---|---|---|
| 2,3-DCP | 3500 | 79 | 10.97 | 230.32 |
| 2,4-DCP | 4000 | 79 | 9.98 | 286.41 |
| 2,5-DCP | 2400 | 79 | 9.56 | 216.91 |
| 2,4,6-TCP | 500 | 79 | 4.345 | 168.2 |
| 2,4-D | 600 | 79 | 3.145 | 207.98 |

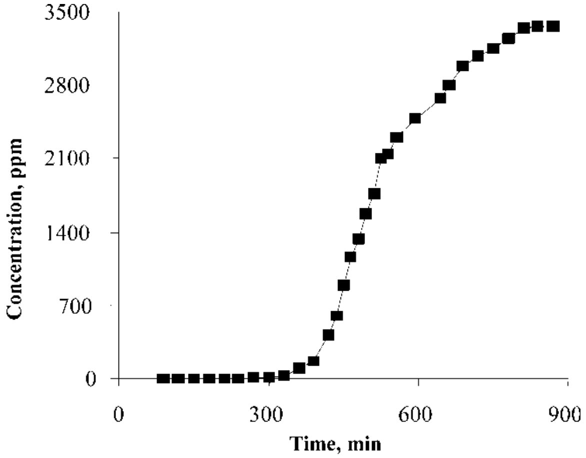


*Figure 5.* Breakthrough curves for 2,3-DCP. Feed concentration = 3500 ppm, adsorbent bed height = 400 mm, diameter of column = 15.6 mm, flow rate of feed = 12 ml/min.

## Column Studies

The design of fixed-bed adsorbers and for scale up requires breakthrough data from laboratory performed tests in similar conditions (18). The scale-up principle is based on the fact that the length of unused bed or unused adsorbents is independent of the total bed length (15, 16). Representative results (for 2,3-DCP) are shown in Fig. 5. The plots show smooth S-shaped breakthrough curves for all of the investigated solutes. The capacities at breakpoint and saturation are given in Table 6. Calculations for the length of unused bed were made for compounds investigated. These results are given in Table 6. These values depend on various factors such as diffusivities, adsorbent-adsorbate interactions, and concentration of adsorbate solute used and flow rates (11, 17). Thus from the breakthrough curves for the solutes it can be observed that all solutes can be adequately removed.

*Table 6.* Length of unused bed (LUB)

| Compound | $t_b$ (min) | t* (min) | $L_0$ (m) | LUB (m) |
|---|---|---|---|---|
| 2,3-DCP | 243 | 505 | 0.4 | 0.2078 |
| 2,4-DCP | 345 | 499 | 0.4 | 0.1234 |
| 2,5-DCP | 490 | 707 | 0.4 | 0.1229 |
| 2,4,6-TCP | 1554 | 1976 | 0.4 | 0.0854 |
| 2,4-D | 1574 | 2653 | 0.4 | 0.1627 |

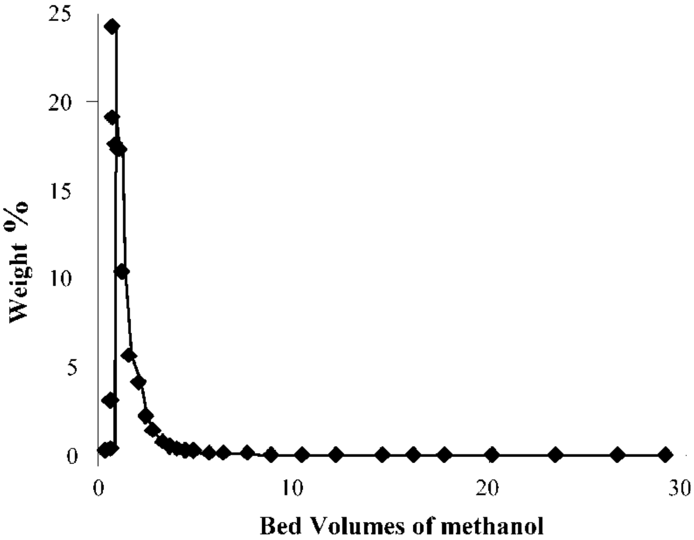


*Figure 6.* Regeneration curve for 2,3-DCP (by methanol). Eluting fluid = Methanol, adsorbent bed height = 400 mm, diameter of column = 15.6 mm, flow rate of eluting fluid = 6 ml/min.

## Regeneration

The eluting solvent methanol was found to have good solubility for the adsorbents studied. A representative regeneration plot for 2,3-DCP is shown in Fig. 6. Complete regeneration was found to be possible with 15–30 bed volumes of methanol. This volume will reduce further, if in actual practice the column is operated upto breakthrough concentration.

The solute concentration increases many fold, when it gets removed/desorbed from the adsorbent surface. The difference in boiling points of solute and methanol can be effectively utilized to separate the solute by distillation.

## Comparison with Literature Results

The toxicity of chlorinated phenols has attracted a number of studies for their removal. Hence, it is not surprising to find a large number of papers in the literatures (3–7, 14–16). Most of the literature is however, focused on degradation of such industrially important compounds rather than their recovery as described in the present study.

The results of this work can be compared with those of Colella et al. (5), who studied equilibrium isotherms of a number of chlorophenols from aqueous medium on wood-based and lignite-based carbons. These investigators obtained a comparatively higher capacity of adsorption. However, the recovery of the adsorbates and regeneration of adsorbents was not studied.

Namasivayam and Kavitha (20) studied the adsorption of 2,4-DCP and reported an equilibrium adsorption capacity of 19 mg/g for coconut coir, which is much less than the present values of 166.78, 174.57, and 457.2 mg $g^{-1}$ for XAD-7, XAD-4, and IMN-2, respectively. Though coir is an inexpensive option, its application in processes may need bulky equipment. Further, the reusability of this material in adsorption/regeneration cycles is questionable. On the other hand the polymeric adsorbents used in the present work are hard cross-linked beads, which allow repeated use.

## CONCLUSION

The study of adsorption of chlorophenols, on commercially available synthetic polymeric adsorbents, shows favorable isotherms. The adsorption capacity shows that the order is IMN-2 > XAD-4 > XAD-7 which is also in increasing order of the surface area. The equilibrium data were correlated using both the Freundlich and Langmuir isotherms. The loading was generally found to be inversely proportional to the solubility in water. Representation of equilibrium adsorption data in terms of a fraction of the pore volume filled at equilibrium and showed that the solutes were not able to swell the polymer matrix. Presence of salt (NaCl and $Na_2SO_4$) increases the equilibrium adsorbent loading confirming a salting out effect.

The breakthrough studies show promising results of removal of studied chlorophenols by adsorbing them on beds of IMN-2 resin and subsequently eluting them by methanol. Thus, it is possible to remove impurities adequately to meet the legislative impositions, simultaneously recovering them for reuse compensating for the treatment costs, thus converting the liabilities into assets.

## NOTATIONS

| | |
|---|---|
| $C_{eq}$ | final equilibrium concentration of the solute, (mmol/l) |
| $C_o$ | initial solute concentrations, (mmol/l) |
| C | solute concentrations, (mmol/l) |
| $F_P$ | fraction of pore volume that is filled at equilibrium, (−) |
| I | ionic strength of solution, (mol/l) |
| k | constant in equation (2) |
| K | equilibrium adsorption constant, (−) |
| LUB | length of unused bed, (m) |
| $L_b$ | length of used bed, (m) |
| m | mass of the adsorbent, (g) |
| $m_s^0$ | distribution coefficient for salt free water, (at s = 0), (−) |
| $m_s^{salt}$ | distribution coefficient in presence of salt, (−) |
| n | constant in equation (2) |
| q | loading capacity, (mmol/g adsorbent) |
| $q_{max}$ | maximum equilibrium loading, (mmol/g adsorbent) |

| | |
|---|---|
| $R^2$ | coefficient of correlation, $(-)$ |
| s | salting out coefficient, $(-)$ |
| $t_b$ | breakpoint time, (min) |
| $t_e$ | bed exhaustion time, (min) |
| $t^*$ | stoichiometric breakthrough time, (min) |
| V | volume of the solution, (l) |
| $V_P$ | specific pore volume of the adsorbent, $(cm^3/g)$ |

## Greek Letters

| | |
|---|---|
| $\rho$ | density of the solute, $(g/cm^3)$ |

## REFERENCES

1. Komesvarakul, N., Scamehorn, J., and Gecol, H. (2003) Purification of phenolic-laden wastewater from the pulp paper industry by using colloid-enhanced ultrafiltration. *Sep. Sci. Tech.*, 38: 2465–2501.
2. Muller, F., Caillard, L., and Chlorophenols (1986) *Ullmann's Encyclopedia of Industrial Chemistry*; Gerhartz, W. (ed.); VCH Verlagsgesellschaft mbH: Weinheim, Germany; Vol. A-7, 1–8.
3. Pritchard, P.H., O'neill, E.O., Spain, C.M., and Ahearn, D.G. (1987) Physical biological parameters that determine the fate of p-chlorophenol in laboratory test systems. *App. Env. Micrb.*, 53: 1833–1838.
4. Mazur, C.S., Jones, W.J., and Tebes-Stevens, C. (2003) $H_2$ consumption during the microbial reductive dehalogenation of chlorinated phenols tetrachloroethene. *Biodegrd.*, 14: 285–295.
5. Colella, L.S., Armenante, P.M., Kafkewitz, D., Allen, S.J., and Balasundaram, V. (1998) Adsorption isotherms for chlorinated phenols on activated carbons. *J. Chem. Eng. Data*, 43: 573–579.
6. Shirgaonkar, I.Z., Joglekar, H.S., Mundale, V.D., and Joshi, J.B. (1992) Adsorption equilibrium data for substituted phenols on activated carbon. *J. Chem. Eng. Data*, 37: 175–179.
7. Kim, J.H., Shin, W.S., Kim, Y.H., Choi, S.J.C., Jeon, Y.W., and Song, D.I. (2003) Sequential sorption desorption of chlorinated phenols in organoclays. *Water Sci. Tech.*, 47: 59–64.
8. Deosarkar, S.P. and Pangarkar, V.G. (2004) Adsorptive separation recovery of organics from PHBA and SA plant effluents. *Sep. Pur. Tech.*, 38: 241–254.
9. Khachane, P.K., Heesink, A.B.M., Versteeg, G.F., and Pangarkar, V.G. (2003) Adsorptive separation recovery of organic compounds from purified terephthalic acid plant effluent. *Sep. Sci. Tech.*, 38: 93–111.
10. Schweitzer, P.A. (1988) *Handbook of Separation Techniques for Chemical Engineers*, 2nd Ed.; Mc Graw-Hill Book Co: New York.
11. Ruthven, D.M. (1984) *Principles of Adsorption and Adsorption Processes*, 3rd Ed.; Wiley-Interscience Publishing: New York.
12. Gusler, G.M., Browne, T.E., and Cohen, Y. (1993) Sorption of organics from aqueous solution onto polymeric resins. *Ind. Eng. Chem. Res.*, 32: 2727–2735.
13. Turner, A. and Rawling, M.C. (2001) Influence of salting out on the sorption of neutral organic compounds in estuaries. *Wat. Res.*, 35: 4379–4389.

14. Rexwinkel, G., Heesink, B.B.M., and van Swaaij, W.P.M. (1999) Adsorption of halogenated hydrocarbons from aqueous solutions by wetted hydrophobic and hydrophilic sorbrnts: equilibria. *J. Chem. Eng. Data*, 44: 1139–1145.
15. Treybal, R.E. (1980) *Mass Transfer Operations*, 3rd Ed.; Mc Graw-Hill Book Co: New York.
16. Collins, J.J. (1967) The LUB/equilibrium section concept for fixed bed adsorption. *Chem. Eng. Prog. Symp. Ser.*, 63: 31–35.
17. Lukchis, G.M. (1973) Adsorption systems Part I: Design by mass transfer concept. *Chem. Eng.*, 80: 111–116.
18. McCabe, W.L., Smith, J.C., and Harriot, P. (2001) *Unit Operations of Chemical Engineering*, 6th Ed.; McGraw-Hill: Singapore, 821–834.
19. Gustafson, R.H., Albright, R.L., Heisler, J., Lirio, J.A., and Reid, O.T. (1968) Adsorption of organic species by high surface area styrene-divinylbenzene copolymers. *I. & E. C. Prod. Res. Dev.*, 7: 107–115.
20. Namasivayam, C. and Kavitha, D. (2004) Adsorptive removal of 2,4-dichlorophenol from aqueous solution by low-cost carbon from an agricultural solid waste: coconut coir pith. *Sep. Sci. Technol.*, 39: 1407–1425.
21. Fluid Process Chemicals (2000) *Dictionary of organic compounds*, sixth ed.; Rohm and Haas, Inc, Vol. III.
22. *Merck Chemical Index*. India, (2003).
23. Verschuren, K. (1996) *Handbook of Environmental Data on Organic Chemistry*, 3rd Ed.; van Nost Reinhold: New York.