Chapter-IV
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SEPARATION AND REMOVAL OF PHENOLS USING IRON OXIDE COATED SAND

Key Words
Iron Oxide Coated Sand
Phenols
Adsorption
Separation
Removal

The phenolic compounds in water environment can arise from natural substance degradation, industrial activities and agriculture practices. Phenolic compounds, especially chlorinated may be life threatening to humans even at low concentrations\(^1,2\). The chlorination in drinking water disinfection treatment may form chlorophenols when phenolic compounds are already present in raw water. Their presence gives nasty smell and taste even at few ppb concentration\(^3\). The Environmental Protection Agency (US - EPA) includes in Federal Register list of eleven substituted phenols retained hazardous for human health and assigns them a maximum admissible concentration range of 60—400 µg/l in relation with their toxicity degree\(^4\).

Treatment of wastewater containing phenol by adsorption is an emerging field of research. Activated carbons\(^5,6\), anion exchange resins\(^7,8\), iron (III) diethanol amine\(^9\), zinc silicate\(^10\), stannic
tungstate\textsuperscript{11}, aluminium magnesium metasilicate\textsuperscript{12}, zinc silicate in Fe (III) form\textsuperscript{13}, iron (III) hydroxide impregnated saw dust\textsuperscript{14} and iron (III) hydroxide loaded marble\textsuperscript{15} have been reported for the separation and removal of phenolic compounds.

The ability of metal oxide in general and iron oxide in particular to adsorb both inorganic ions\textsuperscript{16} and water born humic type compounds\textsuperscript{17, 24} is well known. Iron oxide coated sand has been reported for the adsorption of metal ions\textsuperscript{25} and natural organic matter\textsuperscript{26}.

The present study reports a rapid and effective method for phenol adsorption by use of iron oxide coated sand. This method of phenol removal is advantageous with respect to both solid/liquid separation and cost.

\textbf{MATERIALS AND METHODS}

\textbf{Reagents}

Iron (III) nitrate, iron (III) chloride and sodium hydroxide (BDH, India) were used. All other reagents were of analytical grade.

\textbf{Instrumentation}

An electric rotary shaking machine IEC-56 and Bausch and Lomb Spectronic 20 were used for shaking and spectrophotometric measurements, respectively.

\textbf{Preparation of Iron Oxide Coated Sand\textsuperscript{25}}

In the first step, 80 ml of 2.5 mol dm\textsuperscript{-3} FeCl\textsubscript{3} solution was
poured over 200 ml bulk sand (Kanpur Ganga sand, 100—120 mesh), and the mixture was heated at 550 ± 1°C and stirred for about 3 h, after which the sand was cooled to room temperature in air. At this stage, the coating was dark coloured almost black. Upon rinsing with distilled water, the black coloured fraction washed away, but a dark red coating remained on the sand.

The FeCl₃ solution used to regenerate the coating is strongly acidic, due to hydrolysis of the Fe⁺³ ions by reactions of the type

Fe⁺³ + n H₂O → Fe(OH)ₙ³⁻ + nH⁺

During the heating step, both water and HCl evaporate from the solution, neutralizing and concentrating the residual solution and causing iron oxide to precipitate. Most of this precipitate coats the sand grains, although some oxide precipitates in the space between the grains. The coating has been characterised to be iron oxide mineral hematite (α—Fe₂O₃)³⁵. This material is referred to below as HTM (high temperature media).

In next step, 40 ml of HTM was placed in a heat resistant dish in a layer 1-3 cm deep, and was mixed with a solution of 80 ml of 2.5 mol dm⁻³ Fe(NO₃)₃ and 0.6 ml of 10 mol dm⁻³ NaOH. The mixture was covered loosely, heated at 110 ± 1°C and stirred until it appeared to be dry (10-12 h). HNO₃ is volatilized during heating of Fe(NO₃)₃ solution and the precipitate formed clearly different from that at 550 ± 1°C. After cooling at room temperature, iron oxide coated sand was sieved through 150 mesh sieve to remove free iron oxide particles.
Determination of Iron Loaded on IOCS

IOCS (1g) was treated with hot 20 ml hydrochloric acid (12 mol dm$^{-3}$) and filtered. The iron in the filtrate was determined spectrophotometrically with 1,10-phenanthroline$^{27}$.

Metal Leakage

Iron leakage into the eluting solution was determined by shaking 0.5 g IOCS with a solution for 4 h at room temperature. Iron eluted into the equilibrated solution was determined spectrophotometrically$^{27}$.

Phenol Adsorption Procedure

Phenolic compounds were dissolved in double distilled water or ethanol, depending upon their solubility. The Follin's reagent procedure$^{28}$ was used for spectrophotometric determination of phenols except nitrophenol (directly estimated at 360 nm). To the sample phenol, 5 ml reagent and 15 ml of 20 percent solution of sodium carbonate were added, then diluted upto 50 ml with water and warmed to 30-35°C for 20 min. The absorbance was measured at 520 nm against the reagent black.

Adsorption experiments were performed by shaking 50 ml adsorbate (0.1 g/l) solution and a definite amount of adsorbent (0.1 g) in a stoppered pyrex glass flask for 6 h at 25°C. The biological degradation of phenols was also taken into account by running blank determinations.
Kinetic Measurement

The kinetics of phenol adsorption on IOCS was studied using batch technique. A number of stoppered flasks containing a given volume (20 ml each) of solution of phenols (0.1 g/l) and 0.2 g IOCS were mechanically agitated at predetermined time intervals, separated from the adsorbent material using Whatman no.4 filter paper and analyzed to determine the uptake of phenol.

Breakthrough Capacity

The breakthrough behaviour of different phenols was studied by passing phenolic solutions (1mg/10 ml) through a glass column (1.2 cm i.d.) loaded with 2 g IOCS. The flow rate was maintained at ~ 0.5 ml/min.

Batch Equilibrium

The relative affinities of the adsorbent for 17 phenolic compound were studied by batch equilibrium on IOCS beads in aqueous media of different systems. A decigram of IOCS was equilibrated with 50 ml phenol solutions (100 mg/l) at room temperature (30 ± 2°C) for 6 h in 100 ml pyrex conical flask. Then IOCS was allowed to settle for 1 h, a 5 ml aliquot of the supernatant liquid was carefully withdrawn with a pipette. The amount of phenol was determined spectrophotometrically. The distribution coefficients (Kd values) were calculated from the following equation

\[ Kd(\text{ml/g}) = \frac{\text{Amount of phenol in adsorbent phase per gram}}{\text{Amount of phenol in solution phase per ml}} \]
Column Separations

For quantitative separations of phenols, IOCS (2g) was taken into a column of i.d. 0.4 cm. The column was washed with 20 ml of distilled water and the mixture of phenols was introduced into the column. The phenols were eluted separately using eluents selected on the basis of observed Kd values (Table 4.3).

Filtration Experiment

A small filtration unit was fabricated by connecting a polyvinyl chloride (PVC) tube (40 cm long, 5 cm i.d.) to a Buchner funnel that had been cut to one cm length. A glass fibre filter with nominal particle retention of 2.5 µm was placed above the porous plate of the Buchner funnel (Fig.4.5). The column was filled with 500 g (360 ml) of IOCS up to a height of 19 cm. The IOCS column was washed with about 1 l distilled water. Then the column was connected to a Mariotte bottle, which maintained a constant hydraulic head of 30 cm. Flow rate of the effluent was maintained 1 l/h (empty bed contact time 22 min). The performance of this column was evaluated for removing pyrogallol from ground water (pH 7.2-7.5, hardness 300-320 mg CaCO₃/l, and conductivity 790 - 850 µmhos/cm) spiked to 100 mg/l.

Cyclic Capacity

The desorption of adsorbate and regeneration of column is an important process in wastewater treatment. To assess the cyclic utility of the adsorbent, a glass column 50 x 1.2 cm was
loaded with 2 g IOCS. The phenol solution (100 mg/l, pH~6) was percolated downward at a flow rate of 0.5 ml/min till breakthrough point appeared. The adsorbed phenol was then desorbed by 1 mol dm$^{-3}$ NaOH. The column was washed with distilled water until the washings were neutral and then treated with acidic water (pH~3) and new cycle began.
RESULTS

Adsorption capacity values of nine phenols on iron oxide coated sand were determined. The results are presented in Table 4.1.

Chemical stability of IOCS was determined in water, ethanol, 1 mol dm$^{-3}$ NaOH and 0.1 mol dm$^{-3}$ HCl. The chemical stability data are given in Table 4.2. The rate of adsorption of pyrogallol on IOCS is shown in Fig. 4.1.

The results of experiments carried out to assess the effect of pH on the equilibrium adsorption capacity of IOCS for phenols are presented in Fig. 4.2.

The breakthrough curves of m-cresol, pyrocatechol and pyrogallol on column operation are given in Fig. 4.3.

In order to investigate the selectivity of IOCS, the distribution coefficients (Kd values) of 17 phenols were measured in five different systems. The results are summarized in Table 4.3.

The utility of IOCS was demonstrated by achieving the separations of phenols of great analytical significance. Those achieved experimentally are given in Table 4.4 along with % error. The order of elution and eluents for phloroglucinol-pyrogallol and α-naphthol-β-naphthol are presented in Fig. 4.4a and b.
### Adsorption of Phenols on Iron Oxide Coated Sand

<table>
<thead>
<tr>
<th>No.</th>
<th>Phenol</th>
<th>Adsorption capacity x $10^2$ (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phenol</td>
<td>4.67</td>
</tr>
<tr>
<td>2</td>
<td>Pyrocatechol</td>
<td>7.36</td>
</tr>
<tr>
<td>3</td>
<td>Resorcinol</td>
<td>3.45</td>
</tr>
<tr>
<td>4</td>
<td>o-Aminophenol</td>
<td>3.20</td>
</tr>
<tr>
<td>5</td>
<td>o-Chlorophenol</td>
<td>2.33</td>
</tr>
<tr>
<td>6</td>
<td>2,4,6-Trichlorophenol</td>
<td>2.50</td>
</tr>
<tr>
<td>7</td>
<td>m-Cresol</td>
<td>4.53</td>
</tr>
<tr>
<td>8</td>
<td>p-Nitrophenol</td>
<td>1.80</td>
</tr>
<tr>
<td>9</td>
<td>Pyrogallol</td>
<td>13.80</td>
</tr>
</tbody>
</table>
### TABLE 4.2
Solubility of Immobilized Iron(III) of IOCS in Different Solvents

Amount of IOCS taken = 500 mg

<table>
<thead>
<tr>
<th>No.</th>
<th>Solvents</th>
<th>Amount of Fe(III) released in mg/50ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>Ethanol</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>Sodium hydroxide 1mol dm⁻³</td>
<td>0.00</td>
</tr>
<tr>
<td>4</td>
<td>Sodium hydroxide 2 mol dm⁻³</td>
<td>0.04</td>
</tr>
<tr>
<td>5</td>
<td>Hydrochloric acid 0.1 mol dm⁻³</td>
<td>0.00</td>
</tr>
<tr>
<td>6</td>
<td>Hydrochloric acid 0.5 mol dm⁻³</td>
<td>3.60</td>
</tr>
<tr>
<td>Phenol</td>
<td>Ethanol</td>
<td>$H_2O$</td>
</tr>
<tr>
<td>-----------------------</td>
<td>---------</td>
<td>--------</td>
</tr>
<tr>
<td>Phenol</td>
<td>41.6</td>
<td>47.0</td>
</tr>
<tr>
<td>o-Cresol</td>
<td>15.8</td>
<td>17.6</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>52.0</td>
<td>54.3</td>
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<tr>
<td>p-Cresol</td>
<td>36.4</td>
<td>38.8</td>
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<tr>
<td>o-Aminophenol</td>
<td>53.4</td>
<td>60.5</td>
</tr>
<tr>
<td>m-Aminophenol</td>
<td>28.7</td>
<td>37.6</td>
</tr>
<tr>
<td>p-Aminophenol</td>
<td>22.9</td>
<td>29.6</td>
</tr>
<tr>
<td>Pyrocatechol</td>
<td>63.2</td>
<td>69.5</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>33.2</td>
<td>37.6</td>
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<td>Pyrogallol</td>
<td>240.0</td>
<td>266.9</td>
</tr>
<tr>
<td>Phloroglucinol</td>
<td>32.8</td>
<td>40.2</td>
</tr>
<tr>
<td>α—Naphthol</td>
<td>20.6</td>
<td>28.1</td>
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<tr>
<td>β—Naphthol</td>
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<td>0.0</td>
</tr>
<tr>
<td>p—Nitrophenol</td>
<td>20.0</td>
<td>26.3</td>
</tr>
<tr>
<td>o—Chlorophenol</td>
<td>23.4</td>
<td>31.9</td>
</tr>
<tr>
<td>Picric Acid</td>
<td>16.2</td>
<td>17.6</td>
</tr>
<tr>
<td>2,4,6-Trichlorophenol</td>
<td>28.6</td>
<td>39.0</td>
</tr>
<tr>
<td>Sl. No.</td>
<td>Mixture</td>
<td>Eluent</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------</td>
<td>---------</td>
</tr>
<tr>
<td>1.</td>
<td>Phloroglucinol</td>
<td>0.1 M NaOH 30</td>
</tr>
<tr>
<td></td>
<td>Pyrogallol</td>
<td>0.5 M NaOH 50</td>
</tr>
<tr>
<td>2.</td>
<td>Phenol</td>
<td>0.1 M NaOH 40</td>
</tr>
<tr>
<td></td>
<td>Pyrogallol</td>
<td>0.5 M NaOH 50</td>
</tr>
<tr>
<td>3.</td>
<td>β-Naphthol</td>
<td>H₂O 30</td>
</tr>
<tr>
<td></td>
<td>α-Naphthol</td>
<td>0.1 M NaOH 30</td>
</tr>
<tr>
<td>4.</td>
<td>β-Naphthol</td>
<td>H₂O 30</td>
</tr>
<tr>
<td></td>
<td>o-Aminophenol</td>
<td>0.1 M NaOH 40</td>
</tr>
<tr>
<td>5.</td>
<td>β-Naphthol</td>
<td>H₂O 30</td>
</tr>
<tr>
<td></td>
<td>Pyrocatechol</td>
<td>0.5 M NaOH 40</td>
</tr>
<tr>
<td>6.</td>
<td>o-Chlorophenol</td>
<td>0.1 M NaOH 30</td>
</tr>
<tr>
<td></td>
<td>Pyrogallol</td>
<td>0.5 M NaOH 40</td>
</tr>
</tbody>
</table>
Fig. 4.1 Rate of Uptake of Pyrogallol on IOCS
Fig. 4.2 Effect of pH on Adsorption of Phenols on IOCS. The Aqueous Phase Initially Contained 2 mg Phenol. The pH Was Adjusted by Use of 0.1 mol dm$^{-3}$ Hydrochloric Acid and 0.1 mol dm$^{-3}$ Sodium Hydroxide Solution.
Fig. 4.3 Breakthrough Curves of Phenols on Column Operation.

$C_0$ and $C$ denote the initial and final concentrations in each effluent fraction, respectively.
Fig. 4.4a Separation of Phloroglucinol and Pyrogallol
Fig. 4.4b Separation of $\beta$-Naphthol and $\alpha$-Naphthol
Fig. 4.5 A Small Filtration Unit for Removal of Pyrogallol
DISCUSSION

Adsorption Capacity

The results of adsorption studies presented in Table 4.1 reveal that adsorption capacity varies from $1.8 \times 10^{-2}$ to $13.80 \times 10^{-2}$ mmol/g for different phenols. The retention of phenol on iron-oxide coated sand occurs by virtue of Fe–phenol complex formation on hydrous iron oxide. In this adsorption process mechanism may be assumed to be ligand exchange reaction between ionized phenol molecule and hydroxy group on iron oxide surface.

$$\text{HTM. FeO.OH} + \text{ROH} \rightleftharpoons \text{HTM. FeO.RO} + \text{H}_2\text{O}$$

The selectivity of adsorption process is consistent with the studies of natural organic matter (NOM) removal by coagulation with iron salts$^{30,33}$. In these processes the dominant sorption mechanism is assumed to be ligand exchange reaction between ionized functional groups on the sorbing molecule and hydroxyl groups on the oxide surface$^{18,23,24,34}$.

Chemical Analysis

The results of chemical analysis of iron oxide coating revealed that iron content on IOCS surface (g Fe/g IOCS) is 0.074.

Chemical Stability

The results of chemical stability measurement (Table 4.2) showed that iron oxide coating is fairly stable in water, ethanol, 1 mol dm$^{-3}$ NaOH and acidic solution up to pH 1.
Kinetic Measurement

The rate of adsorption of pyrogallol plotted in Fig. 4.1 shows that equilibrium is reached within 100 min.

Effect of pH

The results of the effect of pH on the equilibrium adsorption capacity of IOCS for phenols (Fig. 4.2) show that adsorption of these phenols is somewhat more efficient in the low pH region than in the high pH region, and remains unaffected within pH range 3-6. It seems due to stronger interaction between positively charged surface of iron oxide particles and phenols at pH <8. The lower adsorption capacity observed in the higher pH region may be due to the competing hydroxide ions.

Breakthrough Capacity

The breakthrough curves of phenols plotted in (Fig. 4.3) reveal that 9 bed volumes of m-cresol, 16 bed volumes of pyrocatechol and 34 bed volumes of pyrogallol, corresponding to a retention of 9, 16 and 34 mg respectively, can be passed through a column of IOCS without any trace being detected in the effluent. On uncoated sand, breakthrough was obtained in the first bed volume only for all phenols.

Batch Equilibrium

The distribution coefficients (Kd values) of 17 phenols were measured in 5 different systems. The results are summarized in Table 4.3. The Kd values reveal that IOCS has differential
selectivity toward phenols. In aqueous media pyrogallol is strongly retained by the adsorbent, m-cresol, o-aminophenol, phenol and pyrocatechol only partially while o- and p-cresol, m- and p-aminophenol, resorcinol, phloroglucinol, α- naphthol, p-nitrophenol, o- chlorophenol, picric acid and 2,4,6-trichlorophenol are scarcely adsorbed. The data show that $K_d$ values decrease with the increasing concentration of NaOH solution. This decrease in $K_d$ values may be due to desorption of phenols by NaOH solution (i.e., $\text{OH}^-$ ligand).

**Column Separations**

The results of separation of phenols (Table 4.4) reveal that positional isomers such as phloroglucinol—pyrogallol, and α-naphthol—β-naphthol have been easily separated on the columns of IOCS. Other binary separations are phenol—pyrogallol, β-naphthol—o-aminophenol, β-naphthol—pyrocatechol and o-chlorophenol—pyrogallol. The % error obtained is within the experimental error range. The order of elution and eluents for phloroglucinol—pyrogallol and α-naphthol—β- naphthol presented in Figs. 4.4a and 4.4b shows that chromatograms are sharp. It is interesting that no significant tailing is observed during the elution of various phenols and only small volumes of eluents were required to give compact chromatograms.

**Cyclic Capacity**

The desorption of adsorbed phenol on IOCS by NaOH solution seems due to ligand exchange reaction (phenol → $\text{OH}^-$) and thus
the sodium phenolic compounds were easily desorbed. The data of cyclic breakthrough capacity determined for pyrocatechol showed that the column can be used for 5 cycles with only 10 per cent loss in capacity.

**Filtration Experiment**

The filtration unit demonstrated for pyrogallol removal from ground water (Fig. 4.5) treated 90 l (250 bed volumes) water in first cycle. 95.8 per cent pyrogallol was recovered during regeneration. The unit treated 86 l (238.8 bed volumes) water in second cycle. The treated water had no pyrogallol content. This unit appeared to be promising for phenol removal from wastewaters.
REFERENCES


