CHAPTER IV

REMOVAL OF TOXIC HEAVY METAL IONS USING MODIFIED ADSORBENT

INTRODUCTION:

In recent years, removal of toxic metal ions from ground water and waste water streams has been a major concern. Water, being an excellent solvent is more severely threatened by pollution due to industrial waste and excessive inputs of population. Toxic metals like Hg, Pb, Cr, Cd, etc. are the necessity of many industries. The hazardous effect of heavy metal ions on public health and environment has prompted governments to implement legislation enforcing the treatment of effluent from toxic heavy metal based industries.

In comparison to ion-exchangers and other adsorbents chelating ion-exchangers have received great attention recently in the field of preconcentration and separation of metal ions. Iron(III) hexamine gel (IHA) was used as a new chelating material for separation and recovery of certain metals. Iron hexamine gel IHA is readily reproducible; fairly stable in water, acids upto 1M and ammonia upto 4M and shows high sorption abilities based on the coordination with the lone pair of nitrogen. Industrial application of chelating materials is limited due to large capital investment and unmodified adsorbents as such are not much successful for the removal of toxic metal ions from effluents.

The objective of study in this chapter is to increase the efficiency of removal of certain heavy metals, by distributing iron(III), hexamine gel on sawdust.

EXPERIMENTAL

Chemical

Iron(III) nitrate (BDH, India) and hexamine (Loba, India) were used. All the other reagents used were of analytical grade.
**Apparatus**

Systronic digital pH meter and Perkin Elmer model 552 spectrophotometer were used for pH and spectrophotometric measurements.

**Preparation of modified sawdust (MSD)**

Saw dust sieved for the desired mesh size (60–100) was stirred with hot demineralized water for 6h to remove the impurities, filtered and dried. 250 ml of 0.1M iron(III) nitrate solution was added to the weighed amount of sawdust and stirred for 2h. Then, 125 ml of 0.4 M hexamine was added and stirring was further continued for 12h. After aging for 24h, the resultant material was filtered, washed with deionized water and finally dried at 60 ± 1°C in an oven.

**Sorption capacity**

The sorption capacity of the adsorbent was determined by batch process. A quarter gram of adsorbent was shaken with 25 ml solution of 0.008M Cr(VI) at pH 6. The supernatant was analysed for un sorbed Cr(VI).

**Sorption of metal ions as a function of pH**

The uptake of various heavy metal ions by modified saw dust has been investigated in terms of sorption capacity at different pH\(^{1-7}\). The adsorbent (0.2 g) was shaken with 25 ml of 0.008M metal ion solutions at different pH (adjusted using 0.25M hydrochloric acid – 0.25M sodium acetate) in a glass stoppered conical flask for 4h. The solution was filtered and analyzed for un sorbed metal ions Pb(II), Mn(II), Ni(II), Zn(II), Cu(II), Hg(II) and Cd(II) were determined by EDTA titration and Cr(VI) was determined spectrophotometrically with diphenylcarbazide\(^{8}\).

**Rate of sorption**

Rate of sorption was determined by batch process. 25 ml of 0.008M solution of Cr(VI) (pH 6) was shaken with 0.2 g of modified saw dust (MSD\(_1\)) for different
time intervals and the amount of unadsorbed Cr(VI) was determined in the filtrate. For comparison, similar studies were performed on untreated saw dust.

**Break through capacity**

The breakthrough behaviour of metal ions was studied by passing solutions of Cr(VI), Pd(II) and Hg(II) (1 mg/10 ml each, pH ~ 6) through a column (30 cm × 0.39 cm²) packed with 2 g MSD₁. The flow rate was maintained 1 ml m⁻¹. For comparison, similar studies were made on untreated saw dust.

**Standard procedure for the removal of metal ions**

The borosilicate column (30 cm × 0.78 cm²) packed with 5 g MSD₁ was preconditioned with the proper pH buffer. Water samples containing metal ions in ppm concentration were passed through the column, at flow rate 2 ml m⁻¹.

**Effect of diverse ions**

1000 ml solution of chromium(VI) (10–50 mg) or, mercury(II) (10–60 mg) containing foreign metal ions: Mn(II), Zn(II), Hg(II) and Cu(II) (5 mg each) were prepared (pH ~ 2). The removal of Cr(VI) or Hg(II) was carried out by standard procedure.

**RESULTS**

The results of sorption capacity of hexavalent chromium on modified saw dust samples and iron(III) hexamine are presented in Table 4.1.

The effect of pH on sorption capacity for different metal ions has been investigated. The uptake of metal ions as a function of pH is plotted in Figure 4.1.

The results of breakthrough behaviour for chromium(VI), lead(II) and mercury(II) are plotted in Figure 4.2.

The results of effect of flow rate on breakthrough capacity are plotted in Figure 4.3.
The data of the removal efficiency for chromium(VI) mercury(II) and lead(II) from water samples are summarized in Table 4.2.

The effect of foreign metal ions such as Mn(II), Zn(II), Ni(II) and Cu(II) on the removal efficiency of Cr(VI) has also been investigated, the data are given in Table 4.3.

DISCUSSION

The distribution of iron(III) hexamine gel on saw dust was found so stable and effective that the material could be utilized for removal of heavy metal ions from aqueous solutions.

The sorption capacity data presented for Cr(VI) (Table 4.6) reveal that the capacity per unit weight of adsorbent decreases as the amount of saw dust increases. However, if we calculate the capacity g\(^{-1}\) of iron(III) hexamine (on the basis of yield), the sorption capacity increases with the increase in saw dust due to increased surface area of Iron hexamine gel IHA available for the sorption of metal ions. The sample modified saw dust MSD\(_1\) has been chosen for detailed studies.

**TABLE 4.1**

PREPARATION AND PROPERTIES OF IRON HEXAMINE MODIFIED SAWDUST (MSD)\(^c\)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Sawdust added (g)</th>
<th>Yield(^a) (g)</th>
<th>Sorption capacity (mg g(^{-1}) MSD)</th>
<th>Sorption capacity(^d) for Cr(VI) (mg g(^{-1}) IHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IHA</td>
<td>0.0</td>
<td>4.580</td>
<td>19.526</td>
<td>26.050</td>
</tr>
<tr>
<td>MSD(_1)</td>
<td>5.0</td>
<td>9.585</td>
<td>14.592</td>
<td>40.679</td>
</tr>
<tr>
<td>MSD(_2)</td>
<td>10.0</td>
<td>9.585</td>
<td>14.282</td>
<td>45.484</td>
</tr>
<tr>
<td>MSD(_3) (^b)</td>
<td>5.0</td>
<td>9.585</td>
<td>19.820</td>
<td>41.464</td>
</tr>
</tbody>
</table>

\(^a\) 250 ml of 0.1 M iron(III) nitrate + sawdust + 125 ml of 0.4 M hexamine;

\(^b\) Mesh size of sawdust was 100-150;

\(^c\) Appearance of adsorbent was dark brown;

\(^d\) Calculated on the basis of yield.
### TABLE 4.2

**REMOVAL OF METAL IONS FROM WATER SAMPLES**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal Ions</th>
<th>Volume of effluent (ml)</th>
<th>Concentration of metal (ppm)</th>
<th>Approximate pH of water sample</th>
<th>Removal*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled Water</td>
<td>Cr(VI)</td>
<td>7000</td>
<td>10</td>
<td>6</td>
<td>100.0±0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8000</td>
<td>10</td>
<td>6</td>
<td>95.8±0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9000</td>
<td>10</td>
<td>6</td>
<td>86.5±0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14000</td>
<td>5</td>
<td>6</td>
<td>100.0±0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16000</td>
<td>5</td>
<td>6</td>
<td>96.0±1.0</td>
</tr>
<tr>
<td>Tap water</td>
<td>Cr(VI)</td>
<td>4000</td>
<td>10</td>
<td>6</td>
<td>100.0±0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5000</td>
<td>10</td>
<td>6</td>
<td>92.3±1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5000</td>
<td>10</td>
<td>2</td>
<td>99.8±1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6000</td>
<td>10</td>
<td>2</td>
<td>93.8±1.2</td>
</tr>
<tr>
<td>Tap water</td>
<td>Hg(II)</td>
<td>5000</td>
<td>10</td>
<td>3</td>
<td>100.0±0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6000</td>
<td>10</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Tap water</td>
<td>Pb(II)</td>
<td>3000</td>
<td>10</td>
<td>6</td>
<td>100.0±1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4000</td>
<td>10</td>
<td>6</td>
<td>89.3±1.6</td>
</tr>
</tbody>
</table>

*Mean and standard deviation for five measurements.*
Fig. 4.1
Sorption of metal ions as a function of pH
TABLE 4.3
REMOVAL OF Cr(VI) AND Hg(II) IN PRESENCE OF FOREIGN METAL IONS Mn(II), Zn(II), Ni(II) AND Cu(II) AT pH 2

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Amount of metal ion taken (mg)</th>
<th>Removal*, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI)</td>
<td>10</td>
<td>100.0 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>100.0 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>99.8 ± 0.8</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>10</td>
<td>100.0 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>100.0 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>99.9 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>91.6 ± 1.4</td>
</tr>
</tbody>
</table>

* Mean and standard deviations for five measurements.

Rate of sorption studies reveal that equilibrium is attained within 30 m in case of MSD1 whilst 6h were required on untreated saw dust. This fast adsorption rate may be explained due to the distributed iron(III) hexamine on modified saw dust. Amine group (chelating site) is responsible for such a fast equilibrium (9–11).

The sorption capacity of eight metal ions studied at different pH (1–7) (Figure 4.1) shows that (i) Cr(VI) and Hg(II) are strongly sorbed on the adsorbent in the pH range 1–7; (ii) Pb(II) and Cd(II) are scarcely sorbed at pH 1, and (iii) Mn(II), Zn(II), Cu(II) and Ni(II) are not sorbed at pH 1. The poor retention of Cd(II) at pH 1 may be due to CdCl42− formation.

The results of breakthrough behaviour (Figure 4.2) show that as many as 36 bed volumes of Cr(VI) (corresponding to 36 mg Cr) could be passed through the treated saw dust without any trace being detected in the effluent but in case of
Fig. 4.2
Breakthrough curves for different metal ions (1 mg/10 ml each) column dimensions 30 cm x 0.39 cm², amount of adsorbent 2 g; flow rate 1 ml m⁻¹. *(For iron (III) hexamine)*
untreated saw dust breakthrough occurred in the first bed volume. For Pb(II) and Hg(II) breakthrough occurred after 43 and 48 bed volumes, corresponding to 43 and 48 mg of Pb and Hg respectively. On iron(III) hexamine breakthrough for Cr(VI) occurred after 46 bed volumes (corresponding to 46 mg Cr). The studies revealed that breakthrough capacity for Cr(VI) on IHA and MSD₁ is 23 mg g⁻¹ of IHA and 37.6 mg g⁻¹ of IHA (calculated on the basis of yield) respectively. This increased capacity in the later case may be due to the increase in surface area of IHA. Similar trend is confirmed by sorption capacity₁²,₁³ (Table 4.1).

Effect of flow rate on break through capacity revealed that the capacity remains same upto flow rate 3 ml m⁻¹ for Cr(VI) when passed through column 30 cm × 0.78 cm² packed with 5 g MSD₁. The effect of column dimensions showed a decrease in breakthrough capacity with the increased cross-sectional area of the column. This may be due to decreased contact time.

The results of effect of diverse metal ions (Table 4.3) Revealed that the removal of Cr(VI) (10–50 mg) and Hg(II) (10–60 mg) is quantitative in presence of Mn(II), Zn(II), Ni(II) and Cu(II) at pH 2. This may be due to the fact that Mn(II), Zn(II), Ni(II) and Cu(II) are eluted at pH 2.

Removal studies of Cr(VI) from water samples (Table 4.2) revealed that distilled water sample having Cr(VI) concentration 10 ppm and 5 ppm could be passed through the column upto 7000 ml and 14000 ml respectively with cent per cent removal of Cr(VI). Total removal of Cr(VI) (10 ppm) from tap water sample was observed upto 4000 ml effluent volume. In case of tap water samples at pH 2, the removal of Cr(VI) was quantitative upto effluent¹⁴–¹⁶ volume 5000 ml. This can be explained due to least possible sorption of metal ions of tap water at pH 2. Similarly, tap water samples containing Hg(II) (pH 3) and Pb(II) (pH 6) (10 ppm
Fig. 4.3
Breakthrough capacity for Cr (VI) as a function of flow rate; column dimensions 30 cm x 0.78 cm²; amount of absorbent 5 g
each) were passed through the column of modified saw dust MSD1 with quantitative metal ion removal up to effluent volumes 5000 and 3000 ml respectively.

Saw dust is waste material of saw mills. The efficiency of removal of toxic metal ions can be improved by distributing iron(III) hexamine gel on saw dust. Regeneration of the adsorbent has been tried by eluting the adsorbed metal ions using appropriate eluants in order to restore the column for further use.
CHAPTER IV

REFERENCES