Removal of Copper (II) using Synthesized 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of Wood flour

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ABSTRACT
5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of wood flour has been used for the removal of Cu(II) metal ions from Synthetically Prepared waste water. The adsorption process was studied as a function of PH(3-6), Contact time (0-120 min.), Initial Concentration (20-55 mg/L), doses of wood flour (1-4g) and Temperature (30±1°C), it was observed that the PH has marked effect on Cu(II) uptake. Result shows that about 66% removal of Cu(II) takes place over the PH range of 5.5 to 6.0 and contact time of 1 hour at initial concentration of 20mg/L, the adsorption of Cu(II) was tested by Plotting Calibration Cure between Absorbance and Concentration.

Key Words: Copper, Wood Flour, Adsorption, Metal Removal, Calibration Curve, 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of wood flour

INTRODUCTION
Presence of heavy metals in water supplies specially Cu(II) into water is a major environmental concern since these metals are being released in to the water supplies from various industrial sources [1-3]. Copper is the first metal known to be employed by man. Copper has many uses in industrial and house hold appliances. Salts of copper are used in controlling biological growths in reservoirs. The toxicity of copper affects the aquatic organisms. Although copper is an essential metal but the inqestion of higher levels of copper may results in nausea, metallic taste, vomiting, jaundice, hypertension, anuria, hemoglobinuria. Absorption of excess amount of copper results in vomiting and liver damage. A maximum concentration of 0.1 ppm copper has been prescribed for drinking water by US environmental protection Agency[4-7].

Many reports are available for removal of Cu(II) from water and waste water using natural products and byproducts. The present work deals with the study of removal of Cu(II) from waste water using 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of wood flour [8]. The wood flour is selected because it is easily available at anywhere. It may prove economically viable substance for water treatment.

MATERIAL AND METHODS
Synthesis of Cross Linked Wood Flour (Epoxy Ether of Wood Flour)
486g wood flour (corresponding to three anhydroglucose unit) was taken in round bottom flask and it was slurried with dioxane 15ml of 40%(w/v) sodium hydroxide was added to it, to make it alkaline, till pH reached 8.5. The contents of the flask were slurried magnetically at 45°C. Then 92.53g (1 mole) epichlorohydrin was added with constant stirring. The stirring was further continued for four hours at 45°C.

The reaction mixture was allowed to settle down. The supernatant liquid was decanted off and the product was filtered under vaccum and washed with 80% aqueous methanol containing few drops of nitric acid, to remove inorganic impurities and excess alkali in the contents. The washed product was dried in an oven at 40°C. Obtained cross linked flour was further used for derivatization. Synthesis of 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of wood flour [9].

In a round bottom flask 0.1 mole of crosslinked wood flour was taken and it was slurried with 70% aqueous isopropanol, 5ml of 50% (w/v) aqueous sodium hydroxide was added to it gradually with continuous stirring magnetically at constant speed on a water, heated at 50°C. Then 0.05 mole of 5-Amino-2-Hydroxy Benzene Sulphonic Acid was added slowly with stirring to the content of flask. The
stirring and heating was continued for 6 hours. The product thus formed was filtered on a Buchner funnel under vacuum. Then washing of product was done with 50% aqueous methanol containing few drops of nitric acid to remove excess alkali, free 5-Amino-2-Hydroxy Benzene Sulphonic Acid and inorganic impurities. The washed product was dried in air and then was suspended in 0.1N HCl and filtered immediately. The filtered product was successively washed with 0.1N NaOH and 0.1 N HCl. The supernatant liquid was decanted and resin was washed several times to remove suspended particles and other impurities. The final washing was carried out with absolute alcohol and the product was dried under vacuum. The product was brownish powder.

![Chemical structure of 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of wood flour](image.png)

**Synthesis of 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of wood flour**

**Reagents**
All the chemicals used were of analytical grade obtained from E.Merck. Stock solutions of 2000 mg/L each of the Cu(II) were prepared separately by dissolving required amounts in distilled water. Synthetic solutions of required concentrations were prepared by diluting the stock solutions. The PH of solutions was adjusted using 0.2M sodium acetate and 0.2M acetic acid.

**Instrumentation**
AGRONIC-511 digital PH meter was used to determine PH of the solutions. Spectrophotometric observations were obtained on an AIMIL-MAKE “spectrochem” spectrophotometer. Magnetic stirrers manufactured by metrex scientific Pvt. Ltd. Were used for stirring.

**Experimental Methods**
10ml standard solution of copper(II) was taken in a beaker and 5ml of 20% ammonium citrate solution was added. The PH of solution was adjusted to 9.0 by adding ammonium hydroxide. The solution was cooled to room temperature and diluted it to 25 or 30ml. Transfer the contents of beaker to a separatory funnel. 1.0ml of sodium diethyl dithio carbonate (0.1%aq) was added to the contents of separatory funnel and was shaken with exactly 5ml of carbon tetra chloride. Allowed the carbon tetra chloride layer to settle. When layer was free from water droplets, it was collected in a suitable cell. Aqueous phase remaining in separatory funnel was again extracted with carbon tetra chloride, until the last portion becomes colourless. Absorbance of extract was measured at 435nm comparing against carbon tetra chloride.

Similarly using standard cu(II) solution of different concentrations the calibration curve was plotted. The concentration of unknown solution can be determined by using the calibration curve.

**RESULTS AND DISCUSSION**
Estimation of Cu(II) was carried out through following tables and curves.

| Table 1: Determination of distribution coefficient and percentage removal for cu(II). |
|---|---|---|
| S.No. | Concentration (ppm) | Absorbance |
| 1 | 2 | 0.08 |
| 2 | 4 | 0.15 |
| 3 | 6 | 0.23 |
| 4 | 8 | 0.30 |
| 5 | 10 | 0.38 |
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(a) Chelation of Cu(II) on constant amount of 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of wood flour (AHBSAWF) resin, with varying PH.

Different amounts of 0.2M acetic acid and 0.2M sodium acetate solution were added to get the desired PH (total volume of buffer in each case was 25ml). Now, 0.1g of dry resin and 25ml of 20ppm solution of Cu(II) was added to each flask. The contents were equilibrated by magnetic stirring for 1 hour and filtered. Filterates were analysed for the concentration of Cu(II). The results are given in table 2.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Vol. of 0.2M acetic acid (ml)</th>
<th>Vol. of 0.2M sodium acetate (ml)</th>
<th>pH</th>
<th>O.D. of filtrate</th>
<th>Conc. Of Cu(II) in filtrate (ppm)</th>
<th>Amount of Cu(II) in sol. (mg)</th>
<th>Amount of Cu(II) in AHBSAWF (mg)</th>
<th>Kd</th>
<th>% removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23</td>
<td>2</td>
<td>3.50</td>
<td>0.28</td>
<td>7.4</td>
<td>0.370</td>
<td>0.130</td>
<td>176</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>19</td>
<td>6</td>
<td>4.01</td>
<td>0.22</td>
<td>5.1</td>
<td>0.290</td>
<td>0.210</td>
<td>362</td>
<td>42</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>10</td>
<td>4.50</td>
<td>0.15</td>
<td>4.0</td>
<td>0.200</td>
<td>0.300</td>
<td>750</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>18</td>
<td>5.03</td>
<td>0.10</td>
<td>2.6</td>
<td>0.130</td>
<td>0.370</td>
<td>1423</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>22</td>
<td>5.52</td>
<td>0.13</td>
<td>3.4</td>
<td>0.170</td>
<td>0.330</td>
<td>971</td>
<td>66</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>24</td>
<td>6.02</td>
<td>0.17</td>
<td>4.5</td>
<td>0.225</td>
<td>0.275</td>
<td>611</td>
<td>55</td>
</tr>
</tbody>
</table>

Table 2: Chelation of Cu(II) on constant amount of 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of wood flour (AHBSAWF) resin with varying pH.

Amount of AHBSAWF resin added = 0.1 g  
Initial concentration = 10ppm  
Volume of Cu(II) of 20ppm = 25 ml  
Total Volume = 50 ml  
Temperature = 30±1°C

Inference

It is observed that with the increase of PH the kd values for Cu(II) on AHBSAWF increases. At PH 5.03 the distribution coefficient value is maximum. So Cu(II) can be adsorbed on AHBSAWF resin at PH 5.03 in presence of sodium acetate-acetic acid buffer. The removal of Cu(II) by AHBSAWF at PH 5.03 is 74% kd value is 1423.

(b) Chelation of Cu(II) on varying amount AHBSAWF resin, at constant PH.

Different amounts of AHBSAWF resin were taken in each flask was added 0.2 acetic acid and 0.2M sodium acetate to get the PH 5.03. Again in each set, volume of buffer was maintained to 25ml. Now 25ml (20 ppm) solution of Cu(II) was then added to each set. The contents were stirred magnetically and equilibrated over night. The contents were filtered and analysed. The results are given in table 3.
Table 3: Chelation of Cu(II) on varying amount of AHBSAWF resin, at constant PH.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amount of AHBSAWF added (mg)</th>
<th>O.D. of filterate</th>
<th>Conc. Of Cu(II) in filterate (ppm)</th>
<th>Amount of Cu(II) in sol. (mg)</th>
<th>Amount of Cu(II) in AHBSAWF (mg)</th>
<th>Kd</th>
<th>% removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0.14</td>
<td>3.7</td>
<td>0.185</td>
<td>0.315</td>
<td>851</td>
<td>63</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>0.13</td>
<td>3.4</td>
<td>0.170</td>
<td>0.330</td>
<td>971</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>0.12</td>
<td>3.1</td>
<td>0.155</td>
<td>0.345</td>
<td>1113</td>
<td>69</td>
</tr>
<tr>
<td>4</td>
<td>400</td>
<td>0.11</td>
<td>2.9</td>
<td>0.145</td>
<td>0.355</td>
<td>1224</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>0.11</td>
<td>2.9</td>
<td>0.145</td>
<td>0.335</td>
<td>1224</td>
<td>71</td>
</tr>
<tr>
<td>6</td>
<td>600</td>
<td>0.11</td>
<td>2.9</td>
<td>0.145</td>
<td>0.355</td>
<td>1224</td>
<td>71</td>
</tr>
</tbody>
</table>

Inference
It is observed that with the increase of amount of AHBSAWF the kd values for Cu(II) on AHBSAWF increases. At PH 5.03 in the presence of sodium acetate-acetic acid buffer the maximum removal of Cu(II) by AHBSAWF is 71% kd value is 1224.

CONCLUSION
In the present work, we have synthesized chelating resins derived from a polysaccharide cellulose (wood flour) an easily available wood product. Wood is the most abundant and renewable natural resource easily available to the mankind. The cellulose of wood are linear polymers of D-anhydro glucopyranose and stabilized by hydrogen bonding. Attempts were therefore made to prepare few derivatives from wood flour without any pretreatment with object to the material as adsorbent for different toxic trace metals (elements) versatile chelating agents of –N-O- types; 5-Amino-2-hydroxy Benzene sulphonic Acid is incorporated in hydrophilic wood flour matrix to give wood flour based chelating resins. The highly porous character of wood flour adsorbent permits the diffusion of metal ions inside it, due to law of capillarity.

5-Amino-2-hydroxy Benzene sulphonic Acid derivative of wood flour shows maximum adsorption of Cu(II) at PH 5.04.

REFERENCES


HOW TO CITE THIS ARTICLE