Utilization of Carbamoyethylated Cotton for Heavy Metal Ion Removal

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Abstract: Cotton cellulose in fabric form was rendered ion exchanger via Carbamoyethylation Reaction (CER). The latter was carried out using acrylamide (Aam) and sodium hydroxide. The resulted carbamoyethylated cotton having amide functional groups (CONH₂) was monitored for its ability to adsorb heavy metals from their aqueous solutions. Different factors affecting adsorption of metal ions onto the latter substrate such as metal ion concentration, pH, treatment time and temperature were studied systematically. Results obtained reflect the following findings: (a) the adsorption value increases by increasing the metal ion concentration up to 60 m mol L⁻¹ then levels off, (b) the carbamoyethylated cotton was found to be selective adsorbent for Hg²⁺ at pH 0.5, (c) the adsorption values is higher at 40°C then levels off by raising the temperature to 60 and 80°C, respectively, (d) the adsorption values increase by increasing the treatment time up to 5 h at 40 and 60°C and 3 h at 80°C then levels off and (e) the adsorption values of the aforementioned substrate in question at different metal ions follow the order: Hg²⁺ > Cu²⁺ > Zn²⁺ > Co²⁺ > Pb²⁺.

Key words: Carbamoyethylated Cotton (CEC), adsorption value, metal ions

INTRODUCTION

Environmental pollution caused by toxic heavy metals in industrial effluents is considered as one of the most important problems worldwide[1]. The use of synthetic resins for chelating toxic metal ions in wastewater is considered as a possible way for preventing environmental pollution. These resins are mostly based on petroleum synthetic polymers[2-3] at which secondary environmental pollution take place via their contamination on soil and air. In addition, these synthetic polymers are usually none renewable and non-biodegradable.

So, present research has been directed to use chemically modified cotton as an agriculture biopolymer, low cost as well as renew ability for heavy metal ion removals, instead of original cotton due to it has no chelating or interaction capacity. Hence, several trials have been made to utilize cotton cellulose as a metal scavenger, by using modified cotton containing glycidyl methacrylate, diethyl aminoethyl methacrylate and acrylic acid[4], DEAE-cotton-g-poly (MAA)[5], phosphorylated cotton[6], DEAE, carbamoyl ethyl and poly (Aam)[7], acrylic acid/N-methylol acrylamide mixture[8], cellulose/glycidyl methacrylate/acrylic acid cation exchange composites[9]. This study has been undertaken with the aim to removal of some heavy metals via chelation on the aforementioned carbamoyethylated cotton having the amide groups. The different factors affecting adsorption of metal ions such as metal ion concentration, pH, treatment time and temperature as well as durability were studied in detail.

MATERIALS AND METHODS

Cotton fabric (400 g m⁻², 21 Picks x 61 ends/cm) kindly supplied by Misr Spinning and Weaving Co., El-Mehalla El-Kobra. It was used after purification by scouring for 2 h at the boil using aqueous solution containing 1% sodium hydroxide. It was then thoroughly washed and air-dried at room temperature. Acrylamide, sodium hydroxide, hydrochloric acid, cyclohexane, mercuric chloride, copper sulphate, zinc acetate, nickel chloride and lead acetate were reagent grade chemicals.

Preparation of Carbamoyethylated cotton having 605 mmol amide group/100 g sample (capacity): The freshly prepared catalyst NaOH (1 mL) of concentration 0.25 N and 4 mL cyclohexane was added to complete the total volume to 10 mL. The reaction mixture was shacked very well and allowed to proceed at 40°C for 1 h in a thermostatic water bath.

Metal salts: Hg(NO₃)₂, Cu(COOCH₃)₂H₂O, Zn(COOCH₃)₂, Co(COOCH₃)₂·4H₂O and Pb(COOCH₃)₂·3H₂O were of analytical reagent grade.

Adsorption of metal ions: Aqueous solutions of 0.01 M of different metal salts were prepared and its pH was
adjusted to the specified values. The cotton (0.5 g) was put into a glass bottle containing 50 mL of the metal salts solution and the mixture was occasionally shaken for the desired treatment time. The adsorption value was calculated by estimating the metal ion concentration before and after treatment with carbamoylethylated cotton by titration against standard EDTA.

**Results and Discussion**

**Effect of metal ion concentration:** Figure 1 shows the adsorption values (expressed as m mol/100 g sample) of different metal ions concentration on carbamoylethylated cotton. It is shown in the Fig. 1 that:

- The adsorbed amounts of metal ions increase by increasing metal ions concentration from 20-60 m mol/100 g sample then levels off.
- The maximum adsorption value was 430 m mol/100 g sample for Hg²⁺ and the minimum was 173 m mol/100 g sample for Pb²⁺.
- The adsorption values depend on the metal ion used and follow the order: Hg²⁺>Cu²⁺>Zn²⁺>Co²⁺>Pb²⁺.

This is in accordance with Irving-William's series

**Effect of pH:** Figure 2 represents the adsorption values (expressed as m mol/100 g sample) of different metal ions at different pH values (0.5 - 6.0) of carbamoylethylated cotton. The results obtained reflect the following findings:

- The adsorption values of metal ions in question increases by increasing the pH values within the range studied.
- At pH value 0.5 only Hg²⁺ metal ion adsorbed and the adsorption value was 220 m mol/100 g samples. This reflects the role of amide group in carbamoylethylated cotton as selective adsorbent for Hg²⁺ at pH 0.5.
- At pH value 1 the adsorbed metal ions were Hg²⁺ and Cu²⁺ and the adsorption values were 260 and 40 m mol/100 g samples, respectively.
- At pH range 2.0-6.0 all metal ions used were adsorbed with different values depending on the nature of metal ion and the substrate used.
- The adsorption values depend on the metal ion used and follow the order: Hg²⁺>Cu²⁺>Zn²⁺>Co²⁺>Pb²⁺.

**Effect of treatment time and temperature:** Table 1 clarifies the adsorption of metal ions at different duration (0.5-24 h) and temperatures (40-80°C) of carbamoylethylated cotton.

The adsorption of metal ions increases by increasing treatment time within the range studied to reach a maximum value the levels off. The maximum adsorption values occur after 5 h at 40 and 60°C and 3 h at 80°C, respectively.

![Graph of adsorption value vs metal ion concentration](image)

**Fig. 1:** Effect of metal ion concentration on the adsorption value (expressed as m mol/100 g sample) of different metal ions of carbamoylethylated cotton

Reaction conditions: Carbamoylethylated Cotton, 0.5 g; total volume of metal ion, 50 mL; pH, 6.0, treatment time, 24 h and temperature, 40°C.
Table 1: Effect of changing treatment time and temperature on the adsorption value (m mol/100 g sample) of different metal ions of carbamoylthlated cotton

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>40°C</th>
<th>60°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>½ h</td>
<td>1 h</td>
<td>3 h</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>270</td>
<td>325</td>
<td>380</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>260</td>
<td>300</td>
<td>355</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>235</td>
<td>260</td>
<td>280</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>160</td>
<td>180</td>
<td>205</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>130</td>
<td>145</td>
<td>165</td>
</tr>
</tbody>
</table>

Reaction conditions: Carbamoylthlated cotton, 0.5 g; metal ion concentration, 60 m mol L⁻¹; Total volume of metal ion, 50 mL; pH, 6.0.

Fig. 2: Effect of pH on the adsorption value (expressed as m mol/100 g sample) of different metal ions of carbamoylthlated cotton

Reaction conditions: Carbamoylthlated Cotton, 0.5 g; metal ion concentration, 60 mmol L⁻¹; total volume of metal ion, 50 mL; pH, 6.0, treatment time, 24 h and temperature, 40°C.

Table 2: The adsorption of different metal ions on the Carbamoylthlated Cotton (adsorption and desorption)

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>0 Cycle</th>
<th>5 Cycles</th>
<th>10 Cycles</th>
<th>20 Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg²⁺</td>
<td>430</td>
<td>430</td>
<td>430</td>
<td>430</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>390</td>
<td>390</td>
<td>390</td>
<td>390</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>215</td>
<td>215</td>
<td>215</td>
<td>215</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>173</td>
<td>173</td>
<td>173</td>
<td>173</td>
</tr>
</tbody>
</table>

The adsorption values of metal ions decreases by raising the treatment temperature from 40 to 60°C and then to 80°C. This can be explained in terms of the higher stability of the chelate formed at lower temperatures as generally observed for low molecular weight complexes. This observation is in agreement with that obtained with Nakamora et al. [1].

**Durability:** Carbamoylthlated cotton was used in adsorption and desorption of different metal ions several times (20 cycles) to examine its durability. Table 2 shows that adsorbed metal ions were easily desorbed by treatment with 0.1 M HNO₃ at room temperature. The adsorbed amount of the different metal ions remains unchanged after 5, 10, 15 and 20 cycles, which reflect the excellent durability of the above mentioned substrate (Table 2).

**CONCLUSIONS**

It was found that, higher adsorption value of different metal ion obtained at: metal ion concentration, 60 m mol L⁻¹; pH, 6.0; treatment time, 5 h; treatment temperature, 40°C when using the metal ion solution 50 mL.

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REFERENCES


