

[E003] **CELLULOSE MODIFIED WITH CITRIC ACID AND ITS ABSORPTION OF Pb²⁺ and Cd²⁺ IONS**

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Abstract. Cellulose was modified with citric acid in high temperature. Investigations of its absorption of heavy metal ions (such as Pb²⁺ and Cd²⁺) showed that modified cellulose in conditions 120°C and 12 h and in mass ratio of cellulose :citric acid=1:3 had highest absorption capacity. Absorption capacity of modified cellulose increased in accordance with increase of concentrations of ions. Structure of modified cellulose was confirmed by IR spectra and SEM pictures.

1. INTRODUCTION

Conventional methods for removing metals from industrial effluents include chemical precipitation, electrolysis, membrane separation, ion exchange, and absorption by activated carbon. Most of these methods suffer from some drawback such as high capital or high operational cost or disposal of resulting sludge. In recent years, more and more interest has been directed to the investigation of low-cost materials such as agricultural by products, industrial wastes and biological materials as adsorbents for the removal of heavy metal from industrial wastewater [1–3]. Recently, modified cellulose beads [4] and chelating resins [5] were used to adsorb some heavy metallic ions.

In recent years, cellulose materials (such as cotton, soybean hulls [6], cottonseed hulls, macadamia nut [7], sugar beet pulp [8], rice straw [9], soybean straw [10]) hulls have been investigated for heavy metal removal from aqueous solutions [11–16]. In some attempts, cellulose materials have converted into activated carbons and investigated for

heavy metals and phenol removal from aqueous solutions [17–19]. It has been showed that treating agricultural materials with polyfunctional acids (such as citric, tartaric, phosphoric) at mildly elevated temperatures enhanced their sorption capacity for metal ion [20–26]. By such a treatment, some extra acidic groups can be introduced to the material by forming an ester linkage. Some cellulosic materials including sugar beet pulp have been modified with commercial phytic acid which is an organic polyphosphoric acid and calcium exchanging capacity of the modified product obtained from sugar beet pulp has been found as 2.72 mequiv. g⁻¹ [26]. Marshall et al. [22] have compared the copper sorption ability of soybean hulls modified with different polycarboxylic acids and reported that the use of citric acid (tricarboxylic acid) in modification process gives better results than the use of succinic, tartaric, malic and maleic acids (dicarboxylic acids).

The objective of this study was to determine the lead and cadmium sorption ability of cotton material treated with NaOH and citric acid by a method applied for soybean hulls by Marshall et al. [21, 24]. For this purpose, cotton material was subjected to alkaline treatment with NaOH solution and subsequently heating together with citric acid for improving the cation binding properties. The cotton material modified was characterized and subjected to a systematic lead and cadmium sorption study.

2. Materials and methods

2.1. Adsorbent preparation

Cotton were treated by heating at refluxing with NaOH 2% solution, then washed with distilled water and dried. Dried cotton was cut into segment of 2–3 mm for further pretreatments. Treated cotton samples and citric acid were dried more in an oven at 50°C until constant weight.

The chemical modification of cotton was made according to the similar method previously described by Marshall et al. [21, 24] with modifying in reaction time and reaction temperature. Treated cotton (0.5 g) was mixed with solution of citric acid (1.5 g) in 8 mL of water. After being stirred for 30 min at 20°C, the acid straw slurries were

placed in a porcelain tray and dried at 50°C in a forced air oven. After 24 h, the thermochemical reaction between acid and straw was proceeded by raising the oven temperature to 120°C for 12 h. After cooling, the reacted products were washed with 200mL distilled warm water per gram of products to remove any excess of citric acid. This volume of water was sufficient to remove unreacted citric acid since no turbidity from lead (II) citrate was observed when the washed straw was suspended in 10mL of water to which 10mL of 0.1M lead (II) nitrate was added. Lastly, the citric acid modified cotton (citric acid-WC) was dried at 50°C until constant weight and preserved in a desiccator as adsorbent for further use. Yield 0.58 g. Some another experiments were performed similarly when the reaction time and reaction temperature were changing (Table 1).

2.2. Adsorbent characterization

The morphological characteristics of soybean straw were observed by using a scanning electron microscope (Hitachi S4800, Japan) . The acceleration voltage (Acc.V) was 5.0 kV, and the spot size (SE) was 10 μm. The functional groups present in the adsorbent were characterized by a Fourier transform infrared FT/IR NEXUS 670 Spectrophotometer (Nicolet, USA), using KBr discs to prepare the soybean straw samples.

2.3. Solution preparation

Cadmium and lead solution was prepared by dissolving solid cadmium sulfate or lead nitrate (analytical grade) in distilled water. Diluted HNO₃ and NaOH solutions were used for pH adjustment. All chemicals used in this work were purchased as reagent grade from Merck.

2.4. Pb²⁺ and Cd²⁺ absorption experiments

Batch experiments were carried out at room temperature (20±2°C) in stoppered conical flasks by shaking a fixed mass of 0.1 g of dry cotton adsorbents, with 50mL of Pb²⁺ (or Cd²⁺) solution at 250 rpm until equilibrium was reached. The initial pH values of the solution were previously adjusted with dilute HNO₃ or NaOH using pH meter. In order to ascertain the contact time that was necessary to achieve the equilibrium state

(characterized by unchanging Pb^{2+} (or Cd^{2+}) concentration in the solution), simple preliminary sorption-kinetic experiments were performed stirring in different conical flasks 0.1 g of dry cotton adsorbents with 50mL of 1000 ppm of Pb^{2+} (or Cd^{2+}) solution at initial pH around 5. Samples were withdrawn at pre-determined time intervals. After agitation, samples were withdrawn from each flask and about 25mL of the Pb^{2+} (or Cd^{2+}) solution was separated from the adsorbent by filtration for analysis. The initial and final concentration of Pb^{2+} (or Cd^{2+}) were determined by inductively coupled plasma atomic emission spectrophotometry (PYE UNICAM, Philip, UK).

The measured Pb^{2+} (or Cd^{2+}) concentrations were then used to calculate the absorption capacity, q_e (mg/g) of the adsorbent using the following mass balance equation:

$$q_e = V \cdot (C_o - C_e) / m \quad (1)$$

The percentage of Pb^{2+} (or Cd^{2+}) adsorbed on the adsorbent was calculated by the following equation:

$$p_e (\%) = 100(C_o - C_e) / C_o \quad (2)$$

where C_o, C_e, V , and m are initial Pb^{2+} or Cd^{2+} concentration (ppm), Pb^{2+} or Cd^{2+} concentration at equilibrium (ppm), the volume (L) of the solution and weight (g) of adsorbent, respectively.

The experiments were conducted in duplicate and the negative controls (with no adsorbent) were simultaneously carried out to ensure that absorption was by adsorbents and not by the container.

3. RESULTS AND DISCUSSION

3.1. Adsorbent characterization

Subjecting the cotton material to a simple base extraction significantly enhance the cation exchange ability. The pre-treatment of pectocellulosic materials with dilute NaOH solution may lead to saponification of esters associated with pectic chains (methylated carboxyls), which results in the increasing number of free carboxylate groups in pectic structure. This treatment may also set free primer alcohol groups esterified in cellulose molecules. In addition, extraction with dilute NaOH solutions at mild conditions may

provide stability to the material by removing soluble substances with low molecular weight. This deesterification process increases both the cation uptake ability of pectic fraction and the number of primary alcohol groups which are appropriate sites in cellulosic fraction to be esterified with citric acid. In a study [12] sugar beet pulp has been subjected to a saponification with NaOH following by a modification with formaldehyde and epichlorohydrine.

Authors have reported an increase in cation exchange capacity of base extracted sugar beet pulp due to the decrease in methylation and acetylation degrees in pectic structure. It has been reported no decrease in swelling capacity. In our study, about 34% decrease in swelling capacity and about 65% increase in cation exchange capacity were observed for a base extracted sugar beet pulp.

In the citric acid treatment stage, cellulose enriched in free primary alcohol groups may bind some extra carboxyl groups. Thus, this treatment may further enhance the cation uptake ability of sugar beet pulp. Findings show that citric acid modification applied after the base extraction is much more effective for enhancing cation exchange capacity.

A lower value of chemical oxygen demand, which is a measure of organic pollution due to the solubilization of some organic materials, for base extracted sample may show the stabilization. Much lower values of swelling and water retention capacities for modified cotton indicate that sugar beet pulp gains further stabilization via citric acid treatment. This may be due to crosslinking the cellulose fibrils through the carboxyl groups of citric acid. It can be briefly noted that a base treatment and a subsequent citric acid modification stabilize the modified cotton due to crosslinking and increase its cation uptake ability stemming from carboxylic groups inserted into molecules.

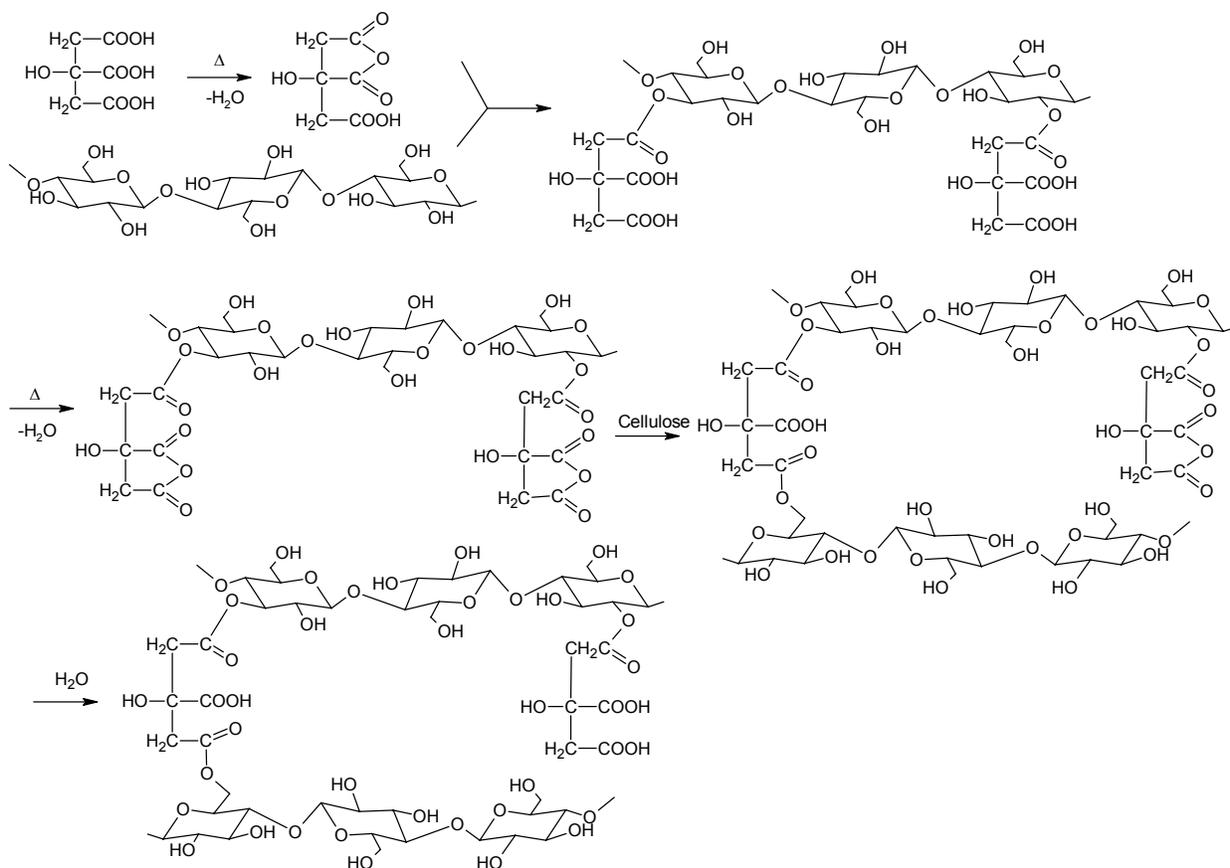


Figure 1. Thermochemical reaction of cotton cellulose and citric acid.

In contrast to hemicellulose that is easily hydrolyzed by dilute acid or base, both of cellulose and lignin are strong and resistant to hydrolysis. After base-washing, the remnant cellulose and lignin can react with citric acid during modification. The citric acid modification is schematically expressed in Fig. 1. The cellulosic hydroxyl groups combined with citric acid anhydride to form an ester linkage and introduced carboxyl groups to the straw fiber. The mechanism could be further confirmed by the FTIR spectra. The FTIR spectra of the soybean straw samples are shown in Fig. 2. As indicated in all the samples, the peaks observed at 2917 cm^{-1} can be assigned to the C-H group, and the peaks around 1063 cm^{-1} are characteristics of C=O group of primary hydroxyl stretching that may be attributed to cellulose structure of the soybean straw. Comparing with the IR spectrum of samples not citric acid modified, it could be seen that there was a strong characteristic stretching vibration absorption band of carboxyl group at 1727 cm^{-1} in IR spectrum of citric acid modified soybean straw

samples. It reflected the result of citric acid esterification [11]. The broad absorption peaks around 3382 and 3353 cm^{-1} also confirms the existence of carboxylic O–H groups (2500–3500 cm^{-1}) after citric acid modification. So, based on the porous structure and the irregular surface, as well as high amounts of introduced free carboxyl groups, it can be concluded that citric acid modified soybean straw presents an adequate physical and chemical characteristics to adsorb metal ions.

Table 1. Cellulose material samples modified by citric acid in different conditions

Entry	Reaction time (h)	Reaction temperature ($^{\circ}\text{C}$)	Mass of citric acid for 0.5 g of cellulose (g)	Yield of sample (g)
1	8	80	1.5	0.50
2	8	80	0.5	0.51
3	8	120	1.5	0.61
4	8	120	0.5	0.60
5	10	100	1.0	0.56
6	12	80	0.5	0.50
7	12	80	1.5	0.51
8	12	120	0.5	0.58
9	12	120	1.5	0.65

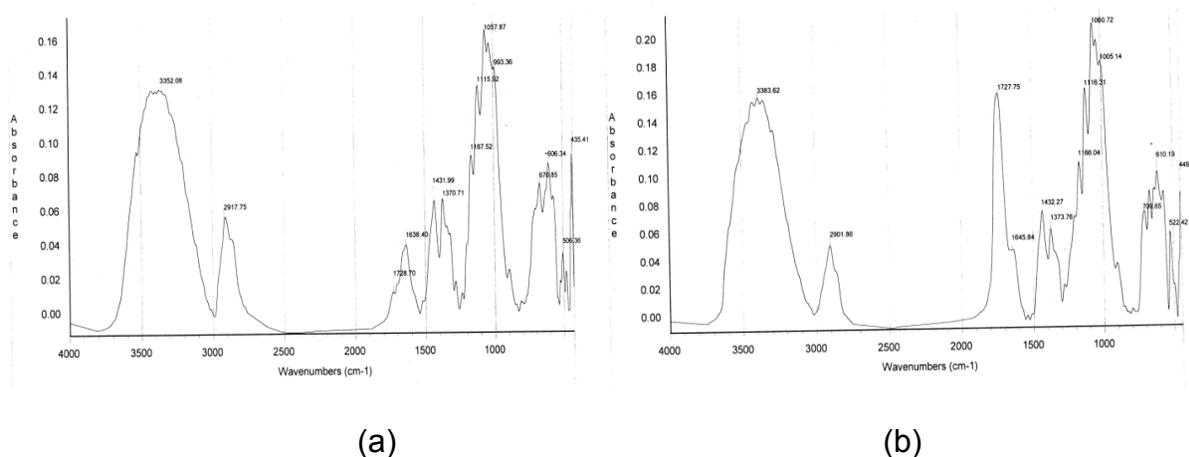


Figure 2. IR spectra of base-treated cotton material (a) and cellulose material samples modified by citric acid (b).

Like all cellulose material, the highly cellular structure gives the cotton skeleton ranging from nanometers to micrometers. Fig. 3 shows the SEM micrographs for the soybean straw samples before and after citric acid modification. Both of the samples are clearly fibrils. The raw sample exhibited rigid and highly ordered fibrils (Fig. 3a). The fibers of milled and sieved sample appeared to be separated from the initial connected structure and fully exposed (Fig. 3b).

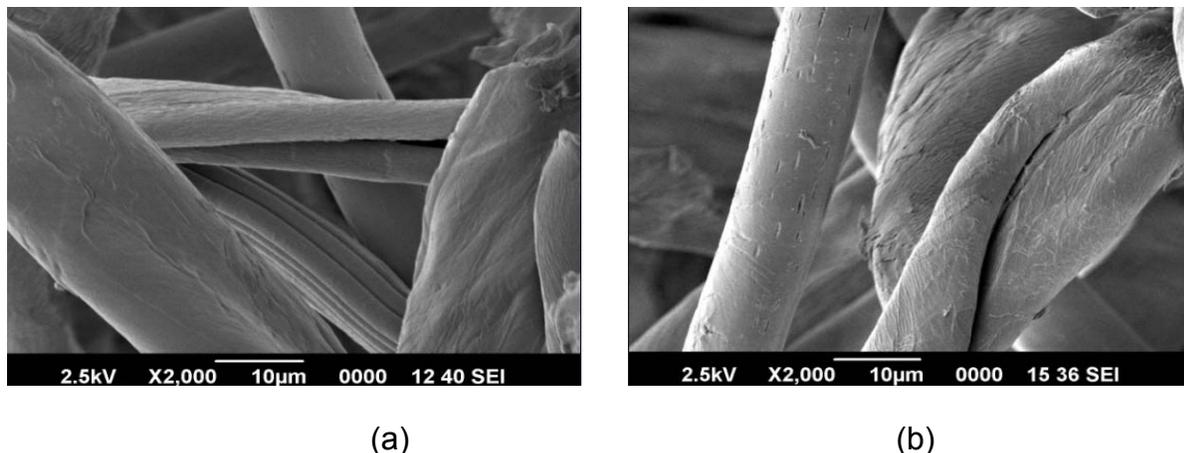


Figure 3. SEM micrographs of cotton material before and after citric acid modification: (a) base washed, (b) base washed, citric acid modified.

3.3. Effect of initial Pb^{2+} and Cd^{2+} concentrations

Several experiments were undertaken to study the effect of initial Pb^{2+} and Cd^{2+} concentrations on the Pb^{2+} and Cd^{2+} removal from the solution. The results obtained are shown in Fig. 3. For all the samples, the data show that the metal uptake increases and percentage absorption of the Pb^{2+} and Cd^{2+} increases with increase in initial Pb^{2+} and Cd^{2+} concentration. This is because at low ion concentrations the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions may interact with the adsorbent and be removed from the solution. However, at high concentrations, the driving force, i.e. concentration gradient is stronger, and the amount of Pb^{2+} and Cd^{2+} adsorbed per unit weight of adsorbent, q_e , is higher. As a result, the soybean straw adsorbent is more efficient for the wastewaters of low ion concentrations, and the

purification yield can be increased by diluting the wastewaters containing high metal ion concentrations [24] (Tables 2 and 3).

Table 2. Pb²⁺ absorption (C_o=1000 ppm) of cellulose modified by citric acid

Entry	C _e (ppm)	q _e (mg/g)
(1). 12h - 120°C - 1.5g	510.0	255.00
(2). 8h - 80°C - 1.5g	797.7	101.15
(3). 12h - 80°C - 1.5g	724.8	137.6.0
(4). 8h - 120°C - 1.5g	504.0	248.00
(5). 12h - 120°C - 0.5g	835.3	82.35
(6). 8h - 80°C - 0.5g	785.0	107.50
(7). 12h - 80°C - 0.5g	724.8	137.60
(8). 12h - 120°C - 0.5g	504.0	248.00
(9). 10h - 100°C - 1.0g	742.0	129.00

Table 3. Values of q_e depending on C_o

C _o (ppm)	Pb ²⁺		Cd ²⁺	
	C _e (ppm)	q _e (mg/g)	C _e (ppm)	q _e (mg/g)
400	176.7	111.65	161.00	119.50
600	252	174.00	276.30	161.85
800	411.8	194.10	460.30	169.85
1000	581.8	209.10	596.30	201.85
1200	701.3	249.35	753.00	223.50
1400	805	297.50	911.40	244.30
1600	962	319.00	1044.30	277.85

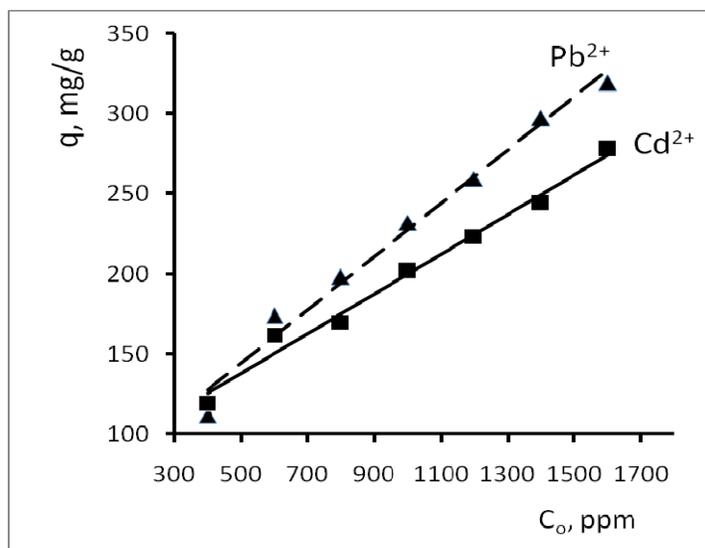


Figure 3. Values of q_e depending on C_o .

4. CONCLUSION

Cellulose samples modified by citric acid were prepared and its absorption with Pb^{2+} and Cd^{2+} ions was estimated. It's shown that cellulose samples which were modified in conditions on reaction temperature $120^{\circ}C$, reaction time 12 h and mass ratio of cellulose: citric acid=1:3 had the most capacity of absorption.

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