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Copper (II) Adsorption onto Sugar Cane Bagasse

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The separation of cupric ion from aqueous solution by adsorption onto sugar cane bagasse, cellulose and oxidized cellulose from sugar cane bagasse was studied. The adsorption equilibrium was attained in 8h at room temperature. The adsorption was found to fit the Langmuir and Scatchard isotherms and the parameter n^s (maximum adsorbent capacity) and b (adsorption intensity) were calculated. The results obtained show that physical and chemical adsorption occur simultaneously and cellulose and oxidized cellulose are better adsorbents than sugar cane bagasse with n^s 0.1669 and 0.1292 mmol g⁻¹ respectively.

Keywords: Adsorption; cupric ion; sugar cane bagasse; cellulose isotherms

INTRODUCTION

Metal ions are known to contaminate the industrial effluents, water supplies, as well as mine waters. The metals of most immediate concerns are chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium and lead [1, 2].

Cupric ion from industrial and mining effluents can eliminate all fish and marine plants from the streams for miles downstream from the source [3].

Treatments methods which should be considered include chemical precipitation, cementation, electrodeposition, solvent extraction, reverse osmosis and ion exchange [1].

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All over the world, a vast amount of agroindustrial residues are available, and the major components present in those materials are cellulose, lignin and hemicellulose. So, various functional groups such as carboxylates, carbonyls, phenolics and aliphatic hydroxyls, etc. are present at the surface.

In the last 20 years several efforts have been made in order to use this biomass as heavy metal adsorbents. Onion skins, bark, peanut skin and dyed cellulosic materials can bind metal ions [2–7]. Lignin, wood and cellulose can bind Cu(II) and Zn(II). Recently we reported the use of corn cob as ion exchange material for cupric ion [8].

In this work the study of sugar cane bagasse, cellulose and oxidized cellulose from sugar cane bagasse is studied.

EXPERIMENTAL

Sugar cane bagasse was obtained from a local alcohol plant production, washed with water and air dried. The air dried sample was ground with a Manesco Ranieri MR 340 knife mill, screened, and the fraction with 60–80 mesh particle size was separated for further work. The separated sugar cane bagasse was extracted sequentially with *n*-hexane, *n*-hexane/ethanol 80:20 and water for 24, 72 and 90 h respectively.

Hemicellulose Extraction

The extracted bagasse was treated with H₂SO₄ 2% at 120°C for 20 min in autoclave.

Cellulose Obtention

The extracted bagasse was treated with NaOH 5% at 80°C for 30 min, filtered and washed until neutralization, and dried at 50°C overnight. The dried sample was treated with formic acid under reflux for 60 min. The sample was washed with formic acid, washed with deionized water until neutralization and dried at 50°C overnight.

The delignified bagasse was treated with NaOCl in acidic media (1% HCl) under stirring for 20 min at room temperature. The sample was filtered and washed with deionized water. The bleached sample was treated with NaOH 0.1 M for 60 min at 60°C. The product was filtered and washed with deionized water, and dried overnight at 50°C.

Adsorption Experiment

Approximately 0.050 g of the adsorbent material were weighted, placed in 50 ml Erlenmeyer flask and 25 ml solution of copper acetate solutions (1.0×10^{-3} – 5.0×10^{-3} mol dm⁻³, was added. The mixtures were agitated occasionally at room temperature for 8 h. After adsorption, the samples were filtered through Whatman N°1 filter paper, and the copper concentration in the solution was determined using a Varian 175 atomic absorption spectrophotometer. The adsorbed copper concentration (Ca) was calculated from the copper remaining in solution after the equilibrium concentration (Ce) and the known initial concentration.

For desorption experiments, the adsorbent obtained in the adsorption process was washed with ~500 ml deionized water, then dried at 50°C for 24 h. Samples of ~40 mg from the adsorbent were weighted, 20 ml HCl 0.1M aqueous solution was added. The mixtures were agitated for 1 h, then filtered and the copper in solution was determined.

All adsorption and desorption data reported matched the average results obtained in at least three identical determinations.

RESULTS AND DISCUSSIONS

Experimental results for the adsorption and desorption of cupric ion onto sugar cane bagasse in batch conditions are shown in Figure 1.

It can be seen that when adsorbent was washed with deionized water, part of the Cu(II) ions were removed. The remaining ions attached to the adsorbent surface were removed with HCl 0.1M solution. The same fact was observed on the four studied samples.

All adsorptions and desorptions obey the Langmuir isotherms as shown in Figures 1 and 2.

Langmuir isotherm can be written in the form

$$Ca = \frac{n^s b Ce}{(1 + b Ce)}$$

—where Ce is the equilibrium concentration (Cu(II) concentration in solution after adsorption) and Ca is the adsorbed amount (moles of Cu(II) adsorbed per gram of adsorbent after adsorption equilibrium). The parameter n^s measures the intensity of the adsorption and b the maximum adsorbent capacity. Both n^s and b were evaluated by curve fitting of the experimental results and are shown in Table I.

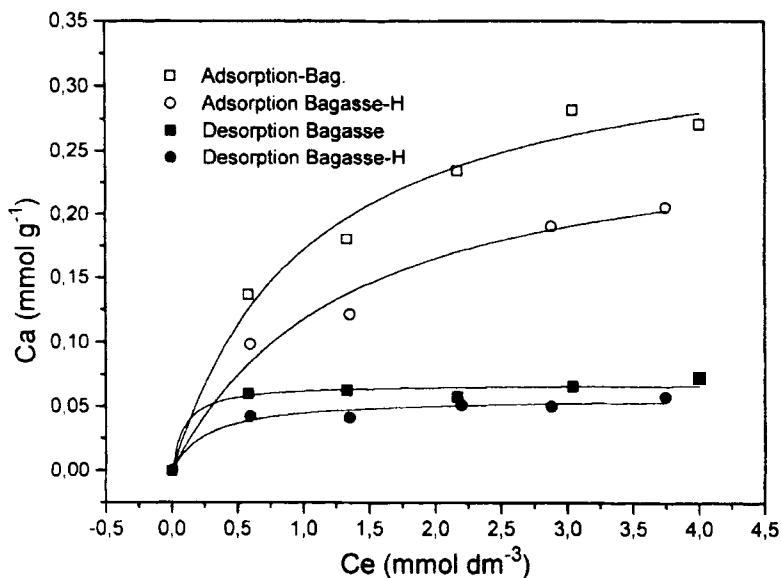


FIGURE 1 Adsorption and desorption isotherms of Cu(II) onto sugar cane bagasse with and without hemicellulose. Symbols are experimental data and solid lines are Langmuir isotherms.

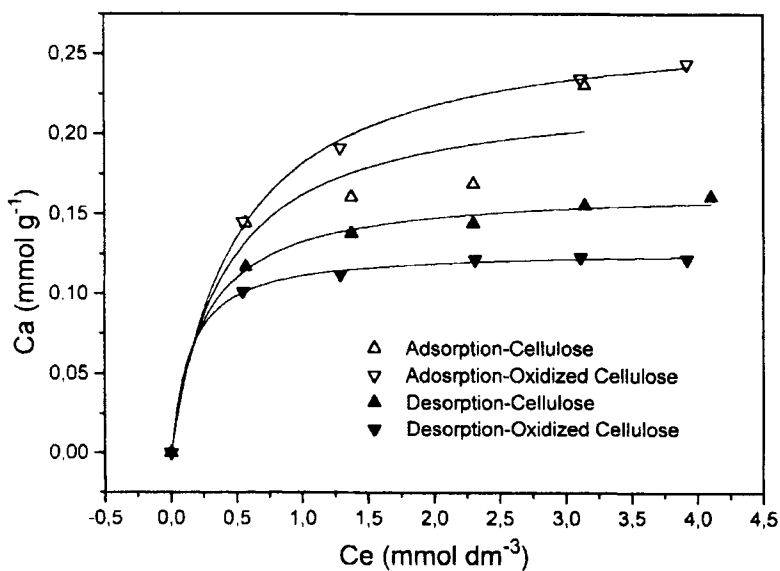


FIGURE 2 Adsorption and desorption isotherms of Cu(II) onto cellulose oxidized cellulose from sugar cane bagasse. Symbols are experimental data and solid lines are Langmuir isotherms.

TABLE I Langmuir parameters for the adsorption and desorption process of Cu(II) onto sugar cane bagasse and derivatives

	Adsorption		Desorption	
	$n^s(\text{mmol g}^{-1})$	$b(\text{dm}^3 \text{mmol}^{-1})$	$n^s(\text{mmol g}^{-1})$	$b(\text{dm}^3 \text{mmol}^{-1})$
Bagasse	0.3539	0.9455	0.0679	10.8701
Bagasse-H ¹	0.2756	0.7455	0.0572	3.6961
Cellulose	0.2279	2.4530	0.1663	3.9563
Cellulose-O ²	0.2731	1.9820	0.1281	6.7623

¹Bagasse without hemicellulose.²Oxidized cellulose.

This table shows lower values of n^s after desorption when compared with its respective values for adsorption as cited early. The b values after water washing present an increase in the interaction metal ion-surface when compared with the adsorption value. Both facts suggest physical and chemical interactions on the adsorption and chemical interactions on the desorption. The interaction strength increase observed when oxidized cellulose is compared with original cellulose is principally due to the carboxyl generation on the cellulose surface after oxidation. In the bagasse case, hemicellulose extraction produce a decrease in the n^s and b values, due probably to the higher surface area generated and weaker lignin-cellulose- hemicellulose-Cu(II) interactions than lignin-cellulose- Cu(II) interactions.

To study possible interactions between adsorption sites we applied the Hill equation [9]

$$\frac{Ca/n^s}{(1 - Ca/n^s)} = K[Ce]^n$$

where n is the Hill coefficient and K a constant (not the equilibrium constant). In the linear form

$$\ln\left[\frac{Ca/n^s}{(1 - Ca/n^s)}\right] = n \ln Ce + \ln K$$

The results are shown in Table II. It is known if there is no interaction between adsorption sites, the Hill coefficient must be equal to unity. In our study, only cellulose satisfies this condition. Oxidized cellulose has a Hill coefficient near 1 and bagasse without hemicellulose have n values very different from unity.

TABLE II Hill parameter for the desorption of Cu(II) onto sugar cane bagasse and derivatives

	<i>n</i>
Bagasse	0.371
Bagasse-H ¹	0.908
Cellulose	1.001
Cellulose-O ²	0.969

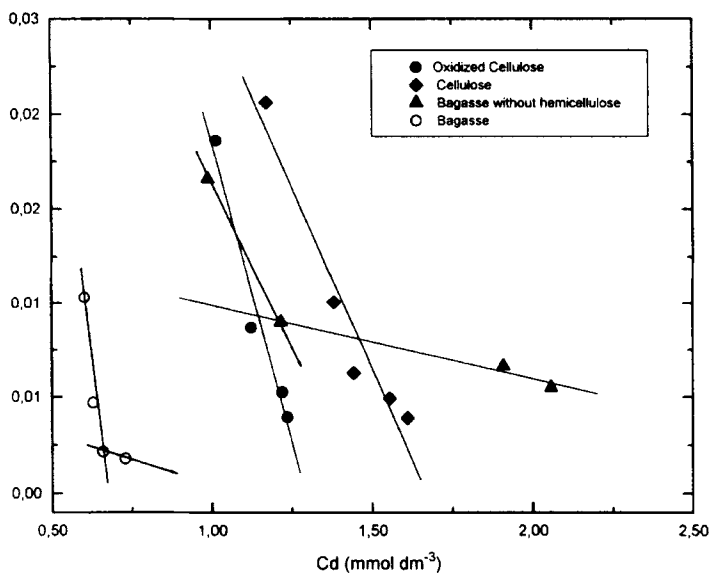
¹Bagasse without hemicellulose.²Oxidized Cellulose.

FIGURE 3 Scatchard plots for the desorption of Cu(II) onto sugar cane bagasse and derivatives.

TABLE III Scatchard parameters for desorption of Cu(II) ion onto bagasse and derivatives

	<i>n</i> ^s (mmol g ⁻¹)	<i>K</i> (dm ³ mmol ⁻¹)
Bagasse	0.0650	21.6154
	0.1098	0.4927
Bagasse-H ¹	0.1486	3.3289
	0.3423	0.3938
Cellulose	0.1669	3.8655
Cellulose-O ²	0.1292	6.3619

¹Bagasse without hemicellulose.²Oxidized Cellulose.

In order to obtain more information about the desorption process we used some mathematical modifications in the Langmuir equation. This equation can be written as

$$\frac{Ca/n^s}{1 - Ca/n^s} = KCe, \text{ Rearranging}$$

$$\frac{Ca}{Ce} = K(n^s - Ca)$$

which is known as the Scatchard equation. Plotting Ca/Ce vs. Ca we obtain a straight line with slope equal to $-K$ and intercept equal to Kn^s . If some concavity is encountered in the plot it implies that binding sites are not identical or not independent [9]. The Scatchard plots are showed in Figure 3 and corresponding K and n^s data in Table III, for the desorption process.

It is clear from figure that cellulose and oxidized celluloses presents only one adsorption site. Two adsorption sites are present in the bagasses. Comparing n values from Langmuir and Scatchard treatment, for the celluloses, we observed that they match very well but for bagasses they are very different.

CONCLUSIONS

All studied materials are able to adsorb Cu(II) ions.

Sugar cane bagasse with and without hemicellulose show more than one adsorption site as showed by Hill plots and Scatchard equation, due probably to the heterogeneous composition (cellulose and lignin) with different functional groups.

Cellulose and oxidized cellulose from sugar cane bagasse presents only one adsorption site, most probably carboxylate groups.

Better adsorbents for Cu(II) ions are cellulose and oxidized cellulose.

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