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TECHNICAL NOTE

Removal of Cupric Ions from Aqueous Solutions by Contact with Corncobs

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ABSTRACT

The separation of cupric ions from aqueous solution by adsorption onto modified corncobs (hemicellulose-free) was studied. The adsorption process was found to take ~15 minutes to attain equilibrium in experiments with continuous agitation at 35°C. The process was found to be pH-dependent, with increasing adsorption as pH increases up to 6.00. There is evidence that the adsorption mechanism is an ion-exchange one involving carboxylate groups, and that two binding sites may be present at the adsorbent. The adsorption was found to fit a Langmuir isotherm, and the parameters n^s (adsorbent capacity) and b (adsorption intensity) were calculated. The results obtained show that corncobs are an interesting adsorbent because they are available in large quantities at several places in the world at little or no cost, and they retain cupric ions rapidly. The corncobs studied also contain aliphatic and phenolic hydroxyl groups that allow for the incorporation of other functional groups and thus increase the adsorbent capacity.

INTRODUCTION

In Brazil, vast amounts of agricultural residues from cereals are available, and the major components of these materials are cellulose, lignin, and hemicellulose with various functional groups, such as carboxylates, carbonyls, phenolic and aliphatic hydroxyls, etc., present at the surface. Such residues represent a valuable raw material for various applications.

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Recent studies show that some natural materials containing proteins, tannins, polyphenolic substances, etc. may be potentially useful for the separation of various contaminants of water. For example, onion skin, bark, peanut skin, and dyed cellulosic materials for binding heavy metal ions (1–6); lignin, wood, and celluloses for binding bile salts, nitrosamines, Cu(II), and Zn(II) (7–9); corncobs for binding dyestuffs (10), etc.

In the present study the behavior of corncobs as an adsorbent for cupric ions in aqueous solution was examined under various conditions of pH, ionic strength, and counterion.

EXPERIMENTAL

The corncobs used in this study as an adsorbent were obtained locally, washed with water, and air dried. This 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 composition of the corncob sample was determined using conventional methods (11), and the following data were obtained: cellulose 32%, hemicellulose 43%, lignin 17%, extractives 6%, ash 2%, humidity 6%. The copper content in ash was also investigated, but it was not detected by atomic absorption.

The corncob sample used in the adsorption experiments (fraction of 60–80 mesh) was treated with sulfuric acid solution (2.5%) at 120°C for 15 minutes (in an autoclave) for hemicellulose extraction.

Stock copper solutions (6.0×10^{-3} mol/L) were prepared from analytical-grade reagents and standardized with EDTA. Approximately 0.1500 g of adsorbent samples were weighed, placed in 50 mL Erlenmeyer flasks, and 20.0 mL of copper solutions (6.0×10^{-3} to 0.5×10^{-4} mol/L) was added. The mixtures were shaken in a Dubnoff-145 Fanem thermostatic bath for a desired contact time period (normally 1.0 hour). Finally, the contents were filtered through Whatman No. 1 filter paper, and the copper concentration in the solution was determined using a Varian-175 atomic absorption spectrophotometer. The adsorbed copper concentration (C_a) was calculated from the copper remaining in solution and the known initial concentration. A digital Micronal B 375 was used for pH measurements with a buffer solution of acetic acid/sodium acetate for pH control. Sodium chloride solutions were used for ionic strength adjustment.

For desorption experiments, the adsorbent obtained in the adsorption process was washed with ~500 mL deionized water, then dried at 50°C for 24 hours. Samples of ~0.1200 g from this adsorbent were weighed, 20.0 mL HCl of a 0.10 mol/L aqueous solution was added, the mixture was agitated for 1.0 hour, then filtered, and the copper content in the solution was determined.

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

RESULTS

Experimental results for the adsorption of cupric ion onto corncobs with various contact times are shown in Fig. 1. Cupric ion adsorption attained equilibrium rapidly, in ~15 minutes, at 35°C with continuous agitation.

Data in Table 1 illustrate the influence of temperature and agitation on cupric ion adsorption onto corncobs. These results show a great increase (~90%) in the adsorbed concentration (C_a) due to agitation, and a small increase (~4%) due to an increase of 5°C in the temperature.

All other experiments were performed at 35°C with continuous agitation and 60 minutes of contact time.

Cupric ion uptake at different ratios of volume per gram of adsorbent are given in Table 2. The cupric ion uptake increases linearly as the volume per gram ratio increases in the range considered. The 132.64×10^{-3} L/g volume per gram ratio was used in all other experiments.

Solutions of acetate, chloride, and sulfate were used for analyzing the counterion effect. The adsorption isotherms obtained are shown in Fig. 2. An increase in cupric ion uptake in the order acetate > chloride > sulfate is evident. This counterion effect is pH-dependent, as can be seen in the data shown in Table 3. The major cupric ion uptake in $CuAc_2$ solution coincides with the higher pH. There is a buffering effect in the acetate

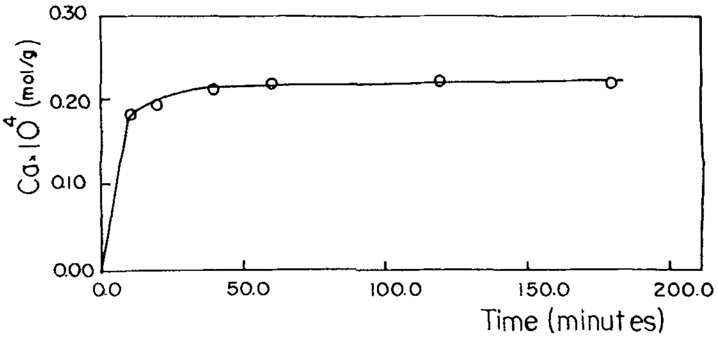

FIG. 1 Effect of contact time on the adsorbed cupric ion concentration onto corncob (C_a). Experimental conditions: $CuCl_2$ solution, initial concentration 1.50×10^{-3} mol/L, unbuffered, continuous agitation; 35°C.

TABLE 1
Effect of Temperature and Agitation in Cupric Ion Adsorption onto Corncobs. Experimental Conditions: $CuCl_2$ Solution 1.00 × 10^{-3} mol/L; 60 minutes

Temperature (± 0.5°C)	Agitation	$C_a \times 10^4$ (mol/g)
25.0	Continuous	0.8607
25.0	Occasionally	0.4391
30.0	Occasionally	0.4684
35.0	Continuous	0.8800

TABLE 2
Cupric Ion Uptake from $CuCl_2$ Solution (initial concentration 1.00 × 10^{-3} mol/L) by Corncobs at 35°C

Volume per gram × 10^3 (L/g)	$C_a \times 10^4$ (mol/g)
39.82	0.1058
49.60	0.2716
66.05	0.4268
132.64	0.8777

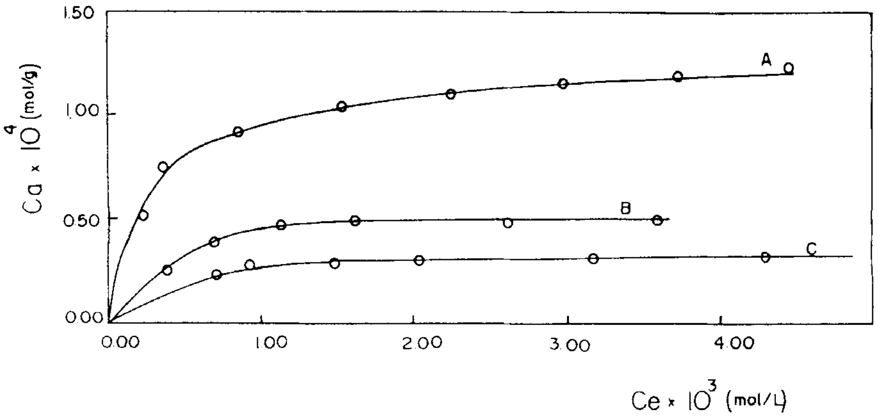

FIG. 2 Adsorption isotherms of cupric ion on corncobs. Experimental conditions: (A) $CuAc_2$ solution, 0.62 × 10^{-3} to 5.4 × 10^{-3} mol/L initial concentrations; (B) $CuCl_2$ solution, 0.59 × 10^{-3} to 3.99 × 10^{-3} mol/L initial concentrations; (C) $CuSO_4$ solution, 0.89 × 10^{-3} to 4.12 × 10^{-3} mol/L initial concentrations.

TABLE 3
pH Data for Adsorption Experiments When the Copper Counterion and the Copper Initial Concentrations Were Varied

	$CuAc_2$ solution pH		$CuCl_2$ solution pH		$CuSO_4$ solution pH	
Exp.	Initial	Final	Initial	Final	Initial	Final
1	6.08	5.18	5.31	4.05	5.10	3.79
2	5.96	5.11	5.24	4.09	5.04	3.74
3	5.95	5.05	5.14	3.95	5.02	3.69
4	5.94	4.97	5.12	3.89	4.92	3.64
5	5.93	4.87	5.06	3.60	4.78	3.60
6	5.91	4.66	5.01	3.60	4.73	3.59
7	5.88	4.60			4.68	3.39
8	5.85	4.58				

solution that minimizes pH variations. The results also show a pH decrease when cupric ion concentration increases (Experiments 1–8 in Table 3) due to equilibrium displacement of the copper complexes in aqueous solution.

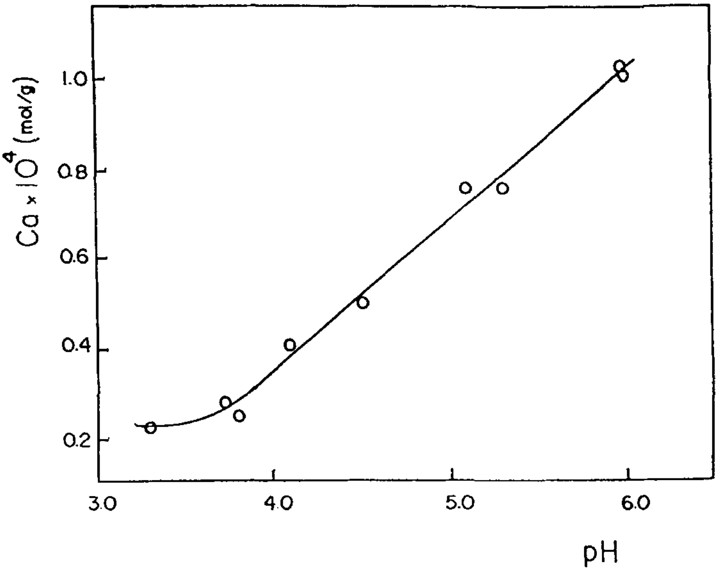

FIG. 3 pH dependence of the adsorption of cupric ion on corncobs. Experimental conditions: initial cupric ion concentration, 1.00×10^{-3} mol/L; 35°C.

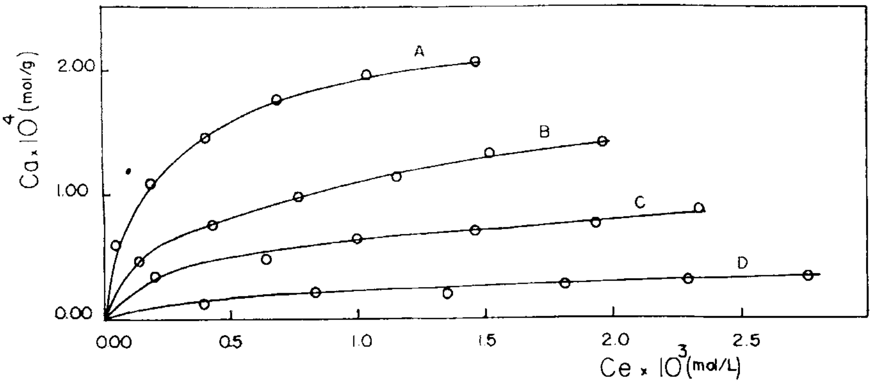

FIG. 4 Adsorption isotherms of cupric ion (from $CuAc_2$ buffered solutions) on corncob at various solution pH values: A, 6.00; B, 5.30; C, 4.50; D, 3.30.

Figure 3 shows the pH effect on adsorbed concentration. In the acidic region the adsorbed concentration is very low (but not zero) and increases from pH ~ 4.0 to pH ~ 6.0. Experiments at higher pH are not possible because of copper hydroxide precipitation.

On the other hand, a decrease of pH after cupric ion adsorption was always observed (Table 3), suggesting an ion-exchange mechanism.

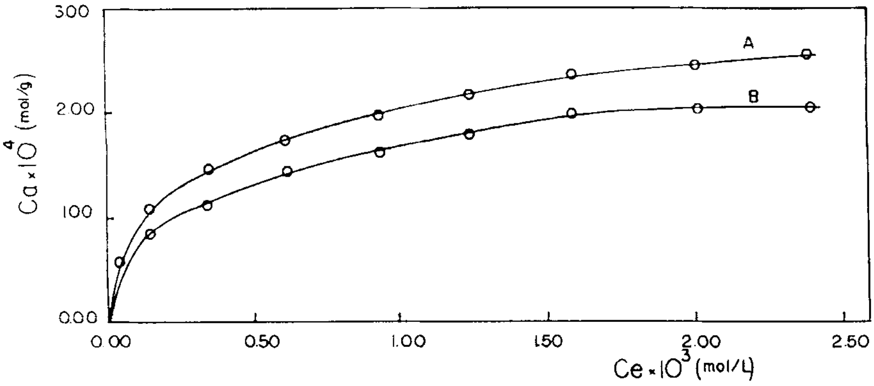

FIG. 5 Adsorptions isotherms of cupric ion ($CuCl_2$ unbuffered solution) on corncob. A: No added salt; B: NaCl 0.9 mol/L.

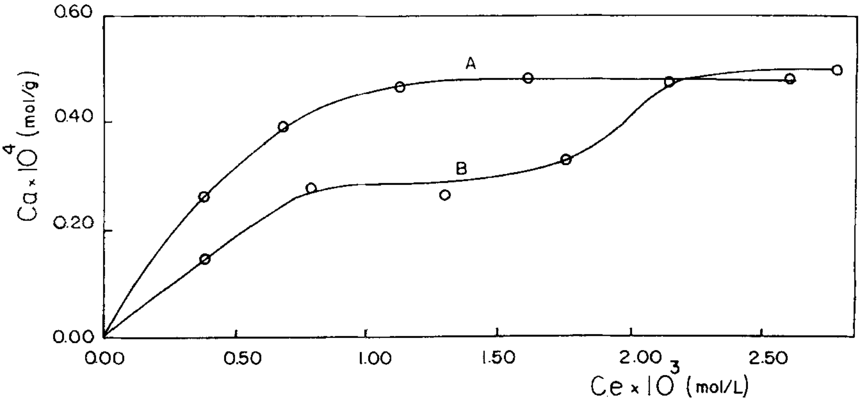

FIG. 6 A: Adsorption isotherm; B: desorption isotherm from adsorbent used in A, washed with deionized water. Buffered $CuAc_2$ solution, pH 6.00, for adsorption isotherm; HCl 0.1 mol/L solution for desorption isotherm.

The isotherms in Fig. 4 were obtained in adsorption experiments using $CuAc_2$ buffered solutions (pH = 3.30, 4.50, 5.30, and 6.00) and also show an increase in C_a as pH increases.

Isotherms obtained by varying the ionic strength (different NaCl concentrations) were also analyzed. Three NaCl concentrations were used: 0.1, 0.5, and 0.9 mol/L. Minimum variations were observed in the corresponding three isotherms. The presence of a neutral salt resulted in a change of the adsorption isotherm shape (Fig. 5). A two-step isotherm was obtained, which suggests there are two binding sites in the adsorbent.

When the adsorbent (separated after contact with cupric ion solution in the adsorption experiments) was washed with water, some Cu(II) ions were removed. The remaining ions attached to the adsorbent were removed with an HCl 0.1 mol/L solution. The results in Fig. 6 illustrate this fact.

DISCUSSION

The adsorption and desorption isotherms obeyed the Langmuir isotherm equation. Such isotherm may be written in linear form as

$$C_e/C_a = 1/n^s b + C_e/n^s$$

where C_e is the equilibrium concentration [Cu(II) in solution after adsorption equilibrium], and C_a is the adsorbed concentration [mols of Cu(II) per gram of corncob after adsorption]. C_a approaches the limiting value n^s at sufficiently high concentrations. The Langmuir parameters n^s and b are measures of the adsorbent capacity and the intensity of the adsorption, respectively (12). Both n^s and b were evaluated from C_e/C_a versus C_e plots. Representative data are collected in Table 4. These results show an increase in the adsorbent capacity when the buffered solution (pH 6.00) is used in the adsorption experiment (see Table 4, Experiments 1 and 4). This great increase in capacity (~160%) corresponds to a variation of ~1.3 in the pH (for the unbuffered solution, the equilibrium pH is ~4.7 at saturation, see Table 4).

Comparison of the adsorption with the corresponding desorption experiments (1 and 5, 4 and 6 in Table 4) shows that the adsorbent capacity decreases as expected because cupric ions are removed when the adsorbent is washed with water. This weakly attached cupric ions removal is also reflected in the b parameter values, which increase in the desorption experiments.

The Langmuir isotherm is valid if adsorption sites and adsorbate molecules are independent and equivalent. Nevertheless, adsorption data for mixtures of adsorbates and adsorbents with different adsorption sites are known to obey the Langmuir adsorption isotherm (10, 13, 14).

In this case, corncobs are mainly cellulose- and lignin-based (hemicellulose was extracted because of its instability and complex structure), so more than one active site is possible. pH influence in the adsorbed concentration is observed, which suggests carboxylate group participation. These carboxyl groups are formed by oxidation of the hydroxy groups of the cellulose. The pK_a of these carboxyl groups is ~4.0 (15), and they should act as weak acidic cation exchangers above pH 4.

The adsorption of cupric ions on corncobs is considerably enhanced by increasing the pH (see Fig. 3), and the use of a buffered solution of pH ~ 6.00 is therefore recommended. The use of a buffered solution is also

TABLE 4
Parameters from Langmuir Isotherms

Experiment	Conditions	$n^s \times 10^3$ (mol/g)	b (mol/L)
1. Adsorption	$CuAc_2$, unbuffered	0.1324	2.324
2. Adsorption	$CuCl_2$, unbuffered	0.0589	3.032
3. Adsorption	$CuSO_4$, unbuffered	0.0359	2.786
4. Adsorption	$CuAc_2$, buffered, pH 6.00	0.3441	1.661
5. Desorption	$CuAc_2$, unbuffered	0.0916	2.970
6. Desorption	$CuAc_2$, buffered, pH 6.00	0.2367	2.414

important because of pH variation with cupric ion concentration and counterion (see Table 3).

There is also minor adsorption in the acidic region, in which all the carboxyl groups should be completely protonated. This fact suggests that some nonelectrostatic binding involving forces such as van der Waals occurs.

On the other hand, by adding a neutral salt (NaCl) in the adsorption experiment, a two-step isotherm is obtained (Fig. 5). This change of isotherm shape was also observed in other systems (9) and was tentatively attributed to modification in functional groups conformation to give two binding sites. The hypothesis that a cupric ion can attach itself to two adjacent hydroxyl groups (3), thereby releasing hydrogen ions into solution, can also take place with phenolic hydroxyl groups, principally in the higher pH region.

CONCLUSIONS

Adsorption of Cu(II) ions onto corncobs take a few minutes when the system is continuously agitated at 35°C. The adsorption process is pH-dependent and increases up to pH 6.00.

The maximum adsorbed concentration attained was 0.3441 mmol/g. The decrease of pH after adsorption suggests an ion-exchange mechanism involving carboxylate groups. Two binding sites may be present at the adsorbent according to the shape of isotherms obtained with variations of the ionic strength. Adsorption and desorption isotherms obey the Langmuir equation, thus allowing for estimation of n^s (adsorbent capacity) and b (adsorption intensity).

The results reported here show that corncobs seem to be good substrates for the binding and recovery of cupric ions in aqueous solutions. This conclusion is also supported by recent work from this laboratory showing that some simple chemical modifications can increase the adsorbent capacity several times. Corncobs may represent a promising and cheap alternative to expensive commercial ion-exchange resins.

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