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Effects of Temperature and pH on Adsorption Isotherms for Cupric and Cadmium Ions in Their Single and Binary Solutions Using Corncob Particles as Adsorbent

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ABSTRACT

The effect of temperature on the adsorption isotherms for cupric and cadmium ions by corncob particles was investigated. The uptake of the two types of ions by corncob particles increased with temperature in the ranges between 25°C and 65°C and between 15°C and 65°C for copper and cadmium, respectively. In addition, a study on the competitive adsorption of copper and cadmium ions from their mixture by the adsorbent was also conducted. The tests showed that the uptake of copper ions in the mixture increased with increasing the total metal ion concentration.

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However, the uptake of cadmium ions from the mixtures first increased, reached a maximum point, and then decreased with increasing the total metal ion concentration resulting in inversed U-shape isotherms. To describe these inversed U-shape isotherms, a new competitive adsorption model with interaction factors was proposed and its constants were estimated. From the tests, it can be concluded that the cupric ions had stronger affinity than the cadmium ions for the corncob particles during the competitive adsorption.

Key Words: Corncob; Copper; Cadmium; Mixture; Competitive adsorption; Isotherm; Model; Temperature.

INTRODUCTION

It has been widely recognized that heavy metal ions in aqueous systems create a lot of problems for humans, animals, and plants. These ions are often found in wastewaters from various industrial processes. Various processes can be applied for their removal from aqueous industrial effluents. Adsorption processes are very often used for this purpose and, in that case, they are influenced by some factors such as the nature and the size of adsorbents, the pH value, temperature, ionic strength, and buffer capability of aqueous solutions. Among them, the pH value and temperature are considered the most important factors. Therefore, effects of these two parameters are reported very often in the literature.[1–11] Temperature is a very important parameter in industrial wastewater treatments and in self-purification of natural water systems. Although the temperature of water in nature can be from above 30°C in the tropics to near 0°C in the frigid zones, industrial wastewaters have a wider temperature range.

Industrial wastewaters often contain two or more kinds of metal ions. The interaction among these ions and the competition for the active sites of adsorbents will influence adsorption equilibrium. There are two approaches for investigating the competitive adsorption of metal ions on adsorbents. One approach is based on the measurement of the uptake of metal ions with the pH change at a constant initial total metal ion concentration, and it provides the adsorption edge curves.[12,13] The other approach is based on monitoring the uptake of metal ions with various initial total metal ion concentrations at an initial pH value, and it results in the adsorption isotherms.[14–17]

In this study, corncob particles were used for the adsorption of cupric and cadmium ions. Its objectives were to:

1. Investigate the effect of temperature on the adsorption equilibrium of the cupric and cadmium ions by corncob particles;

2. Investigate the effect of pH on the competitive adsorption of the cupric and cadmium ions by corncob particles;
3. Propose a novel competitive adsorption isotherm model to describe the inversed U-shape isotherms.

DEVELOPMENT OF A NOVEL EQUILIBRIUM MODEL FOR THE COMPETITIVE ADSORPTION

In the present study of the adsorption of copper and cadmium from their mixture it was observed that the uptake of cadmium by corncob particles first increased, reached a maximum point, and then decreased, resulting in inversed U-shape isotherms,[18] while the uptake of copper increased with increasing the total metal ion concentration. In a competitive adsorption using binary systems, usually, the uptake of both metal ions increases with increasing their concentrations.[16,17] The existing adsorption models, which are applied for mixtures, such as those for the binary Langmuir and Freundlich isotherms, cannot describe this phenomenon because they predict an increase in the uptake of both competitive solutes with an increase in the solute concentration.

In general, the uptake of metal ions in a competitive adsorption is less than that of the individual adsorption. Therefore, it is supposed that the uptake of a kind of metal ion in a competitive adsorption could be described by a formula as the difference between the uptakes of two kinds of metal ions in their individual adsorptions. Since it is impossible to predict precisely a mixture behavior from individual data only, it is necessary to introduce some parameters to this formula. Schay et al.[19] developed a modified binary Langmuir model in which interaction factors were introduced to describe mixture isotherms. In this model the Langmuir parameters from the individual isotherms were applied, whereas the interaction factors were estimated from competitive adsorption data. Therefore, four interaction factors were introduced in the following equations for a competitive adsorption:

$$q_1 = \frac{\delta_1 q_{m1} K_{l1} c_{e1}}{1 + \delta_1 K_{l1} c_{e1}} - \frac{\delta_2 q_{m2} K_{l2} c_{e2}}{1 + \delta_2 K_{l2} c_{e2}} \quad (1)$$

$$q_2 = \frac{\varepsilon_2 q_{m2} K_{l2} c_{e2}}{1 + \varepsilon_2 K_{l2} c_{e2}} - \frac{\varepsilon_1 q_{m1} K_{l1} c_{e1}}{1 + \varepsilon_1 K_{l1} c_{e1}} \quad (2)$$

where subscripts 1 and 2 denote the copper and cadmium ions, respectively, q_m and K_l are the maximum adsorption capacity and the Langmuir equilibrium constant in a single isotherm, while δ and ε are the interaction factors, which are regressed for competitive isotherms, and q and c_e are the uptake by the adsorbent and concentration of metal ion in the solution. It should be noted that Eqs. (1) and (2) are reduced to the Langmuir model for a single component as δ_2 and ε_1 approach zero.

CALCULATION OF ENTHALPY CHANGES, EQUILIBRIUM CONSTANTS OF ADSORPTION

The enthalpy change, ΔH, of adsorption can be calculated from the Van't Hoff equation:[20]

$$\frac{d \ln K_e}{dT} = \frac{\Delta H}{RT^2} \tag{3}$$

Integrating Eq. (3) and taking into consideration the relationship between the free energy and equilibrium constant, and the definition of free energy,[21] the following expression is obtained:

$$\ln K_e = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{4}$$

where ΔS is the entropy change of adsorption, R is the gas constant, and T is the absolute temperature.

Equation (4) shows that the logarithm of the equilibrium constant is an inverse function of temperature. A plot of $\ln K_e$ vs. $1/T$ should yield a straight line from which slope the enthalpy change of adsorption can be calculated.

It is noted that the value of the equilibrium constant depends on the adopted reaction equation. For example, the Langmuir equilibrium constant, K_l, represents the following adsorption reaction:

$$SO^- + Me^{2+} \Leftrightarrow SOMe^+ \tag{5}$$

where SO^- is the unoccupied surface active site at equilibrium, $SOMe^+$ is the occupied surface active site by metal ions at equilibrium, and Me^{2+} is metal ion.

Since the ion exchange between active sites on the cell surface and solutes occurs in the adsorption process, the following reaction may be more appropriate:

$$SOH + Me^{2+} \Leftrightarrow SOMe^+ + H^+ \tag{6}$$

The relationship between the equilibrium constants for reactions (5) and (6) is given by the following equation:

$$K_e = [H^+]K_l \tag{7}$$

EXPERIMENTAL

Material and Methods

The corncobs used in this study were provided by Flynn Produce Ltd. Mississauga, ON, Canada. The crude corncobs were dried at 70°C for 48 h and cut into particles in a granulator (Laboratory Mill, Model 4, Arthur H. Thomas Company). The particles were suspended in deionized water under agitation for 20 min. Ten minutes following the agitation, the supernatant containing some light particles was removed. The washing operation was repeated three times, and the residual solids were dried at 100°C for 48 h.

Metal solutions: 5000 and 1000 mg/l cupric and cadmium stock solutions were prepared from cupric nitrate [$Cu(NO_3)_2 2 1/2 H_2O$, certified A. C. S., Fisher Scientific] and cadmium nitrate [$Cd(NO_3)_2 4H_2O$, certified A. C. S., Fisher Scientific]. The nitrate as an anion was selected since it rarely forms any complexes with metal ions.

Buffers: MES buffer [2-[N-Morpholino]ethanesulfonic acid, $C_6H_{13}NO_4S$, Sigma Chemical Co.], which has been demonstrated to hardly bind with cupric ions,[22] was used for copper in the pH range of 4.0–5.5, and HEPES buffer (N-[2-Hydroxyethyl]piperazine-N′-[2-ethanesulfonic acid], $C_8H_{18}N_2O_4F$, Sigma Chemical Co.) was used for cadmium in the pH range of 6.0–8.3. The buffers were 0.05 M.

Analytical Methods

Cupric and Cadmium Ion Measurement

The cupric and cadmium ion concentrations in the solution were measured by an Atomic Absorption Spectrophotometer (Varian Techtron Pty. Limited, AA1475 Series) at a wavelength of 324.8 nm for copper and 228.8 nm for cadmium. The spectrophotometer was calibrated using a series of standard solutions prepared from 1000 mg/l copper and cadmium reference solutions (Fisher Scientific) for each run.

pH Measurement

The pH of the suspension was measured by a Fisher pH meter (AR50, Fisher Scientific) with a combined electrode (accuTup+, Cat. 13-620-185, Fisher Scientific) and an automatic temperature compensation probe. Buffer solutions for pH 4.00, 7.00, and 11.00 (Fisher Scientific) were used for calibration.

Experimental Techniques

Adsorption Isotherms

Tests were performed in 125 mL Pyrex flasks immersed in a thermostat, which was maintained at required temperatures. First, buffer was prepared according to Perrin and Dempsey[23] by adding 400 mL of deionized water and the required amount of a solid buffer salt into a 1000 mL flask contained in the thermostat. A 2 M NaOH aqueous solution was used to obtain the required pH of the buffer solution. The solution was distributed into eight 125 mL flasks containing 0.500 g corncob particles each. An amount of the cupric and/or cadmium nitrate stock solution of 1000 mg/l was added to each flask to obtain the required metal ion concentration. The final volume in each flask was 50 mL. The flasks were incubated in a shaker at a constant temperature for at least 12 hr. A preliminary study of the adsorption kinetics for these ions by corncob particles showed that the adsorption equilibrium was attained in a 4 hr process even with the highest metal concentration used in the present study.

At the end of the incubation, a 3 mL sample was taken from each flask. Corncob particles were separated from the sample by the vacuum filtration through a 0.45 μm filter paper (Millipore Corporation), and the filtrate was analyzed for these metals as previously described.

When water instead of buffers was used for metal adsorption, the pH of 400 mL of deionized water was adjusted to a desired initial value either with 0.1 M NaOH or 0.1 M HNO_3 solutions (Fisher Scientific). After distributing the water into eight 125 mL flasks containing 0.500 g of corncob particles each, the metal solution was added and the pH was readjusted to the desired initial value. Other treatments of the suspensions were the same as in the case of buffer solutions.

The range of the initial metal ion concentrations for a single component was usually from 20 mg/l to 100 mg/l, but in some cases the maximum concentration was 140 mg/l. In binary systems, the ratio of concentrations of copper to cadmium ions in the solutions was (w/w) 1.00 and 0.565, or (mol/mol) 1.77 and 1.00. The total metal ion concentration range in the binary systems was from 40 mg/l to 200 mg/l.

To check for the appearance of metal precipitate at higher pH values, tests were carried out at a pH of 5.9 for copper and at 8.3 for cadmium. A 6 mL sample was taken from each flask. Three milliliters of the sample were filtrated and the metal concentrations were measured in both the filtrate and in the part of the sample that was not filtrated. Considering that the relative errors between the metal ion concentrations in the nonfiltrated sample and the filtrate were 1.14% and 0.91% for copper and cadmium, respectively, it was concluded that the precipitates were not formed under the tested conditions.

RESULTS AND DISCUSSION

Effect of Temperature on Isotherm

It is well known that a change of temperature can cause a shift of chemical equilibrium (uptake for adsorption) of either exothermic or endothermic reactions. The effect of the temperature on the adsorption isotherms of cupric ions by corncob particles in the presence of MES buffer at pH 5.5 and temperatures 25°C, 35°C, 45°C, 55°C, and 65°C, and cadmium ions using HEPES buffer at pH 7.6 and temperatures 15°C, 25°C, 45°C, 55°C, and 65°C were examined in this study and the results are shown in Figs. 1 and 2, respectively.

It was determined that the uptake of cupric and cadmium ions increase with temperature. This confirms other researchers' observations. Sag and Kutsal[11] reported that the uptakes of Pb^{2+}, Cr^{6+}, and Fe^{3+} by the biomass of *R. arrhizus* and *Z. ramigera* increased when the temperature increased from 15°C to 45°C. Aksu and Kutsal[7] also showed that the lead uptake by the biomass of *Chlorela vulgaris* increased with an increase in temperature from 15°C to 35°C. Kuh and Kim[1] indicated that the removal efficiency enhanced to 99.35% at 55°C from 97.61% at 25°C for adsorption of cadmium ion by waste egg shell.

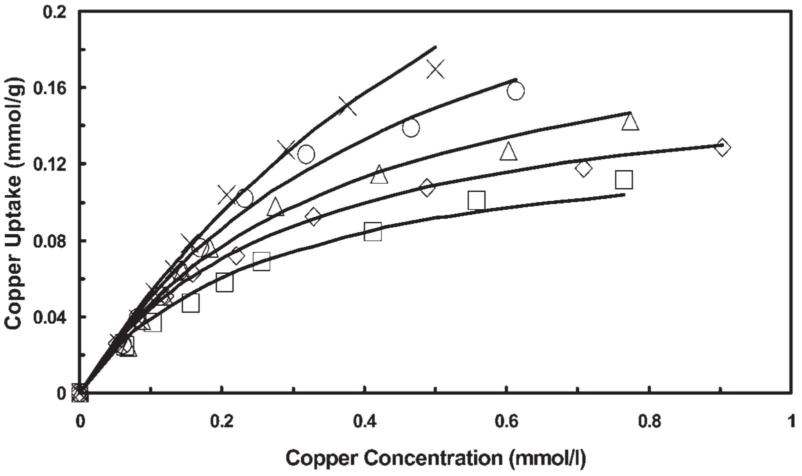

Figure 1. Temperature effect on copper isotherms in MES (mixed size of particles—corncob conc. 10 g/l, pH 5.5). □, 25°C; ◇ , 35°C; Δ, 45°C; ○, 55°C; ×, 65°C. Symbols are experimental data, and solid lines are predicted data using Eq. (8).

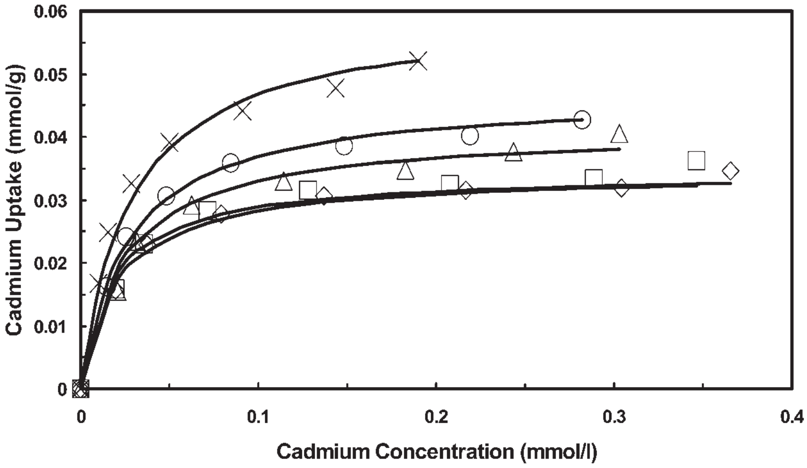

Figure 2. Temperature effect on cadmium isotherms in HEPES (mixed size of particles—corncob conc. 10 g/l, pH 7.6). ◇ , 15°C; □, 25°C; Δ, 45°C; ○, 55°C; ×, 65°C. Symbols are experimental data, and solid lines are predicted data using Eq. (8).

The Langmuir model

$$q = \frac{K_l q_m c_e}{1 + K_l c_e} \tag{8}$$

was fitted to the experimental data in Figs. 1 and 2. The Langmuir equilibrium constants and the maximum adsorption capacities, which are obtained by the fitting, are listed in Tables 1 and 2 for each of the associated isotherm data. These data show that the maximum adsorption capacity of the adsorbent increased with increasing temperature for both of the tested metal ions. This is in agreement with the observations reported in the literature.[5–7] For example, Johnson observed that the maximum adsorption capacity of goethite for cadmium approximately doubled as the temperature increased from 10°C to 70°C.

Table 1. Parameters q_m and K_l in Langmuir model (Eq. 8) for copper in MES at pH 5.5 and various temperatures.

Temperature (°C)	25	35	45	55	65
q_m (mmol/g)	0.140	0.171	0.214	0.294	0.464
K_l (l/mmol)	3.80	3.50	2.80	2.07	1.28

Table 2. Parameters q_m and K_l in Langmuir model (Eq. 8) for cadmium in HEPES at pH 7.6 and various temperatures.

Temperature (°C)	15	25	45	55	65
q_m (mmol/g)	0.0342	0.0367	0.041	0.0467	0.060
K_l (l/mmol)	53.6	47.2	41.3	37.5	35.0

The data (Tables 1 and 2) also show that the Langmuir equilibrium constant, K_l, decreases with increasing temperature. This suggests, according to the chemical equilibrium principles, that the adsorption processes of cupric and cadmium ions by corncob particles are exothermic. The results also show that the maximum adsorption capacity of corncob particles is more sensitive to temperature change for copper than for cadmium. For example, the ratio of the maximum adsorption capacity for copper at 65°C to 25°C is 3.31, whereas for cadmium it is 1.64.

Figures 3 and 4 show the plots of the natural logarithm of equilibrium constants vs. inverses of absolute temperatures, the slopes and intercepts of which indicate the enthalpy (-19.0 kJ/mol for copper and -6.38 kJ/mol for cadmium) and the entropy [-99.6 J/(molK) for copper and -77.6 J/(molK) for cadmium] changes of adsorption.

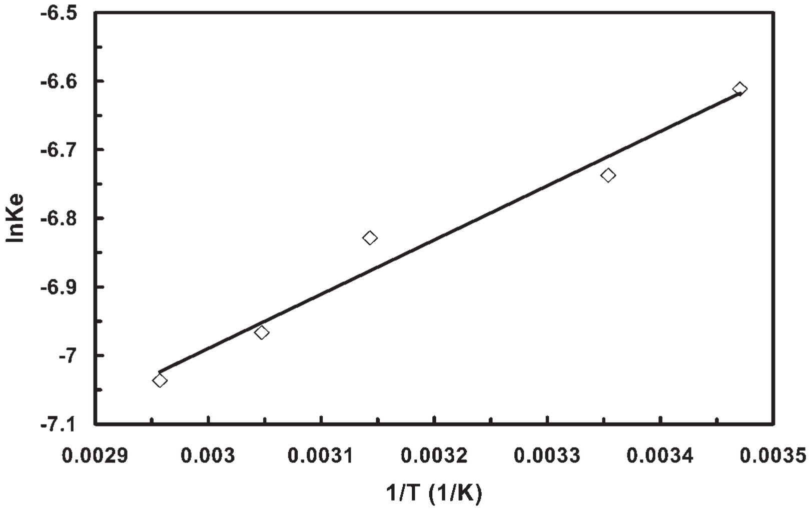

Figure 3. Effect of temperature on equilibrium constant K_e in copper adsorption by corncob particles. ◇ , experimental data. Solid line refers to Eq. (4).

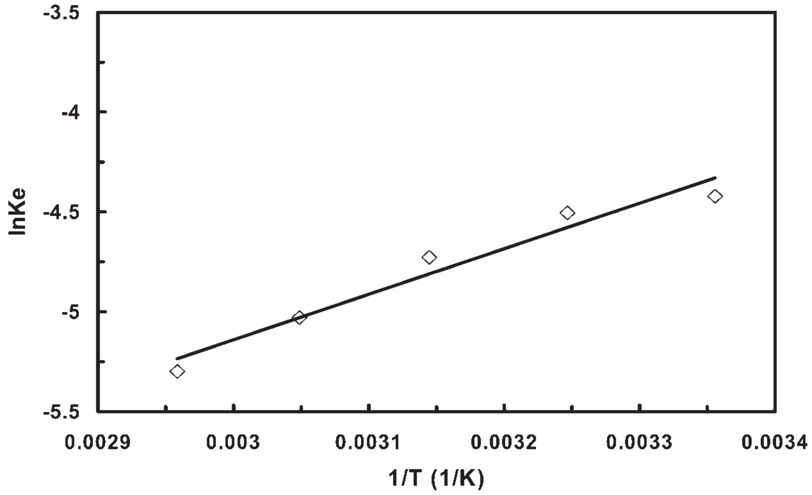

Figure 4. Effect of temperature on equilibrium constant K_e in cadmium adsorption by corncob particles. ◇ , experimental data. Solid line refers to Eq. (4).

The negative values of enthalpy changes show that the adsorption processes of cupric and cadmium ions on the corncob particles are exothermic. Sun and Shi[24] reported that the changes of enthalpy of cupric ion adsorption on sunflower stalks were -6.143 and $-40.57\,\mathrm{kJ/mol}$ for particle sizes <60 mesh and 25–45 mesh, respectively.

In general, gas adsorption processes are exothermic due to the liberation of heat for the change of state of gas.[25] However, for metal ion adsorption in a solution either an exothermic or endothermic process is possible because of the implication of the ion exchange mechanism. In this mechanism, the protons on the surface of adsorbent are replaced by metal ions in a solution. Therefore, in metal ion adsorption processes (Eq. 6), the reactions of the protons desorption (Eq. 9) from the active sites and the metal ions adsorption by the active sites are implicated (Eq. 5).

$$\mathrm{SOH} \Leftrightarrow \mathrm{SO^-} + \mathrm{H^+} \tag{9}$$

Considering that the desorption of protons from the adsorbent surface is an endothermic reaction,[26] and if the absolute value of the enthalpy change (Eq. 5) is greater than the enthalpy change of the desorption of proton (Eq. 9), the adsorption process would be exothermic; otherwise, the process would be endothermic.

From the intercepts of the straight lines in Figs. 3 and 4, the entropy changes of adsorption were calculated, and they are $-99.6\,\mathrm{J/(molK)}$ and $-77.6\,\mathrm{J/(molK)}$ for copper and cadmium, respectively.

Entropy has been defined as the degree of chaos of a system. If the mechanism of ion exchange is considered during the adsorption process, the adsorbate ions upon their association with the surface of the adsorbent lose their degree of freedom. The degree of freedom of the released protons from active sites on the surface is enhanced. According to the statistical thermodynamics, the entropy change is a function of the number of ways Ω. In general, the number of ways of arranging N identical particles of configuration $\{n_1, n_2, \ldots\}$, i.e., n_1, in one group, n_2 in another group, n_3 in another group, and so on, is

$$\Omega = N!/(n_1!n_2!n_3!\ldots n_i!\ldots) \tag{10}$$

where $n_i!$ denotes $n_i(n_i - 1)(n_i - 2)\cdots 1$.[27] Therefore, the numbers of ways do not only depend on the number of identical particles in a system, but also on the particle configuration. Since reaction 7 assumes that a proton is replaced by a metal ion, and cupric and cadmium ions have more configurations than the protons, the negative values of entropy change may be expected.

Effect of pH on Isotherm of Copper and Cadmium in a Mixture: Competitive Adsorption

To study the competitive adsorption behavior between copper and cadmium ions on corncob particles, a series of isotherms for their mixtures with molar ratios of copper to cadmium of 1.77 and 1.00, at various initial pH values, and at a temperature of 25°C are followed (Figs. 5–8). Considering that these tests were not carried out in a buffer solution, the final pH values in suspensions were lower than the initial ones. The final pH ranges for various initial pH values and the two molar ratios of copper and cadmium were listed in Table 4. The average relative standard deviations (RSD) of copper and cadmium concentrations in suspensions from the duplicate experiments for each system were also listed in Table 4. The maximum average RSD for the copper and cadmium concentrations were 5.5% and 2.9%, respectively. The results showed that the uptake of copper in mixtures of copper and cadmium increased (Figs. 5 and 7), whereas the uptake of cadmium first increased, and then decreased, providing inversed U-shape isotherms (Figs. 6 and 8) with increasing the total metal ion concentration. This phenomenon in a dilute solution differs from a number of reported data for metal ion adsorption, which showed that the uptake of both competitive metal ions increased with increasing concentrations.[16,17] However, there are some reported observations of the inversed U-shape isotherms for a binary organic components adsorption in nonaqueous systems when the components are adsorbed by an adsorbent simultaneously.[28,29] In addition, in the present study, the uptake of copper from the mixture (Fig. 5) was slightly lower than that when its adsorption was carried out in a single component system at the same initial pH and equilibrium concentration in the solution,[30] whereas the uptake of cadmium from the mixture (Fig. 6) was much lower than that when cadmium was the only ion in the solution.[30] However, Schwuger and Smolka[28] found that in their inversed U-shape isotherms, the uptake of sodium-n-dodecyl sulfate, which is an anionic surfactant, from a mixture with p-n-octylphenol-polyglycol ethers, which are nonionic surfactants, was even higher, when its concentration was relatively low, than that when the adsorption of the individual component on activated carbon was studied.

When the tests were carried out with the copper to cadmium concentrations of 1.77 (Figs. 5 and 6) and 1.00 (Figs. 7 and 8), the lower uptake for both copper and cadmium ions was noticed at the lower ratio. For example, at the initial pH 5.5 and the equilibrium concentration 0.40 mmol/l, the uptake of copper for the

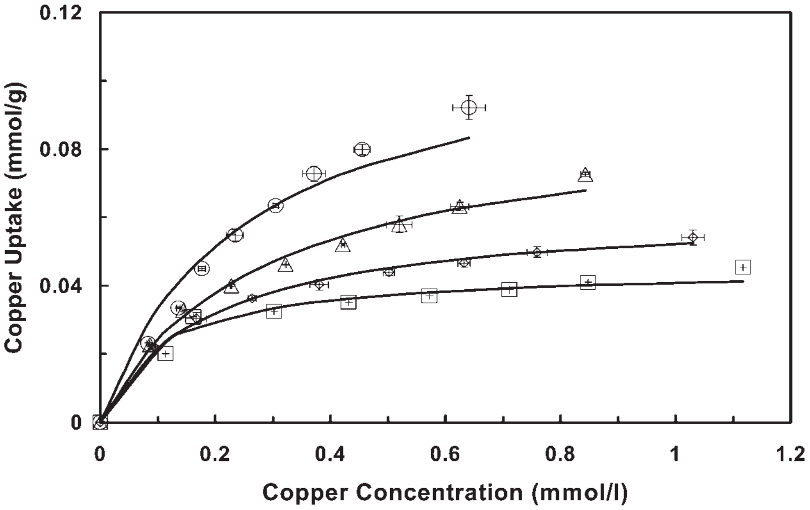

Figure 5. Effect of pH on copper isotherms in mixture with cadmium (mixed size of particles, corncob conc. 10 g/l, copper to cadmium mol. ratio 1.77, temperature 25°C). □, pH 4.5; ◇ , pH 5.0; Δ, pH 5.5; ○, pH 5.9. Symbols are experimental data, and solid lines are predicted data using Eq. (1).

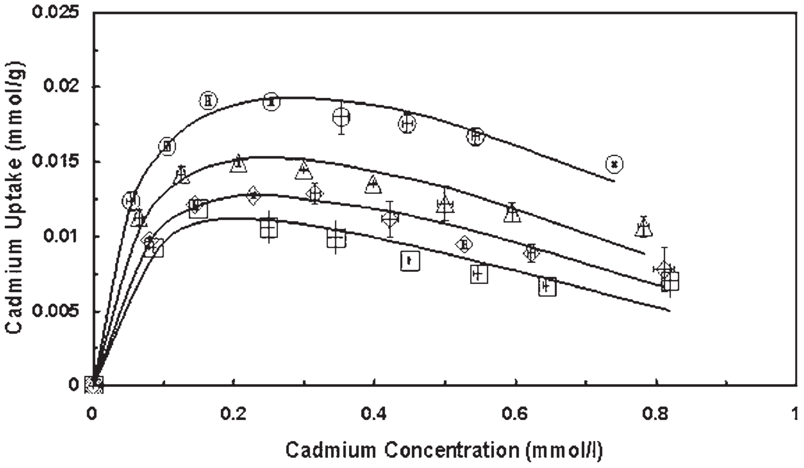

Figure 6. Effect of pH on cadmium isotherms in mixture with copper (mixed size of particles, corncob conc. 10 g/l, copper to cadmium mol. ratio 1.77, temperature 25°C). □, pH 4.5; ◇ , pH 5.0; Δ, pH 5.5; ○, pH 5.9. Symbols are experimental data, and solid lines are predicted data using Eq. (2).

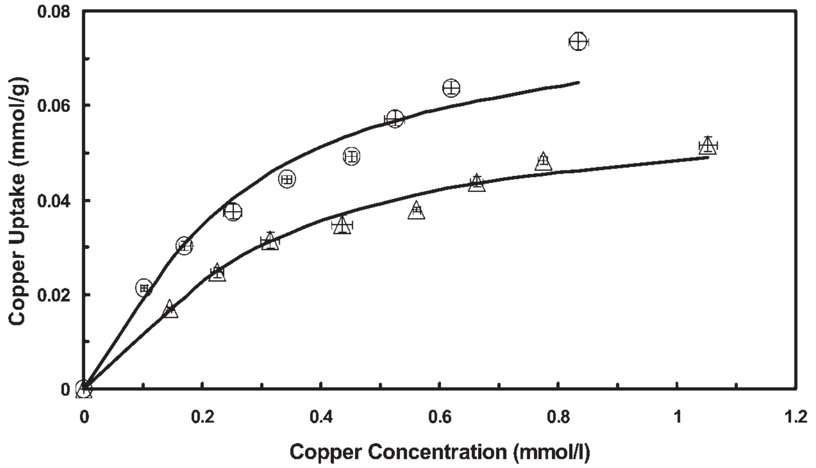

Figure 7. Effect of pH on copper isotherms in mixture with cadmium (mixed size of particles, corncob conc. 10 g/l, copper to cadmium mol. ratio 1.00, temperature 25°C). Δ, pH 5.5; ○, pH 5.9. Symbols are experimental data and solid lines are predicted data using Eq. (1).

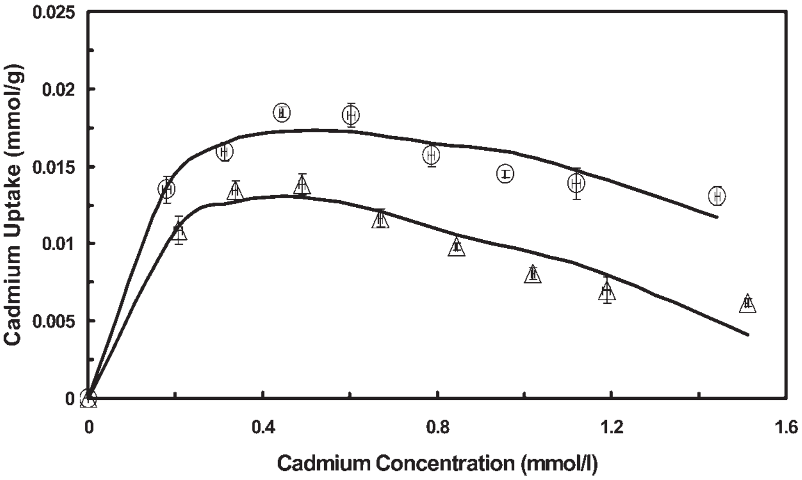

Figure 8. Effect of pH on cadmium isotherms in mixture with copper (mixed size of particles, corncob conc. 10 g/l, copper to cadmium mol. ratio 1.00, temperature 25°C). Δ, pH 5.5; ○, pH 5.9. Symbols are experimental data and solid lines are predicted data using Eq. (2).

ratios 1.77 and 1.00 was 0.052 mmol/g (Fig. 5) and 0.034 mmol/g (Fig. 7), respectively, while the corresponding uptake for cadmium was 0.0135 mol/g (Fig. 6) and 0.0125 mmol/g (Fig. 8). It is obvious that the molecular ratio has a greater effect on the uptake of copper than that of cadmium ions.

The results from this study also indicated that more metal ions with a smaller ion diameter were adsorbed from the mixture than those with a larger ion diameter (Table 3). These results are not in agreement with those published by Tobin et al.,[31] who found that the biomass of *R. arrhizus* adsorbed more ions with a larger ionic radius than those with a smaller one. It is clear that this has an effect on the adsorption equilibrium. The results

Table 3. Metal ion data.

	Cu^{2+}	Cd^{2+}
Atomic weight(33a)	63.54	112.4
Ionic radius (nm)(35)	0.072	0.097
Electronegativity(33b)	1.9	1.69
Polarizability (ground state) (10^{-24} cm^3)(33c)	6.1	7.2
Electron configuration(34)	[Ar]$3d^{10}4s^1$	[Kr]$4d^{10}5s^2$

Table 4. Interaction factors δ_1, δ_2, ε_1, and ε_2 in Eqs. (1, 2), the final pH ranges, and the average RSD for mixture of copper and cadmium at various pH values.

Initial pH	4.5	5.0	5.5	5.9
Cu to Cd mol. ratio 1.77				
Cu				
δ_1	1.20	0.735	0.645	1.16
δ_2	6.20×10^{-10}	1.32×10^{-5}	2.94×10^{-8}	2.97×10^{-16}
Cd				
ε_1	0.0604	0.0488	0.0511	0.0743
ε_2	0.0953	0.0975	0.121	0.165
Final pH range	4.50–4.20	4.64–4.37	5.02–4.88	5.33–5.20
Average RSD Cu%	2.1	5.5	1.8	3.7
Average RSD Cd%	2.3	1.5	2.2	2.9
Initial pH			5.5	5.9
Cu to Cd mol. ratio 1.00				
Cu				
δ_1			1.06	1.69
δ_2			0.298	0.166
Cd				
ε_1			0.0541	0.0609
ε_2			0.0520	0.0594
Final pH range			4.72–4.59	5.12–4.87
Average RSD Cu%			2.8	3.7
Average RSD Cd%			1.2	1.4

from the present study can be explained by a lower molecular weight of cupric ions and, consequently, their higher velocity of diffusion on the surface and in the pores of the adsorbent, than those of cadmium. This results in a higher uptake of cupric ions than those of cadmium. This is especially expressed at higher cupric ions concentrations, when the probability of these ions to bind to the active sites of the adsorbent increases.

The higher adsorption of cupric ions than those of cadmium can also be explained by the electron configuration of these ions. The copper ions have one unpaired electron (Table 3), and they can be easier attracted by the electric field originating from the adsorbent than the cadmium ions the electrons of which are paired.[32]

The curves in Figs. 5–8 and the values of the interaction factors in Table 4 were obtained by fitting Eqs. (1) and (2) to the experimental data for a mixture of copper and cadmium. The very small values of the interaction factor δ_2 for molar ratio 1.77 indicate that copper has greater competitive ability than cadmium in their mixture and that the uptake of the latter ions is affected considerably by cupric ions. This also implies that the adsorption of cadmium ions by corncob particles was reversible, and that with increasing the total metal ion concentration, some cadmium ions adsorbed were replaced by cupric ions. However, this competitive ability of copper depends on the molar ratio of copper to cadmium.

When decreasing the molar ratio from 1.77 to 1.00, the corresponding values of the interaction factors δ_2 increase several orders of magnitude (Table 4). This suggests that the competitive ability of cupric ions decreases tremendously with decreasing the molar ratio.

CONCLUSIONS

It was found in this study that the uptake of cupric and cadmium ions on corncob particles increased with an increase in temperature. The equilibrium constants in the Langmiur model decreased with increasing temperature, which shows that the adsorption processes for copper and cadmium by the corncob particles are exothermic.

The isotherms for copper and cadmium in their mixture have different shapes: the uptake of the former metal ions increased with increasing the total metal ion concentration, whereas the uptake for the latter metal ions has attained a maximum point and then decreased, resulting in an inversed U-shape isotherm with increasing the total metal ion concentration. A novel competitive adsorption model with interaction factors was proposed for this inversed U-shape isotherm. This model is applicable for the experimental equilibrium data for the competitive adsorption. The corncob particles had the larger uptake for cupric ions than for cadmium ions during their competitive adsorption from the binary solution.

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