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Adsorption Isotherms for Cupric and Cadmium Ions on Corncob Particles

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Abstract: The effects of the initial pH and buffer on the adsorption isotherms for cupric and cadmium ions by corncob particles were investigated. The uptakes of the two ions on corncob particles increased with the initial pH. A modified Langmuir model, which considers the effect of pH on the isotherm, has been developed and was used to fit the experimental equilibrium data. The pH at zero-charge point of corncob particles was measured (pH_{zcp} 4.97) by applying the primary equilibrium method of H^+ and OH^-. A method to determine the chemical free energy in the James-Healy model has been proposed in which the pH_{zcp} is used to distinguish the chemical free energy from the solvation and coulombic free energies in that model. The calculated results indicate that the chemical and solvation free energies contribute much to the adsorption free energy. The chemical free energy is constant, while the solvation free energy increases with increasing pH; their effects are opposite. The adsorption free energy increases with the pH value during the adsorption processes of cupric and cadmium ions on corncob particles.

Keywords: Corncob, copper, cadmium, adsorption, equilibrium, isotherm, model, pH_{zcp}, James-Healy model

INTRODUCTION

Today's society is concerned about the fate of heavy metal ions in the environment. With increasing industrial activities, more and more wastewater containing heavy metal ions is discharged into streams and rivers. It is well

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known that heavy metal ions can cause various diseases in humans and animals, retard the growth of plants and agricultural crops, and even cause mutations of living organisms (1). Unlike organic pollutants, heavy metal ions cannot be degraded by microorganisms in the soil, rivers, and activated sludge in wastewater treatment plants. This is the reason why chemical and physical treatments become main methods for removal of heavy metal ions from wastewater.

Among those treatments, the adsorption process has been widely applied to purify various industrial and municipal wastewaters. However, the traditional adsorbents such as activated carbon are expensive, and their application is limited (2). Recently, a number of new low-cost biosorbents have been reported (3–9). These biosorbents can be grouped into two categories with respect to their origins: the microorganisms such as algae, fungi, and bacteria, and the agricultural byproducts such as corncobs, peanut shells, soybean hulls, and rice hulls. Compared to the microorganisms, the advantages of the agricultural byproducts as biosorbents are that they do not have to be specially produced for this purpose, because they are byproducts or waste from agricultural processes, and they are already available in large quantities. It is estimated that agricultural byproducts as a whole exceed 3.2×10^8 metric tons/yr (10). Their cost is low. Because of these advantages, biosorbents made from agricultural byproducts may have a wide application in the future.

Taking into account that various mechanisms can be implicated in adsorption, a number of models based on the considered mechanisms of adsorption have been proposed. One of them is the James-Healy model (Ion-Solvent Interaction model) in which chemical, solvation, and coulombic free energies, representing the corresponding interaction mechanisms, contribute to the overall free energy (11). The main drawback of this model is the chemical free energy, the value of which has to be initially assumed and fitted to the experimental data resulting in an uncertainty, because the fitting result often changes with the assumed value of that energy (12, 13). A method suggested in this study is evaluating the chemical free energy by using pH at zero charge point of the adsorbent at which the coulombic free energy is zero, and the solvation free energy can be calculated.

The objectives of this study, in which corncob particles were used for the adsorption of cupric and cadmium ions, were to:

1) Investigate the effects of initial pH and buffer on the adsorption equilibrium of cupric and cadmium ions by corncob particles;
2) Modify the Langmuir model to include the effect of pH on the metal adsorption;
3) Propose a method to determine the chemical free energy in the James-Healy model, and estimate the solvation and coulombic free energies in that model.

DEVELOPMENT OF A NOVEL EQUILIBRIUM MODEL

A Modified Langmuir Model That Includes Effect of pH

Langmuir model

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

is widely used in adsorption.

Considering that its parameters for the maximum adsorption capacity (q_m) and equilibrium constant (K_l) change with pH, Esposito et al. (14) have proposed the following equation which shows the relationship between q_m and pH:

$$q_m(pH) = \frac{q_0 \exp(k\ pH)}{1 - \{q_0[1 - \exp(k\ pH)]\}/q_\infty} \tag{2}$$

where q_0, q_∞ and k are regression constants. Substituting this equation into the Langmuir model (1), the following expression is obtained:

$$q = \frac{K_l q_m(pH) c_e}{1 + K_l c_e} \tag{3}$$

Unfortunately, Esposito et al. (14) did not give the physical meaning of q_0 and q_∞. In general, the adsorption of metal ions on adsorbents can be caused by electrostatic forces and non-electrostatic forces such as the van der Waals force. The former can be attributed to the charged active sites, while the latter to those which are not charged. Therefore, in the present study of corncob particles as the adsorbent, it is supposed that there are two kinds of active sites on the cell wall of corncob particles: charged and noncharged active sites. At the pH of zero-charge point (pH_{zcp}) it can also be assumed that only the noncharged active sites on the cell wall of these particles participate in adsorption because of the absence of the coulombic effect. Considering this, the following empirical equation for the correlation among q_m, pH, and pH_{zcp} is suggested:

$$q_m(pH) = q_{mzcp} \exp[k(pH - pH_{zcp})] \tag{4}$$

where q_{mzcp} and k are the regression constants, and q_{mzcp} represents the maximum uptake of the noncharged active sites at pH_{zcp}. Since the pH_{zcp} of an adsorbent can be measured by the primary equilibrium of H^+ and OH^- (15, 16) or the titration curves (17), Eq. (4) with two constants is simpler than Eq. (2).

Substituting Eq. (4) into Eq. (1) yields

$$q = \frac{K_l q_{mzcp} c_e}{1 + K_l c_e} \exp[k(pH - pH_{zcp})] \tag{5}$$

Further, assuming that the Langmuir equilibrium constant is

$$K_l = K_0 \exp[n(pH - pH_{zcp})] \tag{6}$$

where K_0 and n are the constants for regression, K_0 is the equilibrium constant at pH_{zcp}. Substituting this expression into Eq. (5), the following equation is obtained:

$$q = \frac{K_0 q_{mzcp} c_e}{1 + K_0 \exp(n\ pH) c_e} \exp[(k + n)(pH - pH_{zcp})] \tag{7}$$

This equation has four constants and can describe the uptake of the solute with changes of both the solute concentration and the pH value.

EXPERIMENTAL

Material and Methods

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

Some corncob particles were treated with 1 M NaOH aqueous solution to remove corncob components soluble in alkali to test for their contribution to the adsorption process. Ten grams of corncob particles were added into 100 mL of 1 M NaOH. The suspension was heated to the boiling point and kept at that temperature for 20 min with stirring. After cooling, the suspension was filtered though filter paper (No. 42, Whatman), and then washed with deionized water. This operation was repeated three times. Finally, the filter cake was dried at 100°C for 48 h. After drying, about 2.0 g of dry matter was obtained. Hence, approximately 80% of components from the corncob particles were extracted.

Metal solutions: 5000 and 1000 mg/l cupric and cadmium stock solutions were prepared from cupric nitrate ($Cu(NO_3)_2 2.5H_2O$, certified A. C. S., Fisher Scientific) and cadmium nitrate ($Cd(NO_3)_2 4H_2O$, certified A. C. S., Fisher Scientific).

Buffers: MES buffer (2-[N-Morpholino]ethanesulfonic acid, $C_6H_{13}NO_4S$, Sigma Chemical Co.), for which it has been demonstrated that it does not bind with cupric ions (18), 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.

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 by 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 (pH 4.00, 7.00, and 11.00, Fisher Scientific) were used for calibration.

EXPERIMENTAL TECHNIQUES

Adsorption Isotherms

Experiments were performed in 125 mL Pyrex flasks placed in a thermostat, which was maintained at required temperatures. First, buffer was prepared according to Perrin and Dempsey (19) by adding 400 mL of deionized water and the required amount of solid buffer salts 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 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 h. A preliminary study of the adsorption kinetics of these ions by corncobs particles showed that the adsorption equilibrium was attained in a 4 h 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 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. Some tests were carried out in duplicate. The relative errors of the duplicates were less 0.58%.

To check for the appearance of metal precipitate at higher pH values, equilibrium 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 milliliter of the sample was filtered and the metal concentrations were measured in both the filtrate and in the part of the sample that was not filtered. Considering that the relative errors between the metal ion concentrations in the nonfiltered 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.

Measurement of pH at Zero Charge Point of Corncob

The primary equilibrium method of H^+ and OH^- was adopted for measurement of pH at zero charge point (pH_{zcp}) of corncob particles in this study (15, 16). Fifty milliliter of 0.1 M sodium nitrate solution was added into a 125 mL flask as a background electrolyte. Carbon dioxide from the solution was purged with nitrogen and the rest of the test was carried out under the nitrogen atmosphere. After adjusting the pH of the solution to the required initial value with 0.1 M HNO_3, 0.500 g of corncob particles was added. The pH of the suspension increased or decreased, depending on the initial pH of the solution. After about 5 min, the pH value was stable, and it was considered the final point. The same test was repeated several times, but with a different initial pH value of the background electrolyte, until the final pH in the suspension was equal, or approximately equal, to the initial pH of the solution. This value was considered as the pH at zero charge point (pH_{zcp}) for this adsorbent. The results showed that pH_{zcp} was 4.97 for the mixture of various sizes of corncob particles used in this study.

RESULTS AND DISCUSSION

Effect of pH on Isotherm

Since a biosorption is similar to an ion exchange process, it can be assumed that the pH value of the aqueous solution has a significant effect on the metal uptake. This is the reason why the effects of pH on the isotherms of adsorption of cupric and cadmium ions from water and buffer solutions by corncob particles were studied at various initial pH values. The obtained results show that the uptake of cupric ions (Figs. 1 and 2) and cadmium

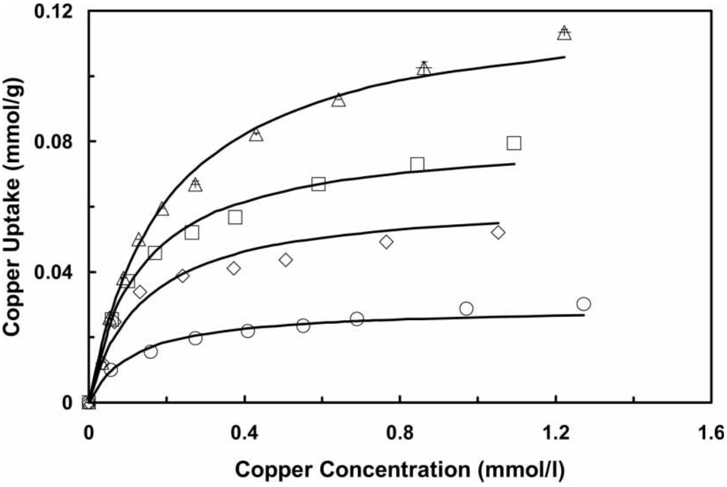

Figure 1. Effect of pH on copper isotherms in water suspension (corncob concen. 10 g/l), ○: pH 4.0, ◇: pH 5.0, □: pH 5.5, △: pH 6.0. Symbols are experimental data, and solid lines are predicted data using Eq. (1).

ions (Figs. 3 and 4) increased with an increase in the initial pH values of the metal solutions. For example, when the initial pH was increased from 4.0 to 5.5 at the solute equilibrium concentration of 0.60 mmol/l in solution (Fig. 1), the copper uptake increased from 0.024 mmol/g to 0.068 mmol/g

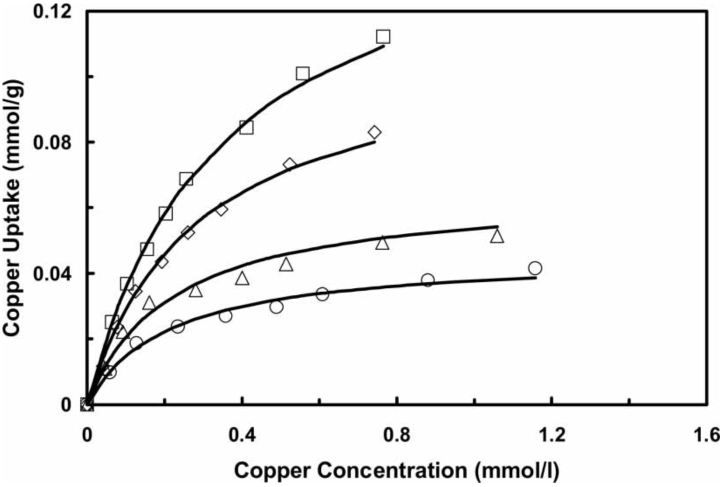

Figure 2. Effect of pH on copper isotherms in MES (corncob concen. 10 g/l). ○: pH 4.0, △: pH 4.5, ◇: pH 5.0, □: pH 5.5. Symbols are experimental data, and solid lines are predicted data using Eq. (1).

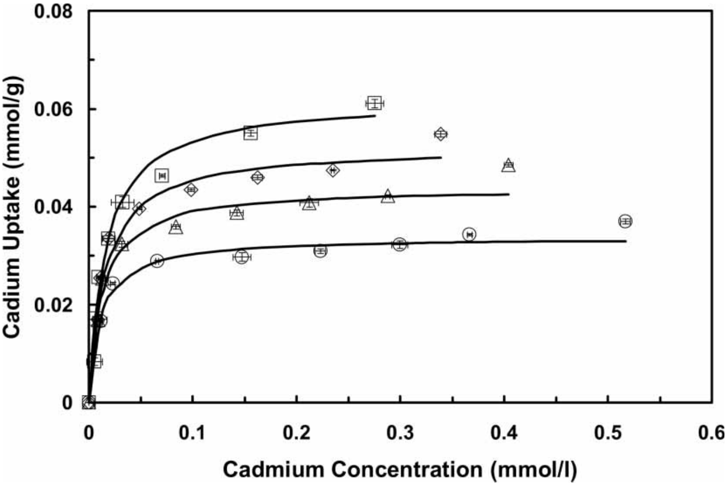

Figure 3. Effect of pH on cadmium isotherms in water suspension (corncob concen. 10 g/l). ○ pH 6.0, △ pH 7.0, ◇ pH 7.6, □ pH 8.3. Symbols are experimental data, and solid lines are predicted data using Eq. (1).

in the water solutions, while in the presence of the buffer for the same equilibrium concentration and pH range, the uptake of copper increased from 0.035 mmol/g to 0.10 mmol/g (Fig. 2). The same trend was noticed for the adsorption of cadmium by the corncob particles in the water and buffer

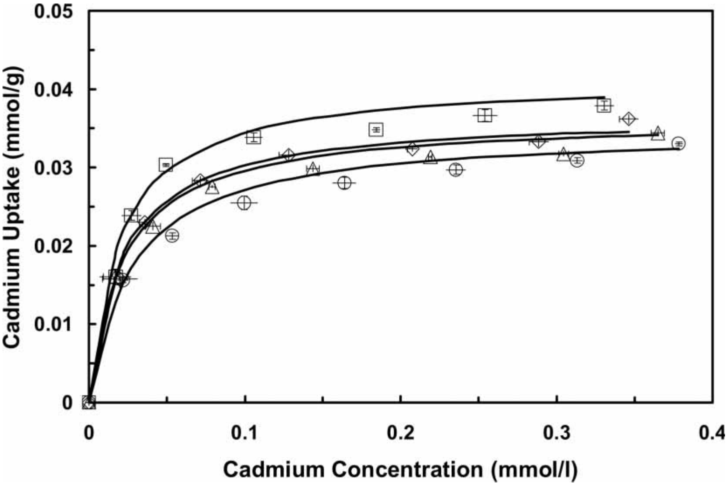

Figure 4. Effect of pH on cadmium isotherms in HEPES (corncob concen. 10 g/l). ○ pH 6.0, △ pH 7.0, ◇ pH 7.6, □ pH 8.3. Symbols are experimental data, and solid lines are predicted data using Eq. (1).

solutions (Figs. 3 and 4). This indicates that the pH is an important parameter in the adsorption of cupric and cadmium ions by corncob particles. Since the change of the initial pH in solution influences both the active sites on the cell wall and the metal solution chemistry, the following three explanations can be considered for this phenomenon. The first explanation is the difference between the pH of solution and pH_{zcp} (or the pH at isoelectric point) of biosorbents. The bonding formed between metal ions and active sites on the cell wall can be attributed to chemical and coulombic factors. The latter can be estimated from the difference between pH_{zcp} and pH in solution (Nernst's law) (20) using the following expression:

$$\Psi_o = 0.059(pH_{zcp} - pH) \tag{8}$$

where Ψ_o is the surface potential (**v**) of the cell wall. The surface of the cell wall with a negative potential favors the adsorption of the positively charged metal ions. When the pH value of suspensions increases above the pH_{zcp}, the absolute value (negative potential) of the surface potential increases, the coulombic contribution to adsorption increases, and then the uptake capacity increases.

The second explanation is a competition between protons and metal ions. At a low pH value, there are many protons in the solution, and the metal ions compete with these protons for the active sites on the cell surface. This competition decreases significantly at a high pH value when the concentration of protons is substantially decreased.

The third explanation is the effect of ligands on the cell wall. At a lower pH, the ligands on the cell wall are more positively charged than at a higher pH value. The active sites on the cell wall favor to associate with protons, because metal ions experience stronger repulsive forces from the positive ligands on the cell wall than protons (21). As the pH increases, more ligands become negative, and they easily attract positively charged metal ions.

The uptakes of copper in the presence of MES buffer (Fig. 2), which does not form complexes with cupric ions (18), are greater than those in water (Fig. 1) at the same initial pH and copper ion equilibrium concentrations in the solution. The reason is that the uptakes in the presence of the buffer (Fig. 2) are at a constant pH, while the uptakes in water (Fig. 1) occur at lower pH values than the initial ones. However, the uptakes of cadmium with HEPES buffer (Fig. 4) are lower than those in water (Fig. 3). The reason may be that HEPES binds with cadmium ions or occupies the active sites on the cell wall and decreases the ions adsorption.

The two constants (K_l and q_m) in the Langmuir model [Eq. (1)] were determined from the linearized representation of the results shown in Figs. 1–4, and are shown in Tables 1 and 2. The maximum adsorption capacity, q_m, increased with increasing pH for the isotherms in the water and the buffer suspensions, both for copper and cadmium. The equilibrium constant K_l decreased in all cases except for cadmium ion uptake in HEPES. This

Table 1. Langmuir model parameters q_m and K_l (Eq. 1) for copper adsorption at various pH values

Initial pH	4.0	5.0	5.5	6.0
In water				
q_m (mmol/g)	0.0291	0.0623	0.0900	0.123
K_l (l/mmol)	8.70	7.17	5.65	2.88
Final pH range	4.00–3.82	5.00–4.50	5.37–4.93	5.73–5.30
R	0.988	0.975	0.990	0.990
SRD	3.60	5.05	2.10	4.17
Initial pH	4.0	4.5	5.0	5.5
In MES				
q_m (mmol/g)	0.0458	0.0653	0.106	0.140
K_l (l/mmol)	4.706	4.581	3.90	3.80
Final pH range	stable	stable	stable	stable
R	0.996	0.990	0.990	0.990
SRD	2.52	3.94	2.72	2.91

R, Correlated coefficient.

SRD, Standard relative derivation.

shows that the pH of the suspensions affects these constants, and it is in agreement with some already reported data. For example, Guibal et al. (22) showed that the q_m and K_l increased with pH in their study of the uranium sorption on chitosan. However, they also reported that the q_m parameter

Table 2. Langmuir model parameters q_m and K_l (Eq. 1) for cadmium adsorption at various pH values

Initial pH	6.0	7.0	7.6	8.3
In water				
q_m (mmol/g)	0.0337	0.0439	0.0522	0.062
K_l (l/mmol)	88.62	78.25	65.99	62.0
Final pH range	5.58–5.26	6.11–5.75	6.36–6.11	7.30–6.69
R	0.998	0.971	0.956	0.975
SRD	1.81	3.30	4.39	2.91
Initial pH	6.0	7.0	7.6	8.3
In HEPES				
q_m (mmol/g)	0.0348	0.0362	0.0367	0.0413
K_l (l/mmol)	35.36	45.14	47.22	50.37
Final pH range	stable	stable	stable	stable
R	0.962	0.972	0.990	0.954
SRD	3.66	3.09	0.87	2.09

was almost a constant and K_l decreased with an increase in pH for the uranium adsorption on glutamate glucan.

Using Eqs. (4) and (6), the correlation between the maximum adsorption capacities and the equilibrium constants (Tables 1 and 2) with pH can be predicted reasonably well (Figs. 5–8). The values of the regression constants q_{mzcp}, k, K_0, and n in Eqs. (4) and (6) are shown in Tables 3 and 4. Using these constants in Eq. (7), a good prediction of the uptake of copper and cadmium can be obtained for various concentrations of these metals and the initial pH values of these systems (Figs. 9 and 10).

Effect of Pretreatment of Corncob Particles with Sodium Hydroxide

To investigate the effect of the pretreatment of corncob particles with sodium hydroxide, some corncob particles were treated with 1 M sodium hydroxide aqueous solution. The results of the alkali treatment showed that about 80% of the mass of the corncob particles had been removed. The isotherms for copper using residuals of the corncob particles treated with sodium hydroxide and those without the treatment of particles are shown in Fig. 11.

The isotherms show that the uptake is much lower when the residuals of the treated corncob particles were used. For example, at an equilibrium concentration of 0.50 mmol/l in solution, the uptakes are 0.034 mmol/g for the pretreated corncob particles and 0.082 mmol/g for the untreated corncob particles (Fig. 11).

As reported by Vaughan et al. (3), 85% of the content of corncob particles are cellulose and hemicellulose. The cellulose is degraded into various organic

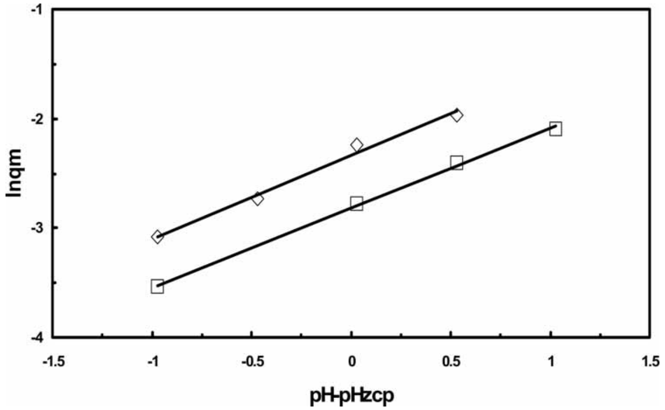

Figure 5. Effect of pH on the Langmuir isotherm parameter q_m for copper adsorption □ in water, ◇ in MES. Symbols are experimental data, and solid lines are predicted data using Eq. (4).

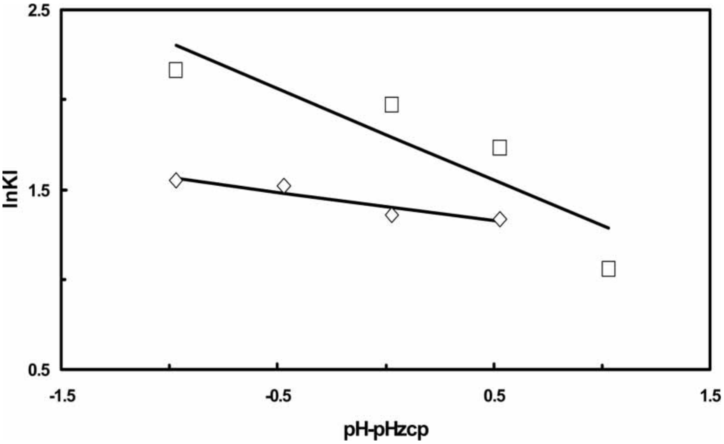

Figure 6. Effect of pH on the Langmuir isotherm parameter K_l for copper adsorption □ in water, ◇ in MES. Symbols are experimental data, and solid lines are predicted data using Eq. (6).

acids with a higher concentration of alkali such as 1 M NaOH above 80°C (23). The lower copper uptake by residuals of the pretreated corncob particles indicates that the cellulose and hemicellulose in the corncob particles were hydrolyzed and lost during the pretreatment process. Consequently, it can be concluded that the cellulose and hemicellulose in the corncob particles are the components that are mainly responsible for the adsorption of metal ions.

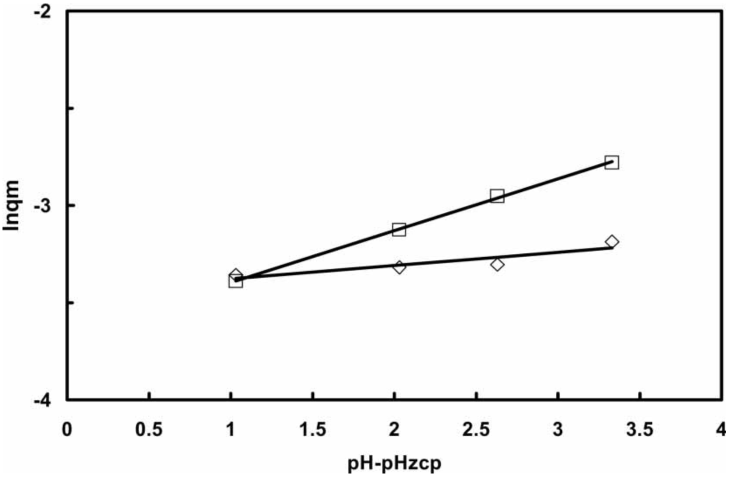

Figure 7. Effect of pH on the Langmuir isotherm parameter q_m for cadmium adsorption □ in water, ◇ in HEPES. Symbols are experimental data, and solid lines are predicted data using Eq. (4).

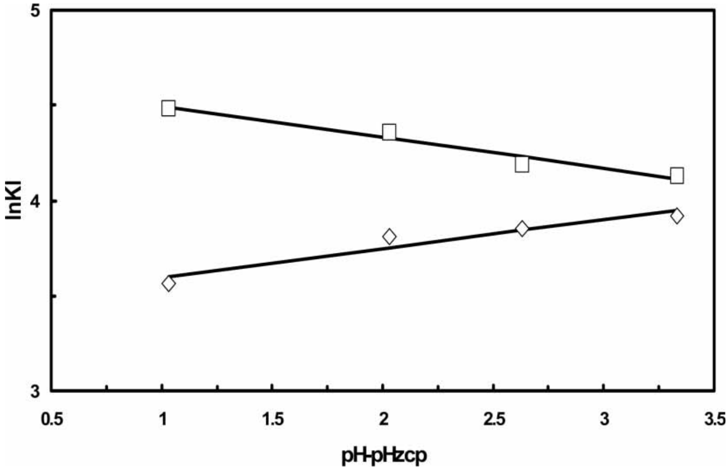

Figure 8. Effect of pH on the Langmuir isotherm parameter K_l for cadmium adsorption □ in water, ◇ in HEPES. Symbols are experimental data, and solid lines are predicted data using Eq. (6).

Estimation of Free Energy of Adsorption for Various pH Values at 25°C

Assuming that the various adsorption mechanisms act independently, the free energy of adsorption, ΔG_{ads}, can be expressed as the sum of contributions of the chemical, solvation, and coulombic mechanisms (11), and it is given by the following expression:

$$\Delta G_{ads} = \Delta G_{chem} + \Delta G_{coul} + \Delta G_{solv} \tag{9}$$

Table 3. Parameters q_{mzcp}, k, K_0, and n in Eq. (7) for copper adsorption

	Cu	
	In water	In MES
q_{mzcp}	0.0598	0.0966
k	0.727	0.767
R	0.999	0.995
SRD	0.0309	0.0596
K_0	6.104	4.081
n	−0.505	−0.1605
R	0.900	0.948
SRD	0.264	0.0426

Table 4. Parameters q_{mzcp}, k, K_0, and n in Eq. (7) for cadmium adsorption.

	Cd	
	In water	In HEPES
q_{mzcp}	0.0256	0.0319
k	0.267	0.0685
R	1.00	0.906
SRD	0.008	0.0383
K_0	105.6	31.31
n	−0.1639	0.1524
R	0.982	0.960
SRD	0.0376	0.527

And the free energy is represented by

$$\Delta G_i = -RT\ln K_i \tag{10}$$

where K is the equilibrium constant, and the subscript i represents the apparent adsorption, coulombic, solvation, and chemical, respectively.

The coulombic equilibrium constant, therefore, the change of coulombic free energy, in Eq. (10) is related to the surface plane potential and the inner

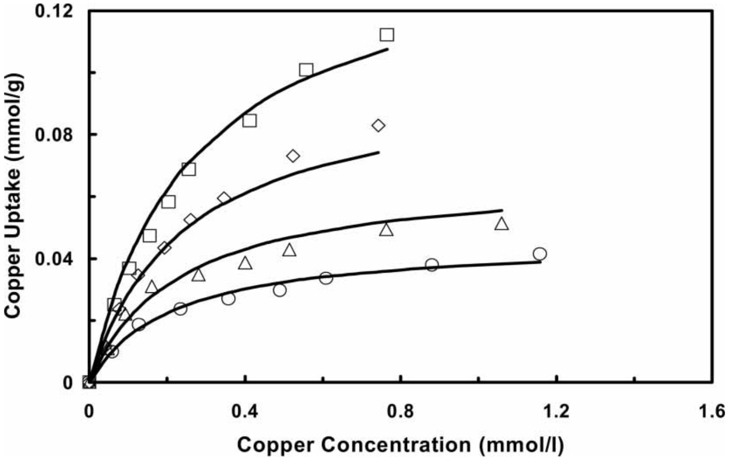

Figure 9. Effect of pH on copper isotherms in MES (corncob conc. 10 g/l). ○: pH 4.0, △: pH 4.5, ◇: pH 5.0, □: pH 5.5. Symbols are experimental data, and solid lines are predicted data using Eq. (7).

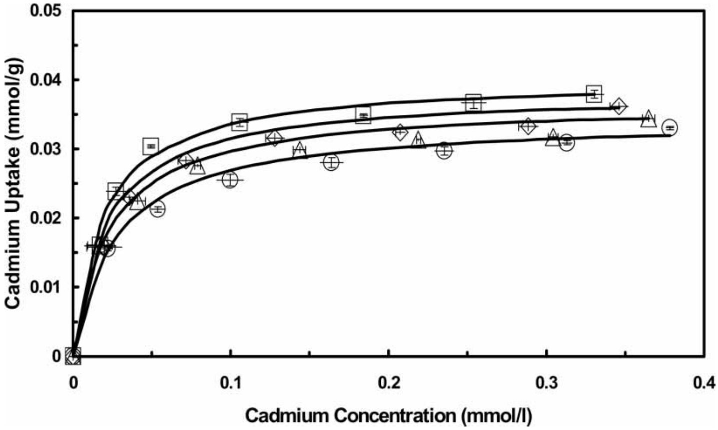

Figure 10. Effect of pH on cadmium isotherms in HEPES (corncob conc. 10 g/l). ○ pH 6.0, △ pH 7.0, ◇ pH 7.6, □ pH 8.3. Symbols are experimental data, and solid lines are predicted data using Eq. (7).

Helmholtz plane potential at a constant temperature, i.e.

$$K_{coul} = \frac{\exp[(-2F\Psi_{\beta})/(RT)]}{\exp[(-F\Psi_{o})/(RT)]} \tag{11}$$

where ψ is the potential (v) in the electrical double layer, and subscripts o and β denote the surface and inner Helmholtz planes of the electrical double layer,

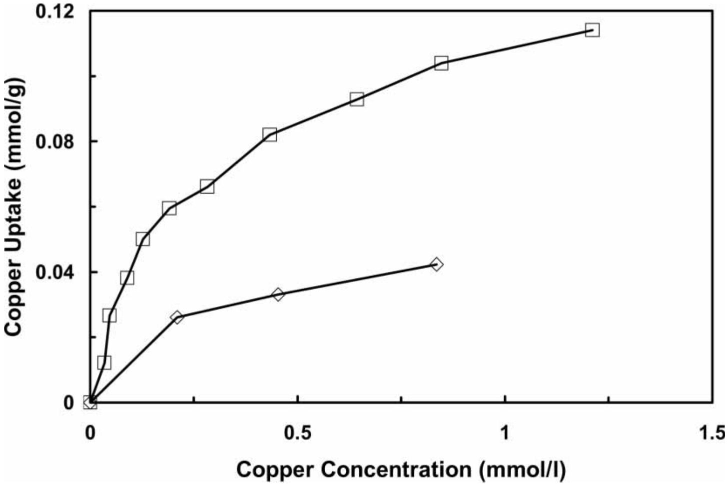

Figure 11. Effect of NaOH pretreatment of corncob particles on copper isotherms ◇: pretreatment, □: no pretreatment.

respectively. The former potential can be estimated from the difference between pH_{zcp} and pH in solution [Eq. (8)]. To estimate the latter potential, an electrical double layer model is required. Electrical double layer models, such as the diffusion layer, constant capacitance, basic stern, and triple layer models, were summarized by Westall (24). In the present study, the diffusion layer model was adopted, since the estimation of capacitance in the other models is difficult. According to this model,

$$\sigma_o + \sigma_d = 0 \tag{12}$$

and

$$\psi_\beta = \psi_d = \psi_o \tag{13}$$

where σ is the charge density (C/m^2) of the planes, and subscript d denotes the outer Helmholtz plane of the electrical double layer. Substituting Eqs. (8) and (13) into Eq. (11), and applying it to Eq. (10). The following expression for ΔG_{coul} is obtained:

$$\Delta G_{coul} = F\Psi_o = 0.059F\left(pH_{zcp} - pH\right) \tag{14}$$

where F is the Faraday's constant (96485 C/mol).

The solvation energy term depends on the difference between the inverse of the dielectric constant in the bulk solution and the inverse of that on the interface, and it can be estimated by Eq. (15) (11).

$$\Delta G_{solv} = \left(\frac{z_i^2 e^2 N}{16\pi\varepsilon_o}\right)\left[\frac{1}{r_{ion} + 2r_w} - \frac{r_{ion}}{2(r_{ion} + 2r_w)^2}\right]\left(\frac{1}{\varepsilon_{\text{int}}} - \frac{1}{\varepsilon_{bulk}}\right) + \left(\frac{z_i^2 e^2 N}{32\pi\varepsilon_o}\right)\left(\frac{1}{r_{ion} + 2r_w}\right)\left(\frac{1}{\varepsilon_{ads}} - \frac{1}{\varepsilon_{\text{int}}}\right) \tag{15}$$

where

$$\varepsilon_{\text{int}} = \left[\frac{\varepsilon_{bulk} - 6}{1 + 1.2 \times 10^{-17}(d\Psi/dx)}\right] + 6 \tag{16}$$

$$\frac{d\Psi}{dx} = -2\kappa\frac{RT}{zF}\sinh\left(\frac{zF\Delta\Psi_x}{2RT}\right) \tag{17}$$

$$\Delta\Psi_x = \frac{2RT}{zF}\ln\left\{\frac{\exp(ZF\Psi_o/2RT) + 1 + [\exp(ZF\Psi_o/2RT) - 1]\exp(-\kappa x)}{\exp(ZF\Psi_o/2RT) + 1 - [\exp(ZF\Psi_o/2RT) - 1]\exp(-\kappa x)}\right\} \tag{18}$$

and

Debye length $\kappa = 0.328 \times 10^{10}\,I^{1/2}$

$x = (r^{ion} + 2r_w)$

z_i = sign and number of charges on the adsorbing ion.

z = 1(for 1:1 background electrolyte).

ε_{int}, ε_{bulk}, ε_{ads}, and ε_o are the dielectric constants of the interface, solvent (water), solid (adsorbent), and vacuum (8.85×10^{-12} C/vm), respectively, r_{ion} and r_w are radii of metal ion and water (m), N and e are the Avogadro's constant (6.022×10^{23}/mol) and the elementary charge (1.60×10^{-19} C), respectively, I is the ionic strength of the background electrolyte, and κ is the Debye length (m). When pH is equal to pH_{zcp}, then Ψ_o, $\Delta\Psi_x$, and $d\Psi/dx$ are equal to zero, and ε_{int} is equal to ε_{bulk} (the dielectric constant of water 78.5). Considering this, Eq. (15) for the solvation free energy at pH_{zcp} is reduced to:

$$\Delta G_{solv,zcp} = \left(\frac{z_i^2 e^2 N}{32\pi\varepsilon_o}\right)\left(\frac{1}{r_{ion} + 2r_w}\right)\left(\frac{1}{\varepsilon_{ads}} - \frac{1}{\varepsilon_{bulk}}\right) \tag{19}$$

The radii of copper and cadmium are 0.72 Å and 0.97 Å (25), respectively. If the dielectric constant of corncob is taken 2.4, i.e., equal to that of cellulose (26), because 85% of corncob is cellulose and hemicellulose, the solvation free energies of 80.5 KJ/mol for copper and 75.1 kJ/mol for cadmium at pH_{zcp} are obtained using Eq. (19).

The free energies of adsorption ΔG_{ads} can be estimated from Eq. (10) for which K_e is calculated using Eq. (20) and K_l from Table 1.

$$K_e = [H^+]K_l \tag{20}$$

The reason for using K_e rather than K_l is 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:

$$SO^- + Me^{2+} \Longleftrightarrow SOMe^+ \tag{21}$$

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

$$SOH + Me^{2+} \Longleftrightarrow SOMe^+H^+ \tag{22}$$

The relationship between the equilibrium constants for reactions (21) and (22) is given by Eq. (20). The values of ΔG_{ads} increase from 1.87 kJ/mol at pH

4.5 to 11.0 kJ/mol at pH 5.5 for copper, and from 8.28 kJ/mol at pH 6.0 to 20.5 kJ/mol at pH 8.3 for cadmium.

It is noted that ΔG_{coul} and ΔG_{chem} are only a function of pH of solution and temperature, respectively. At pH_{zcp}, the free energy of adsorption is equal to the sum of the chemical free and the solvation free energies. The chemical free energy (−72.6 kJ/mol for copper and −72.4 kJ/mol for cadmium with mixed particle size) can be estimated from the difference between the adsorption free energy and the solvation free energy at pH_{zcp} [Eq. (9) in which ΔG_{coul} is equal to zero at pH_{zcp}]. Furthermore, with increasing pH, ΔG_{coul} decreases from 5.52 kJ/mol at pH 4.0 to −3.02 kJ/mol at pH 5.5 for copper, and from −5.86 kJ/mol at pH 6.0 to −19.0 kJ/mol at pH 8.3 for cadmium. When ΔG_{ads}, ΔG_{coul}, and ΔG_{chem} are known, ΔG_{solv} for various pH values can be calculated using Eq. (9). ΔG_{solv} increases from 69.0 kJ/mol at pH 4.0 to 86.6 kJ/mol at pH 5.5 for copper, and from 86.5 kJ/mol at pH 6.0 to 112 kJ/mol at pH 8.3 for cadmium (Figs. 12 and 13). The results from Figs. 12 and 13 show that chemical and solvation free energies are major contributions to the adsorption free energy, while the effect of the coulombic free energy is smaller. The results also indicate that the chemical free energy is constant, while the solvation and adsorption free energies increase, and coulombic free energy decreases with increasing pH during adsorption processes of cupric and cadmium ions on corncob particles.

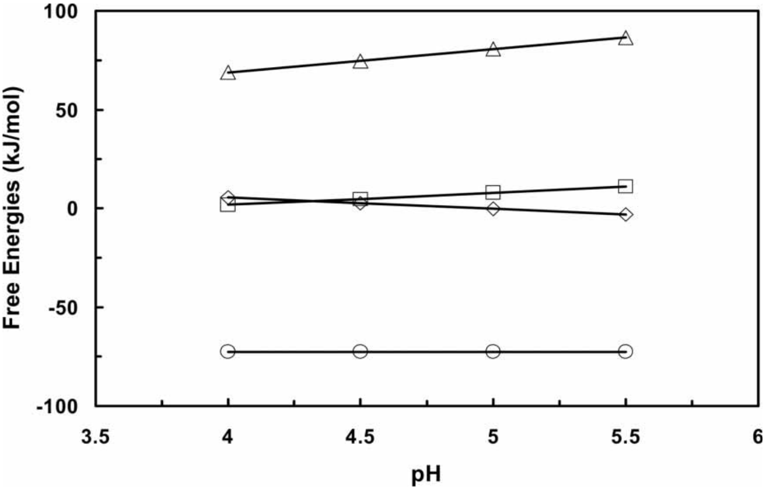

Figure 12. The relationship between free energies and pH for copper. The data were calculated by using (Eqs. 9, 10, 14). □: changes of adsorption free energies, ◇: changes of coulombic free energies, △: changes of solvation free energies, ○: changes of chemical free energies.

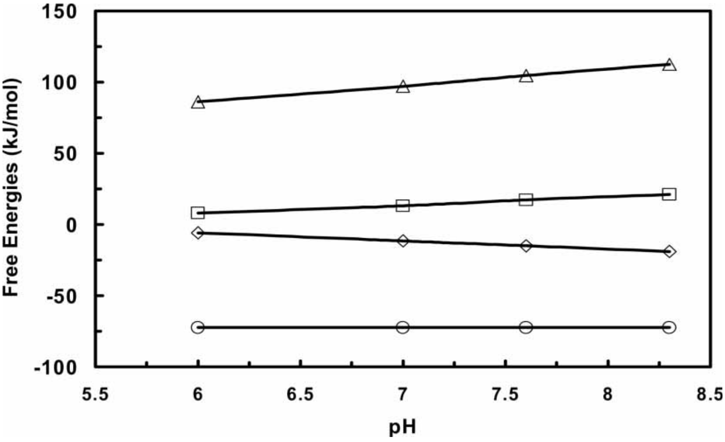

Figure 13. The relationship between free energies and pH for cadmium. The data were calculated by using [Eqs. (9), (10), (14)]. □: changes of adsorption free energies, ◇: changes of coulombic free energies, △: changes of solvation free energies, ○: changes of chemical free energies.

CONCLUSIONS

Corncob, an agricultural byproduct, has a low cost and good ability for binding metal ions. At initial pH values in the range of 4.0–6.0 for copper and pH 4.0–8.3 for cadmium, corncob particles have considerable affinity for the two metal ions. The adsorption characteristic can be described by the Langmuir model in these initial pH ranges and below equilibrium concentrations in solution of 1.2 mmol/l for copper and 0.37 mmol/l for cadmium. The corresponding maximum adsorption capacities for copper and cadmium increased with increasing the initial pH, while the Langmuir equilibrium constants decreased except for cadmium with HEPES, which increased.

A modified Langmuir isotherm model correlating the maximum adsorption capacity and the equilibrium constant with pH and pH_{zcp} can describe the changes of the uptake of the metal ions by the corncob particles studied at various pH values.

The chemical, solvation, and coulombic free energies in James-Healy model (11) were estimated by means of the equilibrium constants with pH and the pH_{zcp}, which was determined by the primary equilibrium method of H^+ and OH^- on corncob particles. These results indicated that the chemical and solvation free energies are two main factors that affect adsorption, and their effects are opposite. The adsorption free energy will increase with pH during the adsorption processes of cupric and cadmium ions on corncob particles.

REFERENCES

1. Volesky, B. (1990) Removal and recovery of heavy metals by biosorption. In *Biosorption of Heavy Metals*; Volesky, B., ed.; CRC Press, Inc: Boca Raton, Florida, USA, 9–20.
2. Al-Asheh, S. and Duvnjak, Z. (1998) Binary metal sorption by pine bark: Study of equilibria and mechanisms. *Separation Science and Technology*, 33 (9): 1303–1329.
3. Vaughan, T., Seo, C.W., and Marshall, W.E. (2001) Removal of selected metal ions from aqueous solution using modified corncobs. *Bioresource Technology*, 78: 133–139.
4. Sun, G. and Shi, W. (1998) Sunflower stalks as adsorbents for the removal of metal ions from wastewater. *Ind. Eng. Chem. Res.*, 37: 1324–1328.
5. Al-Asheh, S. and Duvnjak, Z. (1996) Adsorption of copper by canola meal. *Journal of Hazardous Materials*, 48: 83–93.
6. Lehrfeld, J. (1996) Conversion of agricultural residues into cation exchange materials. *Journal of Applied Polymer Science*, 61: 2099–2105.
7. Marshall, W.E. and Champagne, E.T. (1995) Agricultural byproducts as adsorbents for metal ions in laboratory prepared solutions and in manufacturing wastewater. *J. Environ. Sci. Health*, A30 (2): 241–261.
8. Periasamy, K. and Namasivayam, C. (1994) Process development for removal and recovery of cadmium from wastewater by a low-cost Adsorbent: adsorption rate and equilibrium studies. *Ind. Eng. Chem. Res.*, 33: 317–320.
9. Marshall, W.E., Evans, W.J., and Champagne, E.T. (1993) Use of rice milling byproducts (hulls & bran) to remove metal ions from aqueous solution. *J. Environ. Sci. Health*, A28 (9): 1977–1992.
10. Wing, R.E. (1996) Corn fiber citrate: Preparation and ion exchange properties. *Ind. Crops Prod.*, 5: 301–330.
11. James, R.O. and Healy, T.W. (1972) Adsorption of hydrolysable metal ions at the oxide-water interface. *J. Colloid Interface Sci.*, 40 (1): 65–81.
12. Crawford, R.J., Harding, I.H., and Mainwaring, D.E. (1993) Adsorption and coprecipitation of single heavy metal ions onto the hydrated oxides of iron and chromium. *Langmuir*, 9: 3050–3056.
13. Agashe, K.B. and Regalbuto, J. (1997) A revised physical theory for adsorption of metal complexes at oxide surfaces. *Journal of Colloid and Interface Science*, 185: 174–189.
14. Esposito, A., Pagnanelli, F., and Veglio, F. (2002) pH-related equilibria models for biosorption in single metal systems. *Chemical Engineering Science*, 57: 307–313.
15. Ahmed, S.M. (1966) Studies of the dissociation of oxide surfaces at the liquid-solid interface. *Canadian Journal of Chemistry*, 44: 1663–1670.
16. Tewari, P.H. and Campbell, A.B. (1976) Temperature dependence of point of zero charge of cobalt and nickel oxides and hydroxides. *J. Colloid and Interface Science*, 55 (3): 531–539.
17. Akratopulu, K.Ch., Vordonis, L., and Lycourghiotis, A. (1986) Effect of temperature on the point of zero charge and surface dissociation constants of aqueous suspensions of γ-Al_2O_3. *J. Chem. Soc., Faraday Trans. I*, 82: 3697–3708.
18. Good, N.E., Winget, D., Winter, W., and Connolly, T.N. (1966) Hydrogen ion buffers for biological research. *Biochemistry*, 5 (2): 467–477.
19. Perrin, D.D. and Dempsey, B. (1974) *Buffers for pH and Metal Ion Control*; Chapman and Hall: New York, 43.

20. Fokkink, L.G.J., DeKeizer, A., and Lyklema, J. (1989) Temperature dependence of the electrical double later on oxides: Rutile and hematite. *J Colloid Interface Sci.*, 127: 116–131.
21. Zhou, J.L. and Kiff, R.J. (1991) The uptakes of copper from aqueous solution by immobilized fungal biomass. *J. Chem. Tech. Biotechnol.*, 52: 317–340.
22. Guibal, E., Jansson-Charrier, M., Saucedo, I., and Le Cloirec, P. (1995) Enhancement of metal ion sorption performances of chitosan: Effect of the structure on the diffusion properties. *Langmuir.*, 11: 591–598.
23. Biermann, C.J. (1996) *Handbook of Pulping and Papermaking*, 2nd Ed.; Academic Press, Inc: San Diego, California, 407.
24. Westall, J. and Hohl, H. (1980) A comparison of electrostatic models for the oxide/solution interface. *Advances in Colloid and Interface Science*, 12: 265–294.
25. Lide, D.R. (1998) *CRC Handbook of Chemistry and Physic*; 78th Ed.; Frederikse, H.P.R CRC: Boca Raton, Fla, 10–201.
26. Mizumachi, H. (2001) Wood-polymer composites. In *Wood and Cellulosic Chemistry*; Hon, D.N.-S. and Shiraishi, N., eds.; Marcel Dekker Inc: New York, 717.