

CHEMICAL UTILIZATION OF BIOMASS II: PREPARATION OF ADSORBENTS FROM WHEAT STRAW TO ELIMINATE CUPRIC AND ZINC IONS OF INDUSTRIAL WASTEWATERS

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Agricultural residues represent a cheap and environmentally safe source of raw material for the preparation of ion exchangers and adsorbents that may be useful for removal of metals and/or colour from different wastewaters. Metal ions (Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni and Zn) are known to contaminate the industrial effluents, water supplies, as well as mine waters. Fish and textile plants may apply this method to eliminate contaminants in case of low ion concentrations far away from their source. The simultaneous biosorption of Cu and Zn ions from aqueous solution by straw based oxidised cellulose was studied. The adsorption equilibrium was attained in 24 h at room temperature. The adsorption was found to fit the modified Langmuir type isotherms, and the parameters of the maximum adsorbent capacity and the adsorption intensity were calculated.

Keywords: adsorbents, straw, bio-based products

Introduction

The sorption of heavy metal ions onto biosorbents from aqueous solution has been studied for single systems (Xie, Chang & Kilbane, 1966). The influence of a second metal has also been investigated (Trujillo, Jeffers, Ferguson & Stevenson, 1991). Chong and Volesky (1996) reported a description of a two metal biosorption equilibrium using Langmuir-type models. There have been several extended Langmuir models applied to multicomponent sorption systems. Jain and Snoeyink (1973) developed an extended Langmuir model by adding a term based on the hypothesis that in a multicomponent system adsorption occurs both with and without competition. A two-term expansion of the isotherm for competition equilibrium of the two components of a binary mixture has also been reported (Levan & Vermeulen, 1981). The present paper investigates the binary sorption of copper and zinc ions onto oxidised cellulose using three molar ratios of Cu:Zn. The model has been developed by

incorporating an interaction factor correlation into the multicomponent Langmuir equation. This model was originally developed by Marton et al. (1981).

Materials and Methods

The batch sorption experiments for single-component systems were carried out using a constant temperature shaking water bath and a series of capped 125 ml conical flasks. In the sorption isotherm tests, 0.5 g of straw sample was thoroughly mixed with the metal ion solution (125ml). The concentrations of the two metal, copper and zinc ions system ranged from 0.2 to 3 mmol/dm³. A similar procedure was used for the bi-component studies. Three different systems were examined using copper and zinc in the molar ratios of 1:1, 1:2 and 2:1 (Cu:Zn) and in the concentration range of 0.5-4 mmol/dm³ for both Cu and Zn ions.

Materials

Stock solutions of CuSO_4 and ZnSO_4 were prepared in distilled water. Wheat straw was obtained from a local agro-refinery with the fraction 60-80 mesh particle size. Pretreatment procedure consists of a cc. HNO_3 and H_3PO_4 (1:1) treatment at 80 °C for 120 min and water washing.

Preparation of oxidized cellulose (OC)

Nitric acid (69.7%w/w) and phosphoric acid (85% w/w) were mixed in a 1:1 ratio. 5.0 g of straw sample was added to a 70 ml solution of the acid mixture. It was completely soaked and 1.0 g of sodium nitrate was added. An immediate formation of reddish brown fumes occurred. To prevent the release of these fumes into the air, the reaction container was covered with a Petri dish. The reaction mixture was allowed to react at room temperature, with occasional stirring using a glass rod, for 12, 24, 36 or 48 h. The reaction mixture, which appeared green, was diluted by adding an excess of water (about five times the volume of the reaction mixture). The diluted reaction mixture was filtered, and washed with water until the filtrate showed a pH of about 4. It was finally washed with acetone and then air-dried at room temperature. The dried OC was ball milled for 24 h and then sieved. The solid product of the reaction contained particles ranging between 74 and 105 μm was used for the adsorption investigation.

Determination of carboxyl content

This was performed according to the method described in the United States Pharmacopoeia (USP, 1995). Approximately 0.5 g of the sample was weighed and suspended in 50 ml of a 2% (w/w) calcium acetate solution for 30 min. The mixture was titrated with 0.1M NaOH using phenolphthalein as an indicator. The volume of NaOH solution consumed was corrected for the blank. The carboxyl content in the sample was calculated using the following relationship:

$$\text{Carboxyl groups (\% w/w)} = \frac{49 \cdot M \cdot V}{\text{Weight of sample (mg)}} \cdot 100$$

where M is the molality of NaOH, and V is the volume of NaOH in ml consumed in titration, after correcting for the blank.

The carboxyl content of our product was 18.2%.

Isotherms

Equilibrium sorption studies provide the capacity of the sorbent, which can be described by a sorption isotherm characterised by certain constants whose values express the surface properties and affinity of the sorbent. Sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that of the interface. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms. The data were determined and analysed in accordance with some of the most frequently used isotherms.

The Langmuir sorption isotherm (Langmuir, 1916) is the best known and the most often used isotherm for the sorption of a solute from liquid solution:

$$\frac{C_e}{q_e} = \frac{1}{Qb_1} + \frac{C_e}{Q} \quad (1)$$

where q_e is the sorption capacity at the equilibrium solute concentration C_e (mmol/g); C_e is the concentration of sorbate in solution (mmol/dm³); Q is the maximum sorption capacity corresponding to complete monolayer coverage (mmol/g); b_1 is a Langmuir constant related to the energy of sorption (dm³/mmol).

Butler and Ockrent (1930) developed a model for competitive sorption based on the Langmuir equation. This isotherm is applicable when each single-component obeys Langmuir behaviour in a single-component system. It is widely used to calculate the Langmuir constant Q , the amount of solute sorbed per unit weight of the sorbent, in the multicomponent systems. The common form for depicting the sorbate distribution is to correlate the amount of solute sorbed per unit weight of the sorbent with the residual solute concentration remaining in an equilibrium state. If there are two solutes present together in the sorption system the extended Langmuir isotherms are:

$$q_1 = \frac{Q_1 b_1 C_1}{1 + b_1 C_1 + b_2 C_2} \quad (2)$$

$$q_2 = \frac{Q_2 b_2 C_2}{1 + b_1 C_1 + b_2 C_2} \quad (3)$$

where q_1 and q_2 are the amounts of solutes 1 and 2 sorbed per unit weight of the sorbent at equilibrium concentrations C_1 and C_2 respectively.

Q_1 and Q_2 are the maximum sorption capacities of 1 and 2, respectively. These are determined from single-component systems and, therefore, correspond to a monolayer coverage of the sorbent. b_1 and b_2 are the Langmuir constants and are a function of the energy of sorption of solutes 1 and 2, respectively. These are also determined from single-component systems. These Langmuir equations are simple extensions of the single-component isotherms to multicomponent sorption. They assume that each component adsorbs onto the surface according to the ideal solute behaviour under homogenous conditions with no interaction or competition taking place between the molecules.

Extension of the Langmuir and BET theory for the description of multicomponent liquid-phase adsorption

According to the original Langmuir hypothesis, the free area available for adsorption of component i is:

$$S_i = \tau_i z_i \sigma_{0i} N \left(Q_i - \sum_{j=1}^n S_j \right) \quad (4)$$

Let us assume that the ratio of free and occupied area of the adsorbent is:

$$\frac{S_i}{\sum_{j=1}^n S_j} = \frac{N \tau_i z_i \sigma_{0i} Q_i}{\sum_{j=1}^n N \tau_j z_j \sigma_{0j} (Q_j - \delta_{ij})} \quad (5)$$

where δ_{ij} is the surface-area-excess accounting for the difference in size and energy-state of the competing adsorbing components. By definition $\delta_{ij} = 0$ for each $i = j$, while for $i \neq j$ it may be a positive or negative number, or zero.

By substituting Eq. 5 into Eq. 4 we obtain:

$$S_i = \tau_i z_i \sigma_{0i} N \left[Q_i - \frac{S_i}{N \tau_i z_i \sigma_{0i} Q_i} \sum_{j=1}^n N \tau_j z_j \sigma_{0j} (Q_j - \delta_{ij}) \right] \quad (6)$$

Let us introduce: $\tau_i z_i \sigma_{0i} N = b_i C_i$ (7)

Let us make use of the statement of BET theory, i.e. that at low concentration of the adsorbent component:

$$S_i = \left(1 - \sum_{i=1}^n k_i C_i \right) q_i \quad (8)$$

By substituting Eq. 7 and 8 into Eq. 6 we obtain:

$$q_i = \frac{b_i C_i Q_i}{1 + \frac{1}{Q_i} \sum_{j=1}^n b_j C_j (Q_j - \delta_{ij})} \cdot \frac{1}{\left(1 - \sum_{i=1}^n k_i C_i \right)} \quad (9)$$

Let us introduce:

$$b_{ji} = \frac{b_j (Q_j - \delta_{ij})}{Q_i} \quad (10)$$

For two components Eq. 9 becomes:

$$q_1 = \frac{b_1 Q_1 C_1}{1 + b_1 C_1 + b_2 C_2} \cdot \frac{1}{1 - k_1 C_1 - k_2 C_2} \quad (11)$$

$$q_2 = \frac{b_2 Q_2 C_2}{1 + b_2 C_2 + b_1 C_1} \cdot \frac{1}{1 - k_1 C_1 - k_2 C_2} \quad (12)$$

k_1 and k_2 in the equations 11 and 12 are so called interaction factors.

Results and Discussion

The data were examined by linear regression analysis using equations 11 and 12. Table 1 shows the modified Langmuir parameters for the adsorption of Cu(II) and Zn ions. Comparison of measured and calculated data (Fig 1) produced an excellent (>0.98) correlation coefficient for the bi-component system.

Table 1: Modified Langmuir parameters for the adsorption of Cu(II) and Zn(II) for the eq. 11 and 12.

Sample	Q_1	Q_2	b_1	b_2	k_1	k_2
	mmol/g		dm ³ /mmol			
Untrd. straw	0.072	0.066	0.52	0.37	0.021	0.013
Oxidized straw	0.321	0.293	0.98	0.83	0.043	0.080

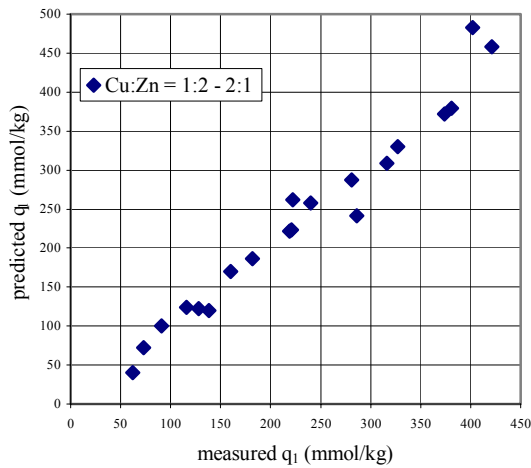


Figure 1: The relationship between measured and predicted amount of adsorbed component of Cu ion in the presence of Zn ion.

Conclusions

A series of modified extended multicomponent Langmuir isotherms have been used to correlate binary copper-zinc equilibrium sorption study results using oxidised wheat straw. Because of complexity of the mechanism of biosorption a new interaction factor-combined equilibrium model has been developed.

SYMBOLS

- A specific surface area of adsorbent, m^2/kg
 b adsorption energy coefficient, m^3/mol
 c_i concentration of i-th component, mol/m^3
 k_1 BET constant, m^2/mol
 N Avogadro's number, $1/\text{mol}$
 q_i amount of adsorbed component, mol/kg
 Q ultimate uptake capacity, mol/kg
 R universal gas coefficient, $\text{m}^2 \text{bar}/\text{K mol}$
 S_i surface covered by i-th solute, m^2
 z_i collision frequency factor of i-th solute
 σ_{0i} actual area of one adsorbed molecule, m^2
 τ_i residence time on the surface of i-th solute, h

SUBSCRIPTS

- i, j ..., ..., n component
 c calculated
 m measured

REFERENCES

1. Xie J. Z. and Chang H. L.: (1996) *Biores. Techn.* 57, 127-136
2. Trujillo E. M; Jeffers T. H.; Ferguson and Stevenson, H. Q.: (1991) *Environ. Sci. and Technol.* 25, 1559-1565
3. Le Van M. D. and Vermeluen T.: (1981) *Journ. of Phys. Chem.* 85, 3247-3250
4. Marton G.; Dencs J.; Szokonya L. and Illés Z.: *Hung. Journ. Ind. Chem.* (1981), 9, 251-262