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Technical Note

Determining the Overall Mass Transfer Coefficient for Adsorption of Cu^{2+} Ions onto Ca-Alginate in Fixed Bed Column

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ABSTRACT

In this study, adsorption of trace amounts of dissolved Cu^{2+} ion was investigated. The polymeric Ca-alginate particles was used as adsorbent. The pH of the solution affected the metal uptake capacity of the Ca-alginate and optimum initial pH of the solution was found as 4 at 25°C constant temperature for this study. The experiments were done at the same volumetric rates and different initial solute concentrations in the fluid. The equilibrium concentration in the fluid, c*, does equal to zero for irreversible adsorption and it is practically zero until the solid concentration is over half the saturation value. The adsorption isotherm of Cu^{2+} ion onto the above mentioned spherical Ca-alginate particles is indeed sharply convex and the corresponding value of equilibrium concentration, c*, is at a negligible level and the assumption c*=0 is valid. The Cu^{2+} ion equilibrium concentration is approximate zero even for the maximum adsorbate loading conditions of fixed bed sorption with recycle experiments. The overall mass transfer coefficient of K_e was obtained without the assumption $(\partial c/\partial t)=0$. © 2002 SDU. All rights reserved.

Keywords: Adsorption; Fixed bed column; Heavy metal; Overall mass transfer

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1. INTRODUCTION

Environmental pollution due to developments in technology is one of the most important problems. Heavy metals such as chromium, copper, lead, cadmium, etc., found in waste water are hazardous to the environment and effect on our biological ecosystem. Because they are toxic. Treatment of waste waters containing heavy metal ions involves concentration of the metals into a smaller volume followed by recovery or secure disposal. Heavy metal ions can be removed by adsorption process. Adsorption processes are typically carried out in beds consisting of large columns packed with a multitude of small pellets to promote contact between fluid and solid). A study of the evolution of accumulated metal in the beads revealed two possible accumulation phases. Accumulation differences between free and immobilized microalgal cells were investigated and resulted in no differences for copper, and small differences for zinc (Moreno *et al.*, 2002). The efficiency of the laboratory-scale continuous flow bioreactor loaded with alginate-immobilized cells and fed chromium solution was compared at different flow rates (Khattar *et al.*, 2002). The alginate beads and both entrapped live and heat inactivated fungal mycelia of Phanerochaete chryosporium were used for the removal of Hg^{2+} and Cd^{2+} ions from aqueous solution (Kacar *et al.*, 2002). A kinetic study of cadmium and lead biosorption to a brown alga Kjellmaniella crassiforia was investigated and average apparent diffusion coefficient of about $9\times10^{-6}cm^2.s^{-1}$ was found for both cadmium and lead ions (Seki *et al.*, 2002). Copper adsorption by free and immobilized mycelia of *Aspergillus niger* B77 in batch as well as in column mode experiments

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was investigated (Tsekova *et al.*, 2001). Microcystis aeruginosa immobilized in a natural polymer was tested for its potential to remove Cu^{2+} ions from aqueous solution in a continuous, downflow packed columnar reactor (Pradhan and Rai, 2001).

A comprehensive treatment of mass transfer in adsorption processes has been investigated (Vermeulen *et al.*, 1984). Approximate expressions for the rate of adsorbate uptake by spherical pellets were derived for linear and non-linear systems (Yao and Tien, 1992). The problem of determining intraparticle transport coefficients for multicomponent adsorption from experimental kinetic curves was analyzed (Carl and Morgenstern, 1992). In fixed-bed adsorption, the concentrations in the fluid phase and the solid phase change with time as well as with position in the bed. If the mass transfer coefficients and the equilibrium isotherm informations are known, the design of a fixed-bed adsorber and the prediction of the length of the adsorption cycle between reservoir and column might be easily carried out. The solute continuity equation for a fixed-bed adsorber, with provision for axial dispersion, is given as

$$\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial x} + \frac{(1-\varepsilon)}{\varepsilon}\frac{\partial q}{\partial t} = D_a \frac{\partial^2 c}{\partial x^2} \tag{1}$$

for "dilute" system (i.e., systems for which v is essentially constant). Eq. (1) has been widely employed in mass transfer coefficient measurement studies on packed beds. Solutions were derived by assuming the accumulation rate in the fluid $(\partial c/\partial t)=0$ (Radcliffe *et al.*, 1982; Cooney, 1991).

In this study the overall mass transfer coefficients were determined without the assumption $(\partial c/\partial t)=0$. Another advantage of the proposed technique arises from the fact that the determination of mass transfer coefficients is not based on column inlet and effluent fluid concentration measurement. Hence, overall mass transfer coefficients can be determined for a wide variety of operating conditions. For this purpose, fixed bed sorption with recycle system was envisaged, where a stream was taken from a reservoir, fed to a sorbent bed, and then recycled back to the reservoir. Investigators presented solutions for a process involving fixed bed sorption with recycle for the calculation of sorbent bed concentration profiles (Cooney and Shieh, 1972; Chang *et al.*, 1973). The purpose of the research presented in this article is to determine the overall mass transfer coefficients for adsorption of heavy metal ions to sorbent. Morever, the concentration-time profiles predicted by the model were compared with those obtained by substituting different overall mass transfer coefficient values in the model until the predicted profiles fitted the experimental reservoir concentration-time measurements.

2. MATERIALS AND METHOD

Ca-alginate spherical particles were employed in this study. 2g of Na-alginate were blended and mixed with water to 100ml, with continuous stirring in order to obtain a homogeneous solution. The solution was dropped into 400g/L calcium chloride solution by syringe pump (Braun Melsungen, type 871122). The exchange of sodium ions with calcium ions caused hardening and spherical sorbent particles were obtained. The average diameter of particles was 3.5mm.

Experiments were conducted using a percolation column with 12cm height and with 2.2cm internal diameter; 19.2g wet Ca-alginate particles were added to the column. The bed height of the sorbent particles in the column was 10.5cm. The porosity of the bed was found by first filling the column with water up to the packing height and then emptying it. The water volume then was used for the calculation of the bed porosity (ε=0.3). A recirculation system (reservoir volume=0.5L, temperature=25°C, pH of Cu^{2+} ion solution=4) as shown in Figure 1 was used and the adsorption of Cu^{2+} ion was investigated for the different initial concentrations of Cu^{2+} ion (134 and 238mg/L), at the constant volumetric flow rate was 12.4ml/min. The change of Cu^{2+} ion concentration with time was monitored by UV spectrophotometre (Nourbakhsh, 1991). The adsorption isotherm of Cu^{2+} ion onto the above mentioned spherical Ca-alginate particles was investigated. During the course of experiments, spherical sorbent particles were immersed in Cu^{2+} ion solutions at different initial concentrations in 250ml flasks at 25°C with initial pH=4. Jars containing sorbent particles and Cu^{2+} ion solutions at different initial concentrations were continuously shaken with a water bath shaker. A 150 minute contact time was established as an equilibrium were determined by UV spectrophotometre.

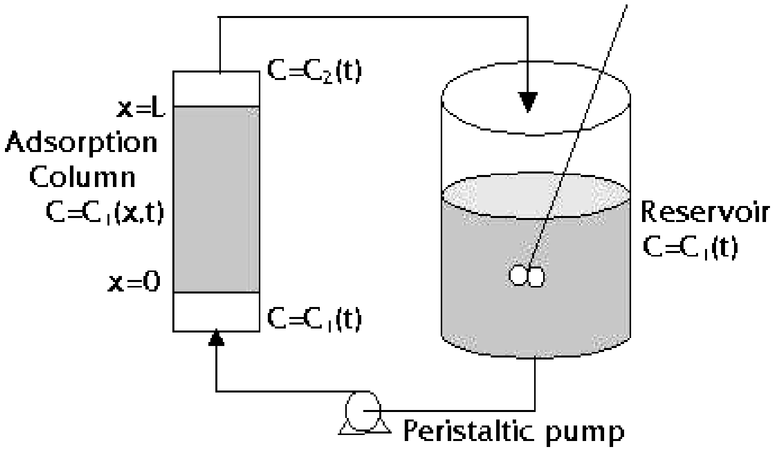

Figure 1. Reservoir-adsorbent system with recirculation

3. THEORY

For the fixed bed column system shown in Figure 1, the axial dispersion was neglected (D_a=0), because the fluid phase was liquid. The equation that characterizes this case is then given by

$$\frac{\partial c}{\partial t} + v.\frac{\partial c}{\partial x} + \frac{(1-\varepsilon)}{\varepsilon}.\frac{\partial q}{\partial t} = 0 \qquad (2)$$

The first term on the left hand side of Eq. (2) is the time rate of accumulation in the fluid and the third term corresponds to the time rate of accumulation in the solid. The mechanism of transfer to the solid includes diffusion through the fluid film around the particle and diffusion through the film around the particle and diffusion through the pores to internal adsorption sites.

The transfer process approximated using an overall mass transfer coefficient and an overall driving force. Therefore,

$$\frac{\partial q}{\partial t} = K_e a(c - c^*) \qquad (3)$$

Noting that the equilibrium concentration in the fluid, c* does equal to zero for irreversible adsorption and it is practically zero until the solid concentration is over half the saturation value (McCabe *et al.*, 1985), one obtains

$$\frac{\partial c}{\partial t} + v.\frac{\partial c}{\partial x} + 3.\frac{(1-\varepsilon)}{\varepsilon}.\frac{K_e}{R}.c = 0 \qquad (4)$$

Solving for c as a function of x and t, with the initial and boundary conditions that (c(0,0)=0, c(0,0)=c_1, c(0,0)=c_2), yields (Ozdural, 1994).

$$c_2 = c_1.\exp\left[-\frac{3(1-\varepsilon)LK_e}{\varepsilon vR}\right].\left(\frac{c_1}{c_0}\right)^{-(L/vt)} \qquad (5)$$

If the reservoir shown in Figure 1 is a perfectly mixed tank, the mass balance gives

$$\frac{dc_1}{dt} = \frac{1}{\tau}.(c_2 - c_1) \tag{6}$$

Substitution of Eq. (5) in Eq. (6) gives

$$\frac{dc_1}{dt} = \frac{c_1}{\tau}\left[\exp\left(-\frac{3(1-\varepsilon)LK_e}{\varepsilon vR}\right).\left(\frac{c_1}{c_0}\right)^{-(L/vt)} - 1\right] \tag{7}$$

Solution of Eq. (7) gives the change of reservoir concentration with time.

4. RESULTS AND DISCUSSION

The adsorption isotherm of Cu^{2+} ion onto the above mentioned spherical Ca-alginate particles is shown in Figure 2. This figure demonstrates that the adsorption isotherm is indeed sharply convex and the corresponding value of equilibrium concentration, c*, is at a negligible level and the assumption c*=0 is valid, The Cu^{2+} ion equilibrium concentration is approximately zero even for the maximum adsorbate loading conditions of fixed bed sorption with recycle experiments. Consequently, almost a perfect fit is obtained between the model output and the experimental measurements during the first 90min of perfusion studies.

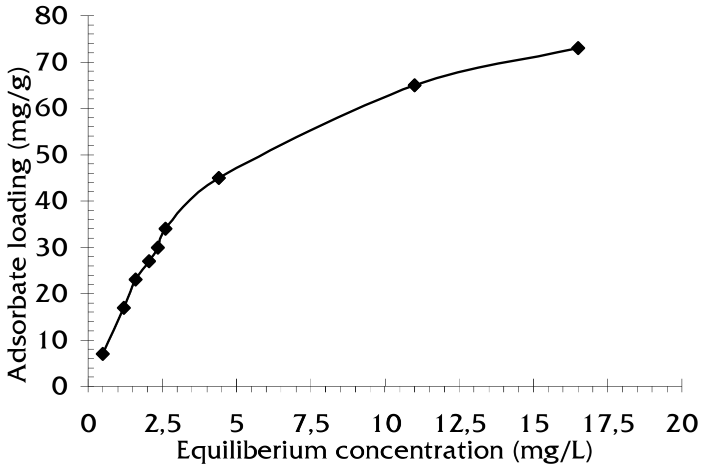

Figure 2. The adsorption isotherm of Cu^{2+} ions onto Ca-alginate (the initial Cu^{2+} ion concentration values are ranged between 25mg/L and 150mg/L, pH=4 and temperature=25°C)

Eq. (7) was solved by numerical integration and using second order Runge-Kutta method. The step size, Δt, to yield a sufficiently accurate solution was determined by successive reductions until no further significant concentration-time profiles (implying which were obtained by trying different K_e values in Eq. (7)) were obtained when compared with those of experimental measurements. When the model-predicted profile fitted the experimental profile, the corresponding K_e value used in Eq. (7) was taken as the overall mass transfer coefficient. Matching between the model predictions and experimental measurements was examined only for the data where solid concentration was well below half the saturation value and the assumption c*=0 held.

Figure 3 illustrates that during the fixed bed recycle experiments, the degree of adsorbate loading is very low. The model predicted reservoir solute concentration time profiles in compliance with the experimental measurements. The overall mass transfer coefficients for the 233mg/L and 138mg/L initial

Cu^{2+} ion concentrations at 12.4ml/min flow rate, was almost $1 \times 10^{-6} m^3/m^2 s$.

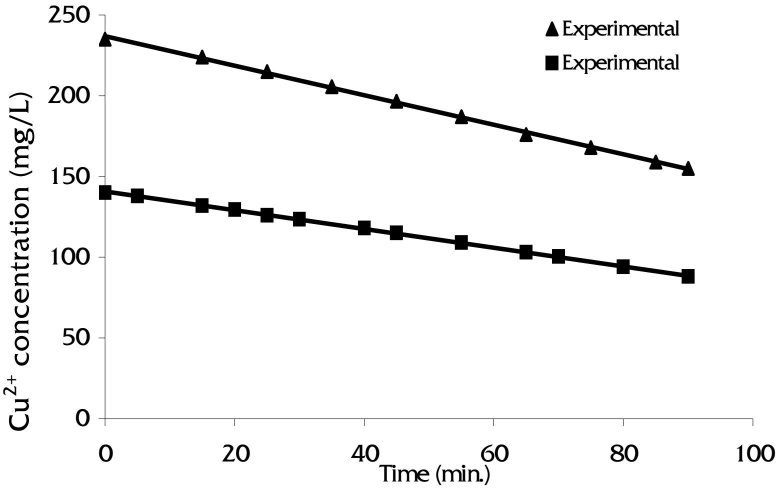

Figure 3. Comparison of the experimental measurements with the model output. (initial Cu^{2+} ion concentrations 233mg/L and 138mg/L, pH=4 and T=25°C)

5. CONCLUSIONS

The model presented in this work describes the adsorption process in recycling systems. The model is simple and it provides an effective tool for determining overall mass transfer coefficients in fixed bed sorption columns. In this work the model developed requires perfect spherical particles, however, Eq. (7) might still be used for fixed beds composed of nonspherical particles by substituting the equivalent radius instead of R. The adsorption isotherm of Cu^{2+} ion onto the above mentioned spherical Ca-alginate particles is indeed sharply convex and the corresponding value of equilibrium concentration, c^*, is at a negligible level and the assumption $c^*=0$ is valid. The Cu^{2+} ion equilibrium concentration is almost zero even for the maximum adsorbate loading conditions of fixed bed sorption with recycle experiments. In these circumstances, the overall mass transfer coefficient K_e was determined by using this model.

NOTATION

a	external particle surface area, m^2/m^3 solid
c	solute concentration in fluid phase, kg solute/m^3 fluid phase
c_0	initial solute concentration in the reservoir and at column inlet, kg solute/m^3 fluid phase
c_1	solute concentration in fluid phase at column inlet and in the reservoir, kg solute/m^3 fluid
c_2	solute concentration in fluid phase at column effluent, kg solute/m^3 fluid
c^*	equilibrium solute concentration value in fluid phase, kg solute/m^3 fluid
D_a	axial dispersion coefficient, m^2/s
K_e	overall fluid phase mass transfer coefficient, m^3/m^2 s
L	adsorbent bed length, m
q	solute concentration in solid phase, kg solute/m^3 solid
R	adsorbent particle radius, m
t	time, s
v	interstitial fluid velocity, m/s
x	axial distance, m

Greek Letters

ε packed bed porosity, m^3 voids /m^3 bed
τ residence time in reservoir, s

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