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Modelling of breakthrough curves of single and binary mixtures of Cu(II), Cd(II), Ni(II) and Pb(II) sorption onto grape stalks waste

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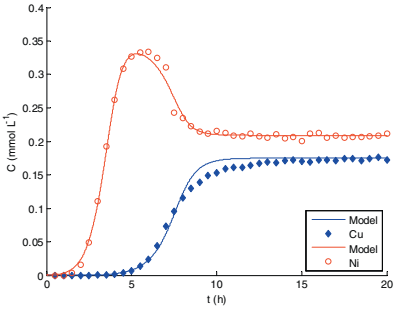
HIGHLIGHTS

- Cu, Cd, Ni and Pb sorption in grape stalks packed columns.
- Metal sorption breakthrough curves modelling (single and binary mixtures).
- Except Pb all the other metal ions suffer overshoot in binary mixtures.
- Satisfactory fit of breakthrough curves.
- Satisfactory fit of elution profile of overshoot metal ion.

GRAPHICAL ABSTRACT

Experimental data and predictive breakthrough curves for metal sorption onto grape stalks from Cu–Ni binary mixture.



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ABSTRACT

Few studies deal on metal sorption from multi-metal solutions, though in real situations more than one metal ion are present in solution and interactions between them occur. Interaction takes place when the different metal ions compete for the same sorbent active sites. In this work, sorption of Cu(II), Cd(II), Ni(II) and Pb(II) onto grape stalks waste in single and binary mixtures has been investigated. Sorption studies were carried out in continuous mode by using packed columns with grape stalks waste. The obtained metal ions breakthrough curves in binary mixtures showed that lead is not overshoot in binary mixtures with copper, cadmium and nickel. Copper is only overshoot in binary mixtures with lead. Nickel and cadmium suffer >60% overshoot metal sorption loose in binary mixtures with copper and lead. A model based on the Homogeneous Surface Diffusion Model (HSDM) has been developed to describe breakthrough curves. Langmuir model and Extended Langmuir Model (MEL) have been incorporated into the kinetic HSDM for breakthrough curves prediction of single and binary systems, respectively. The proposed model fits successfully the breakthrough curves of metal sorption from single and binary mixtures. In binary mixtures, the model also satisfactorily fits the elution profile of the overshoot metal ion.

1. Introduction

From the different methods used for removing metal ions adsorption is one of the most common and effective process for this purpose [1]. In the last years, most of research focused on metal sorption from single metal solutions. In most of the studies the parameters that most influence metal adsorption (pH, time of contact, metal and sorbent concentration) and the mechanisms of sorption were investigated and the sorbent functional groups involved in the process elucidated [2]. Few studies deal on metal sorption from multi-metal solutions, though in real situations more than one metal ion are present in solution and interactions between them occur. Interaction takes place when the different metal ions compete for the same sorbent active sites.

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In sorption processes in packed-bed columns filled with sorbent materials the competitive sorption is observed with an overshoot in the breakthrough curve. The overshoot is produced by a sudden increase above the input concentration to decrease later to its feeding concentration. The overshoot depends on the adsorption affinity of the sorbates and their concentration; the sorbate with the lower sorption affinity is displaced by the sorbate with higher sorption affinity. A good understanding of the competitive sorption would help to improve the accuracy to predict sorbent behavior in the simultaneous removal of two or more solutes. Literature concerning metal ions removal from multi-metal solutions is relatively scarce, especially when the process is carried out in a sorbent packed column operated in the continuous mode [3–10]. Nevertheless, several authors have made some attempts to describe the sorption breakthrough curves of metal ions and the overshoot suffered by the metal ions with lower affinity in competitive sorption processes. In order to predict results for Cu(II), Zn(II) and Cd(II) sorption onto bone char from binary mixtures [6,7] incorporated the Langmuir and the Sips equations into the ideal adsorbed solution theory (IAST) and developed a multicomponent mass transport model based on the Homogeneous Surface Diffusion Model (HSDM). The same author had previously developed the same film-surface diffusion based model to simulate the fixed bed single metal sorption of these metal ions onto bone char [8]. Vilar et al. [9], used a mass transfer model for the adsorption and desorption process considering an external and intraparticle film resistance to simulate an algae sorption column performance to sorb metal ions from Pb/Cu and Pb/Cd binary mixtures. Similar models based on HSDM have also been developed to describe sorption breakthrough curves of organic solutes from binary mixtures [11–14]. In this study, a model based on the Homogeneous Surface Diffusion Model for describing fixed bed sorption of binary mixtures of Cd, Cu, Ni and Pb onto grape stalks has been developed.

2. Materials and methods

2.1. Materials, reagents and instrumentation

Grape stalks (GS) waste generated in wine production (supplied by a wine manufacturer from Castilla la Mancha region, Spain) was rinsed three times with distilled water, dried in an oven at 110 °C until reaching constant weight, cut and sieved for a particle size of 0.25–0.50 mm.

Metal solutions were prepared by dissolving appropriate amounts of $CuCl_2{\cdot}2H_2O$, $NiCl_2{\cdot}6H_2O$, $PbCl_2$, $CdCl_2 \cdot 2\frac{1}{2}H_2O$ in Milli-Q grade water. Acid and base solutions prepared from HNO_3 (67%) and NaOH (pellets) were used to adjust the solution pH to the desired value.

Metal concentration was analysed by flame atomic absorption spectroscopy (FAAS) using a Varian SpectrAA 220FS equipment coupled with an automatic dilutor Varian SIPS and autosampler Varian SPS3. Metal standard solutions of 1000 mg L^{-1} were used for FAAS calibration.

Measurement of pH was performed using a pHmeter PHM 250 (Meterlab). All metal reagents were purchased from Panreac (Terrassa, Spain).

2.2. Batch equilibrium studies

Equilibrium isotherms for each metal ion were obtained in batch by contacting 0.1 g of grape stalks with 15 mL of different metal solutions (Cd, Cu, Ni and Pb) for 24 h in continuous agitation at 20 ± 2 °C. The range of initial metal concentration was within (5–1000 mg L^{-1}) and each solution pH was adjusted to the initial value 5.2. The sorbent was separated from the liquid by filtration through a 0.45 μm filter, the filtrates were acidified and analyzed for metal concentration by FAAS.

2.3. Column experiments procedure

Fixed bed sorption experiments were carried out in glass columns of 10.0 cm length and 1.0 cm inner diameter (Omnifit). Columns were packed with approximately 0.5 g grape stalks waste (dry weight) previously rinsed with abundant water until no release of colored compounds was observed. By doing this, a bed height around 6.7 cm was obtained. Sorption process was carried out in the up-flow mode to avoid possible short-circuiting by clogging and channelling. The solutions were pumped at room temperature (20 ± 1 °C) upwards the grape stalks packed column by a peristaltic pump at a flow rate of 30 mL h^{-1}. By using an automatic fraction collector (Gilson FC 203B), samples of 5.5 mL were collected at different times. The pH of the collected samples was recorded. The solutions were then acidified to avoid possible metal precipitation and analysed by FAAS. Breakthrough curves were obtained by plotting C/C_0 ratio (concentration of metal ions in the effluent/concentration of metal ions in the influent) versus time. Each experiment was carried out in duplicate and the average results are presented.

2.3.1. Sorption from single metal solutions

For single metal solutions runs, the feeding solution of Cu(II), Cd(II), Ni(II) and Pb(II) concentration was 0.2 mM. Initial pH was adjusted to 5.2 and the automatic fraction collector was programmed to take a sample (5.5 mL) each hour.

2.3.2. Sorption from binary mixtures

Equimolar concentration of 0.2 mM of Cu(II)–Ni(II), Cu(II)–Cd(II), Cu(II)–Pb(II), Ni(II)–Pb(II), Ni(II)–Cd(II), Pb(II)–Cd(II) binary mixtures were used as feeding solution in binary mixtures experiments. Initial pH was adjusted to 5.2 and the automatic fraction collector was programmed to take a sample (5.5 mL) each 30 min.

2.4. Modelling of adsorption process

2.4.1. Equilibrium models

Single-solute sorption equilibrium isotherms of Pb, Cu, Cd and Ni onto grape stalks were described by Langmuir isotherm:

$$q_e = \frac{q_{max} b C_e}{1 + bC_e} \tag{1}$$

where q_e is the equilibrium solid-phase concentration (m mol g^{-1}), q_{max} is the monolayer capacity of Langmuir equation (m mol g^{-1}), b is the Langmuir isotherm constant (L m mol^{-1}) and C_e is the equilibrium liquid-phase concentration (m mol L^{-1}).

Sorption equilibrium isotherms of binary mixtures were described by the Modified Extended Langmuir (MEL) [10,14]. This model, based on the mechanism of direct competition for adsorption sites, is one of the simplest and most widely used models and is represented by the equation:

$$q_{e,1} = \frac{K_1 b_1 (C_{e,1}/\eta_1)}{1 + b_1(C_{e,1}/\eta_1) + b_2(C_{e,2}/\eta_2)} \tag{2}$$

$$q_{e,2} = \frac{K_2 b_2 (C_{e,2}/\eta_2)}{1 + b_1(C_{e,1}/\eta_1) + b_2(C_{e,2}/\eta_2)} \tag{3}$$

where K_1 and K_2 are the MEL constants (m mol g^{-1}); η_1 and η_2 are the Langmuir correction coefficients and b_1 and b_2 are the Langmuir isotherm constants (L m mol^{-1}).