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A fast and easy approach to the simulation of binary mixtures sorption kinetics

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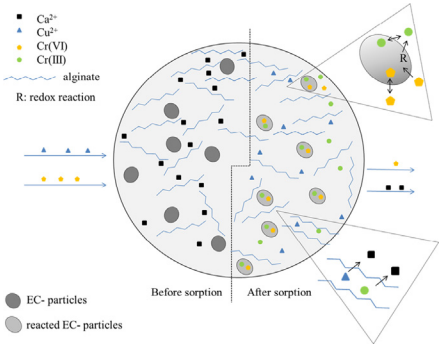
HIGHLIGHTS

- Cr(VI) and Cu(II) sorption onto exhausted coffee encapsulated in gel beads
- Complex system: Sorption, redox reaction and ion exchange mechanism taking place
- Bench and pilot scale kinetics data modelling by Linear Adsorption Model (LAM)
- Development of an empirical model to quickly determine LAM parameters
- Simulation of process kinetics by combining LAM and the empirical model developed

GRAPHICAL ABSTRACT



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ABSTRACT

Diffusivity of a component in a binary mixture is affected by the presence of a second component. The knowledge of the influence on each other component diffusivity is very useful for the prediction of sorption kinetics of binary mixtures. In this work kinetic studies of Cr(VI) and Cu(II) binary mixtures sorption onto exhausted coffee encapsulated in calcium alginate beads were carried out in both bench and pilot scale experiments. The spectroscopic analysis evidenced the complexity of the process since different mechanisms such as adsorption, redox reaction and ion exchange are involved. Experimental data were fitted to the Linear Adsorption Model (LAM). An empirical quadratic model was developed to estimate LAM parameters (D_e) and $\alpha = C_f/(C_i - C_f)$ as a function of the initial concentration of metals in the mixture. The empirical model developed enables to estimate the LAM parameters (D_e and α) of metal ions binary mixtures provided that the initial concentration of the metal ions is included in the range of concentrations studied. The estimated parameters introduced in LAM equation allow simulating the corresponding binary mixtures sorption kinetics. This study constitutes a fast and easy approach to the modelling of sorption kinetics of complex systems in which different processes take place simultaneously.

1. Introduction

Sorption processes in porous natural materials as a way to decontaminate wastewaters has attracted the attention of researchers during the last two decades. In our previous works exhausted coffee waste (EC)

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was investigated for Cr(VI) sorption in single and binary mixtures with Cu(II) (Fiol et al., 2008; Liu et al., 2015). In those works it was concluded that: Cr(VI) sorption by EC comprises reduction and sorption of Cr(VI) and Cr(III) and the presence of Cu(II) in the binary mixtures exerts a synergic effect on Cr(VI) sorption (Pujol et al., 2013). Exhausted coffee waste like most of bisorbents based on vegetable or agricultural wastes, is fragile and does not present either uniform or spherical shape. These characteristics make such materials unsuitable for large-scale processes. Encapsulation of biosorbents in polymeric matrixes such as calcium alginate has been used by some authors to solve the above mentioned problems. Calcium alginate has been successfully applied for the encapsulation of bacteria (Sag et al., 1995), algae (Aksu et al., 1998) and fungi (Bai and Abraham, 2003) for metal ions removal. More recently, agro food industry wastes such as grape stalks have been encapsulated for Cr(VI) sorption (Fiol et al., 2006; Sillerová et al., 2015; Escudero et al., 2017) while encapsulated sewage treatment plant waste metal (hydr)oxide was tested for arsenic removal (Escudero et al., 2009; Garlaschelli et al., 2017)). Calcium alginate beads themselves have proved to be efficient for divalent and trivalent metal ions removal by ion exchange between the calcium(II) in the beads and metal cations. (Chen et al., 1997; Ibañez and Umetsu, 2002; Cataldo et al., 2013; Escudero et al., 2017).

In this work, exhausted coffee has been encapsulated in calcium alginate beads to study Cr(VI) and Cu(II) adsorption kinetics in binary mixtures. It is well known that the kinetics of adsorption processes involve three consecutive steps: external diffusion of the solute through the liquid film that surrounds the solid particles, adsorption of the solute on the sorbent and internal diffusion across the particle by pore diffusion, surface diffusion or both of them. Depending on which is the rate-limiting step, different models are used to simulate the adsorption kinetics. The external-film diffusion model (Ponnusami et al., 2010; Sag and Aktay, 2000) describes the initial period of adsorption when the driving force is the concentration gradient located at the interface region between the bulk solution and the external surface of the adsorbent particles. The most used models when the adsorption step is considered to be the rate-limiting step are the pseudo-first order equation (Liu and Liu, 2008), pseudo-second order equation (Liu and Liu, 2008), Langmuir kinetic model (Placinski et al., 2009), Statistical Rate Theory (SRT) (Haerifar and Azizian, 2013; Placinski et al., 2009), and Elovich equation (Largitte and Pasquier, 2016). When intra-particle diffusion is the rate-limiting step the models used are the Weber-Morris equation or intraparticle model equation (Largitte and Pasquier, 2016; Liu and Liu, 2008; Sag and Aktay, 2000), the Fickian diffusion model (Ponnusami et al., 2010), the Film-pore diffusion model, the Linear Adsorption Model (LAM) (Chen et al., 1997; Papageorgiou et al., 2006), the Macropore and Micropore diffusion, the Macropore and Micropore parallel, the Shrinking Core Theory model, Homogeneous Surface Diffusion Model (HSDM) (Xu et al., 2013) and the Pore and Surface Diffusion model (Ma et al., 1996). In a multicomponent system as the studied in this work where several physical and chemical processes (sorption, reduction, ion exchange) take place the suitable model would be the Pore and Surface Diffusion model for a non-equilibrium multicomponent system. The use of this model requires estimating a set of unmeasured and hard-measuring parameters which makes the optimization process hard because of the large computational work required. Moreover, a specific experimental design is required to obtain the needed data to solve this complex mathematical problem.

Due to the complexity of the Pore and Surface Diffusion model and the large number of experiments required, the authors of the present study opted for testing simplified models with the least number of parameters that could explain the kinetics of the overall adsorption process of Cr(VI) and Cu(II) on exhausted coffee encapsulated in calcium alginate beads. Several models such as Weber-Morris and the Fickian Diffusion model were tested and the final choice was the Linear Adsorption Model that resulted to be the one that fitted best the experimental data. The advantage of this model is that only two parameters (D_e *and* α) for component of the mixture are needed. Furthermore, these parameters are of easy determination as $\alpha = C_f/(C_i - C_f)$ and D_e is obtained by solving a nonlinear equation. Once these two parameters were determined for each binary mixture, the foreseeable relationship between them and the initial concentration of the metals in the mixture was investigated by a regression model.

2. Experimental

2.1. Materials

Sodium alginate salt from brown algae purchased from Fluka was used as the hydrocolloidal gelling material. As fixing solution a $CaCl_2$ solution from Panreac (Barcelona, Spain) was used. Metal solutions were prepared by dissolving appropriate amounts of $K_2Cr_2O_7$ (Scharlau) and $CuCl_2 \cdot H_2O$ (Merk) in distilled water. NaOH and HCl 32% purchased from Panreac (Barcelona, Spain) were used for pH adjustment. Metal standard solution of 1000 mg/L purchased from Carlo Erba (Milano, Italy) was used for Atomic Absorption calibration.

Exhausted coffee (EC) waste was kindly provided by a soluble coffee production plant from Catalonia region (Spain). The waste was first oven dried at 105 °C until constant weight and then ground and sieved to obtain a particle size of 50–100 μm.

2.2. Preparation of the beads

The beads were prepared according to the procedure followed by Fiol et al. (2005). A 1% (w/v) Na-alginate solution was prepared by solving 1 g of sodium alginate into 100 mL distilled water at a temperature of about 65 °C. Then, the gel was allowed to cool down at room temperature and 2 g of exhausted coffee powder (50–100 μm) was added to the gel with continuous stirring. Once the mixture was homogeneous it was forced through a micropipette tip by a peristaltic pump. The resulting gel droplets were collected in a stirred reservoir containing 200 mL of a chemical "fixing" solution of 0,1 M $CaCl_2$. The beads were allowed to harden in this solution for 24 h. After this time hard spherical beads containing 2% (w/v) of exhausted coffee were obtained. The microbeads were filtered and rinsed several times with distilled water to remove calcium chloride from the bead surface. Then they were stored in distilled water at 4 °C until their use. When calcium alginate beads were used as a blank, the same procedure was followed but in this case there was no addition of exhausted coffee powder. The average diameter of the obtained beads determined by optical microscopy was 3.14 ± 0.14 mm. Once produced the beads were stored in Milli-Q water at 4 °C. The different beads will be referred to as CA (calcium alginate beads) and EC-CA (calcium alginate beads containing exhausted coffee).

2.3. Beads physical characterization

CA and EC-CA beads properties that are likely to be related to their sorption performance namely water content, weight swelling ratio, diameter and density were determined. Morphological and elemental analysis of the beads by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDX) was also carried out. The presence of reduced species of chromium sorbed onto the beads was examined by ESR (Electron Spin Resonance).

2.3.1. Water content and weight swelling ratio (WSR)

The dry weight of 40 beads was determined drying the beads at 40 °C until constant weight was reached. To measure the wet weight the same amount of beads were placed onto a cellulose filter paper

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