Nano-Iron Based Coated Biomass as Packing Material in Fixed-Bed Reactors for Lead Removal from Wastewater: Experimental and Mathematical Modelling

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Abstract

The lead pollution of natural environments is considered a severe issue due to the high toxicity and mobility of lead ionic species. The present study deals with the removal of Pb(II) ions from synthetic wastewater by means of iron-based coated hazelnut shells, used as packing material in lab-scale fixed bed columns. The biomass was coated through the direct precipitation of nano-iron oxide nanoparticles and demonstrated a notable Pb(II) sorption capacity. In detail, the continuous experiments showed a Pb(II) removal efficiency of 80% at an initial Pb(II) concentration of 50 mg/L, a bed height of 6 cm and an inlet flowrate of 4 mL/min. Different operating parameters values were varied (initial Pb(II) concentration, inlet flowrate and bed height) at pH>pH of zero charge of the packing material. The obtained breakthrough curves were fitted by suitable dynamic models, to obtain the regressed model parameter values for a subsequent pilot-scale process simulation and scale-up.

Keywords: Lead; fixed-bed reactor; continuous-process; laminar-flow; nano-iron coating.

1. Introduction

Among the various processes developed for the heavy metals removal and recovery, liquid/solid separation performed by solid sorbent material has demonstrated to be one of the most prominent technology (Mpouras et al., 2017). Through the sorption process the heavy metals can be effectively separated from liquid streams and recovered onto the surface of solid sorbent materials, that can be subsequently washed to concentrate the heavy metals in a solution that, after eventual additional purification steps, can be used in a new industrial cycle. When the sorption process is characterized by fast kinetics and the mean size of the sorbent material is of the minimum order of magnitude of 0.5 mm (to avoid excessive pressure drops) the fixed-bed reactor should be preferred instead of stirred tank, since a higher volume of inlet wastewater can be treated at fixed reactor volume value.

In this work a Pb aqueous solution was used to simulate a heavy metal polluted water, and was treated using hazelnut shells coated by precipitated nano-magnetite particles to increase their sorption capacity and specific surface area value. The obtained particles were used as packing material in lab-scale fixed-bed reactor to treat the synthetic wastewater at low inlet-flowrate. The obtained breakthrough curves were fitted by suitable dynamic models to estimate the film mass transfer coefficient at different fluid dynamics conditions, used to obtain the empirical coefficients of the classical correlations between *Sh*, *Sc* and *Re* numbers.

2. Materials and Methods

2.1. Materials and experimental

All the reagents used were of analytical grade and were purchased from Carlo Erba (Milan). The hazelnut shell particles were obtained by crushing commercial hazelnut shell after washing them with demineralized water and drying them in hoven at 80°C overnight. Subsequently, the particles were sieved and characterized; the complete characterization is reported in a previous work (Vilardi et al., 2019). The particles were characterized by a mean size, d, of 1 mm. The particles were coated with nano-magnetite particles, by a precipitation method (impregnation) reported in a previous work (Han et al., 2015). The pH of zero charge was measured according to the literature (Reymond and Kolenda, 1999) and was equal to 2.93. The coated particles were used as packing material in lab-scale fixed bed reactor, made of glass, with internal diameter of 1.5 cm and length of 15 cm. The bed height, h, was fixed to 6 cm, corresponding to a bed volume V of 10.5 mL using 7 g of packing material (m). Thus, the bed density, ρ_b, was calculated as the ratio among m and V, equal to 666.67 g/L. The inlet flowrate, Q, was varied as 2, 3, 4, 5, 6 and 7 mL/min, corresponding to 1.13, 1.70, 2.26, 2.83, 3.40 and 3.96 m/s of linear velocity v. The Pb solution (50 mg/L) was prepared dissolving $PbNO_3$ in demineralized water and the pH was measured by a Crison pH-meter. The pH was about 6.6, higher than the pH of zero-charge of the sorbent particles that for this reason were negatively charged during the treatment, favoring the sorption process of Pb cations, mainly present as Pb^{2+}. At each time steps (5 min), a liquid aliquot from the outflow from the fixed-bed reactor was withdrawn for the measurement of the residual Pb concentration, up to the saturation of the bed (t_e is the bed saturation time). A Flame Absorption spectroscopy instrument (Agilent) was used for this purpose). The experiments were conducted in triplicate, the average values were reported in the graphs (standard deviation<4%).

2.2. *Data modelling and results*

The maximum column capacity q_{tot} was calculated as:

$$q_{tot} = \frac{Q\int_{t=0}^{t=te} C_{ads}dt}{1000} \quad (1)$$

where C_{ads} is the sorbed Pb concentration. The total bed sorption capacity, q_e, can be calculated as the ratio among q_{tot} and m, whereas the removal efficiency, R, was calculated as follows:

$$R = 100\frac{1000q_{tot}}{Qt_eC_0} \quad (2)$$

where C_0 is the initial Pb concentration. The obtained breakthrough curves were modelled according to a dynamic model developed in a previous work (Vilardi et al., 2019), considering as limiting resistance to the mass transfer process of Pb from liquid to solid phase the diffusion of Pb cations through the liquid film around the packing material's particles. The regressed model parameters, i.e. the mass transfer coefficient k_f at different inlet flow-rates, were then used in a non-linear regression procedure using the following empirical correlations between Sherwood, Schmidt and particle's Reynolds numbers:

$$Sh = \frac{k_f d}{D} = aRe_p^e Sc^f \quad (3)$$

where D is the Pb bulk diffusion coefficient, $Re_p = vd/\nu$ ν is the solution kinematic viscosity and a, e, f are the empirical coefficients. Figure 1 displays the main results obtained in this work. It can be observed that increasing the inlet flowrate caused an efficiency decrease (R was in the range 74-80% for Q=2-4 mL/min, whereas it dropped in the range 67-73% for Q=5-7 mL/min), mainly due to a decrease in the contact time between bed and solution. As expected, the k_f value increased with an increase of inlet flowrate, i.e. linear velocity value, since the mass transfer phenomenon was dependent on fluid dynamic conditions established in the reactor and at higher *Re* number values the solute mass transfer from liquid to solid phase resulted enhanced. The value of a was close to 2, typical of spherical shaped particles, whereas the e and f values were in line with those obtained in similar works (Vilardi et al., 2019).

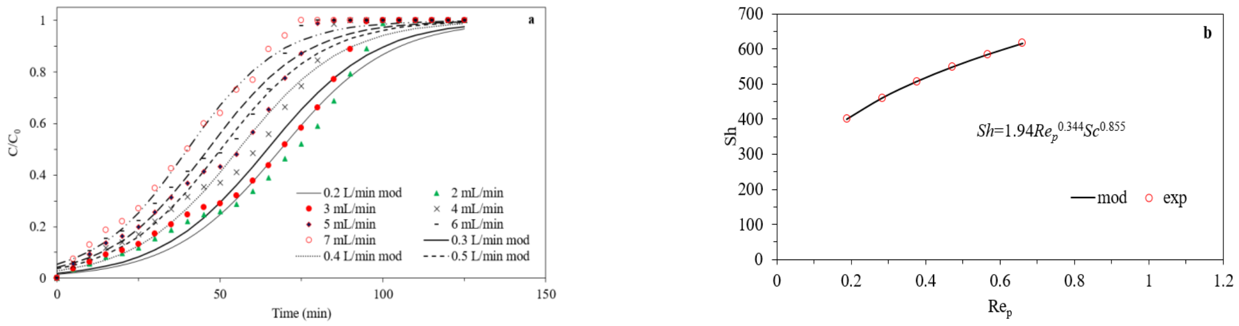

Figure 1. Breakthrough curves at different inlet flowrates (exp and mod, a) and *Sh*, *Sc* and Re_p correlation (b).

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