Removal of Cr(VI) under flow conditions using a green nano-iron loaded resin

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Abstract

A new nanocomposite material, consisting of nanoiron incorporated in cationic resin beads, was evaluated for the removal of Cr(VI) under flow conditions, by conducting column experiments. An aqueous solution containing Cr(VI) 5 mg/L and NaCl 0.01 M as inert electrolyte was introduced in the column applying a continuous up-flow mode. The tests were carried out using a column with diameter 2.6 cm and the flowrate was stepwise increased, reducing the Empty Bed Contact Time (EBCT) from 38 to 2.3 minutes. The reduction of Cr(VI) was found to depend on the residence time of the solution inside the bed of R-nFe, and the pH of flowing solution. The column has treated an amount of solution equivalent to 640 bed volumes without appearance of the Cr(VI) breakthrough. Also, when the feeding solution was spiked with both Cr(VI) and Ni, the effluents were free from the two elements, indicating that the nanocomposite material can be equally efficient in the case of mixed contamination.

Keywords: nanoiron loaded resin, cation exchange resin, hexavalent chromium, column tests

1. Introduction

A very efficient reductant for the remediation of polluted waters is nano zero valent iron (nZVI) (O'Carroll et al. 2013; Mystrioti et al. 2016). However, the direct use of nZVI particles for wastewater treatment, or for the remediation of contaminated groundwater following pumping, must overcome the difficulties to separate the exhausted nanoparticles from the purified aqueous phase. Alternative modes for the exploitation of high nZVI remediation capabilities are investigated, such as the dispersion of the nanoparticles inside the matrix of a granular porous material, like granular activated carbon, chitosan or resin beads (Tseng et al. 2011; Toli et al. 2016, 2018). When nZVI is incorporated in a granular solid, the composite product can be used in a packed bed installation avoiding the solid/liquid separation step. Cationic exchange resins are an interesting porous support for the attachment of iron nanoparticles with an additional characteristic, i.e. the capacity to adsorb the cationic byproducts (Zhao et al. 2011).

İn the present study, the selected support was the macroporous cationic resin Amberlyst 15, with a mean pore size of 38.4 nm. A 'green' synthesis procedure was applied for the incorporation of elemental iron nanoparticles in the resin beads. The synthesis was carried out in two steps: (i)adsorption of Fe(III) cations from a ferric chloride solution and (ii) reduction of adsorbed Fe(III) using the natural polyphenols of green tea extract. In a previous study, the effectiveness of the nanoiron loaded resin (R-nFe) for the treatment of contaminated waters was evaluated by conducting batch tests and using as model contaminant the hexavalent chromium(Toli et al. 2018). The objective of present work was to evaluate the performance of R-nFe under flow conditions and determine the critical design and operating parameters.

2. Materials and Methods

The nZVI loaded resin (R-nFe) was placed in a polyethylene column with a diameter of 2.6 cm. The characteristics of the column are presented in Table 1. The packed column was connected to a peristaltic pump (Alitea, Sweden) and to a reservoir, which contained the fluids prepared for introduction in the column. The feeding of aqueous solutions was carried out in an upflow mode. The column was first saturated with 1L of NaCl 0.01M as inert electrolyte to obtain a steady flow rate. Afterwards, an aqueous solution containing Cr(VI) 5.4 mg/L and NaCl 0.01 M was introduced in the column. For some period the feeding solution was also spiked with Ni at a concentration of 5 mg/L. The flowrate was gradually increased from 1.2 up to 20 mL/min, in order to determine the minimum required contact time. The total amount of solution introduced in the column was equal to 29 liters (corresponding to 640 bed volumes (BV). Column effluents were sampled periodically and analyzed for pH, ORP, Cr(VI) and Ni.

Table 1: Properties and operating conditions

Parameter	Value
Resin mass, M (g)	36.13
Column diameter, d (cm)	2.63
Bed height, L (cm)	8.4
Bed Volume, BV (cm^3)	45.6
Porosity, θ	0.347
Pore volume size, V_{PV} (cm^3) [a]	15.84
Solution flowrate, Q (cm^3/min)	1.2-20
Pore velocity, v (cm/min) [b]	0.64-10.6
Contact time, τ (min) [c]	13.2-0.8
npty bed contact time, EBCT (min) [d]	38.0-2.3

$$^{(a)} V_{PV}=BV*\theta, \quad ^{(b)} v = Q/(\theta \cdot \frac{\pi d^2}{4}), \quad ^{(c)} \tau = V_{PV}/Q, \quad ^{(d)} EBCT = BV/Q$$

3. Results and Discussion

The Cr(VI) concentration in the solution fed to the column was equal to 5.4 mg/L and the pH was equal to 5.3. The Cr(VI) concentration in the effluents and the corresponding pH values are shown in Figure 1. These parameters are shown as a function of the amount of solution passing through the bed (V), expressed as number of bed volumes (N_{BV}) ($V=N_{BV}*BV$). The flow rates which were applied during the operation of the column are also presented in the figure. The initial flowrate was equal to 1.2 mL/min, corresponding to a contact time between the solution and R-nFe equal to 13.2 min, and the concentration of Cr(VI) in the effluent was constantly below detection limit (<6 μg/L). The flowrate was stepwise increased from 1.2 to 2, 5 and 10 mL/min without appearance of any Cr(VI) in the effluents. Approximately 1000 mL (equivalent to 22 bed volumes) was fed to the column at each specific flow rate. When the flowrate was increased to 20 mL/min (contact time 0.79 min), Cr(VI) appeared in the effluent at a concentration equal to 0.75±0.06 mg/L and this value remained constant during the whole operation of the column at this flowrate.

When the flowrate was again decreased from 20 to 10 mL/min the Cr(VI) concentration in the effluent dropped again below detection limit until the supply of 100 more bed volumes (BVs). An increase of Cr(VI) concentration in the range 0.22-0.74 mg/L was recorded between N_{BV} 210 and 540. When the flowrate decreased from 10 to 5 mL/min, Cr(VI) concentration dropped below the value of 0.05 mg/L for 100 more BVs.

As seen in Figure 1, during the initial stages of the operation of the column, the pH of the effluent became very acidic, namely dropped from 5.3 to 2.5. This is due to the fact that during the R-nFe synthesis procedure the cation exchange sites were filled with protons. The Na^+ cations of the feeding solution are exchanged with H^+ and this causes the acidification of the effluent. As the operation of the column continued, the pH of the effluent increased from 2.5 up to 4.2 at the end of the experiment. The results suggest that the removal of Cr(VI) under flow conditions is determined by the residence time of the solution inside the bed of R-nFe, and is also influenced by the prevailing pH conditions. The kinetics of the removal can be described as a first order kinetic law with respect to Cr(VI) and the value of kinetic constant was estimated to range between 2.4 min^{-1} at pH 3 and 1.5 min^{-1} at pH 4.2

Based on the experimental results, it was calculated that if the nanocomposite material is used for the treatment of highly polluted groundwater, with Cr(VI) in the order of 10 mg/L and if the target is to reduce Cr(VI) content below the legal limit of 50 μg/L, the EBCT should be >10.2 min. For the treatment of groundwater with lower Cr(VI) contamination, in the order of 100 μg/L, and target concentration 5 μg/L, level considered as safe for drinking water, the required EBCT was calculated to be 5.8 minutes.

From the results presented in Figure it can be also seen that the column has treated an amount of solution equivalent to 640 bed volumes without appearance of the Cr(VI) breakthrough. When the feeding solution was spiked with Ni (between the 134 and 154 BV), the
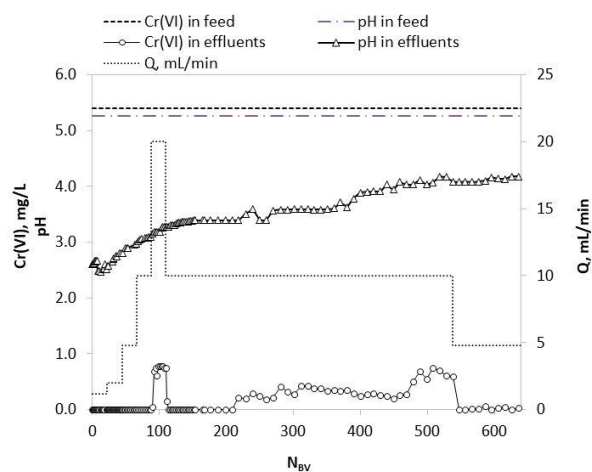
Figure 1. Concentration of Cr(VI) and pH in the effluents under different flow rates as a function of the number of bed volumes N_{BV} were free from both Cr(VI) and Ni indicating that the nanocomposite material can be equally efficient in the case of mixed contamination.

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