Synthesis of kaolin supported nZVI and evaluation for the removal of Cr(VI) and Ni from waste streams

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Abstract

This study involved the synthesis of kaolin-supported nano zero valent iron (K-nZVI) and the evaluation of its performance for the removal of chromates and nickel from contaminated waters. K-nZVI was prepared by mixing a kaolin sample with a $FeCl_3$ solution, followed by the addition of sodium borohydride for the reduction of Fe(III) to the zero valent state. The effectiveness of kaolin supported nZVI for Cr(VI) and Ni removal was evaluated by conducting batch experiments. The investigated parameters included the amount of K-nZVI per solution volume, the concentration of contaminants and the effect of pH. K-nZVI was found to be more efficient for the treatment of Cr(VI) contaminated waters than for the removal of Ni. Using 1 gram of K-nZVI per liter of solution, it was possible to reduce 20 mg/L of Cr(VI) to less than 5 mg/L within 3 hours. Starting with the same concentration of Ni, i.e.20 mg/L, the final concentration after 3 hours was aproximately 17 mg/L at pH 5.6, and dropped to 10 mg/L when the pH of the suspension was regulated to the value of 7.5. The results suggest the K-nZVI has a rather limited efficiency for Ni removal.

Keywords: nano zero valent iron (nZVI), kaolin, nickel, hexavalent chromium, batch tests.

1. Introduction

The presence of heavy metal ions in the environment, such as Cr(VI) and Ni, has caused environmental concerns because of their toxicity and their adverse impacts on the ecosystem. Removal of toxic elements from contaminated water is often carried out by adsorption techniques. However the preferred methods for the treatment of Cr(VI) are based on the use of chemical reduction processes, because the reduced form of trivalent chromium, Cr(III), is not toxic and is removed from the aqueous phase by precipitation as hydroxide (Barrera-Díaz et al. 2012).

Nickel is found in the natural environment at various concentrations and its solubility depends mainly on the temperature and the type of its compounds (Ghrab et al. 2014). Nickel occurs in water as $Ni^{+2}(aq)$ and sometimes as aqueous complex with carbonate ($NiCO_3(aq)$). When introduced in the food chain at elevated amounts Ni can be teratogenic and carcinogenic for mammals.

A promising reducing agent is elemental iron in nanoscale, nZVI (nano zero valent iron) which is characterised by high reactivity (Mystrioti et al. 2018). Many studies have demonstrated that the reactivity of nZVI is enhanced in combination with an adsorptive substrate (Kerkez et al. 2014; Toli et al. 2016, 2018; Ezzatahmadi et al. 2017). In this study kaolin was used as the adsorptive substrate and nZVI as the reducing agent. The structure of kaolin presents cavities that are occupied by ions and water molecules. Because of its structure, the phenomenon of ion exchange and dehydration occurs. Thus, toxic metals are firmly retained in the crystalline structure of kaolin.

The objective of this research is to evaluate the performance of kaolin supported iron nanoparticles (K-nZVI) for the removal of Cr(VI) and Ni from contaminated waters.

2. Materials and Methods

The main stages of kaolin – nZVI (K-nZVI) synthesis involved mixing of 10 g kaolin with a 0.2 M $FeCl_3$ solution of 250 mL for 1 hour and the reduction of Fe(III) to Fe(0) using 250 mL $NaBH_4$ (1.6 M) solution. Iron content in the K-nZVI product, as determined by XRF analysis, was equal to 18% or 3.2 mmol/g.

A first series of batch tests were conducted for the removal of Cr(VI) from aqueous solutions using K-nZVI. The investigated parameters were the initial concentration of Cr(VI) in the range 5-40 mg/L and the amount of kaolin per solution volume at three levels, 1, 2 and 4 g/L. A second series of experiments were also carried out to evaluate the effectiveness of K-nZVI for the removal of Ni. The investigated parameters were the initial concentration of Ni in the range of 10 - 40 mg/L and two different pH values, namely pH equal to 5.6 and to 7.5 in the presence of 1 g/L K-nZVI.

3. Results and Discussion

The experimental results of Cr(VI) removal using the K-nZVI material, at a contact time of 3 hours, are summarized in Table1. The loading of K-nZVI with Cr, q_e (mg/g), was calculated from equation (1):

$$q_e = \frac{(C_0 - C_e)}{M/V} \qquad (1)$$

where C_0 is the initial concentration of Cr(VI) in solution (mg/L), C_e the final concentration (mg/L), M the mass of K-nZVI (g) and V the volume of aqueous solution (L).

The loading q_e as a function of the remaining concentration in solution C_e is presented in figure 1. Most probably, the predominant mechanism of Cr(VI) removal with K-nZVI is the reduction of chromates by nZVI in the trivalent state. However the q_e vs C_e curve can be also described using the formulation of Langmuir adsorption isotherm:

$$q_e = q_{max} \frac{C_e K_L}{C_e K_L + 1} \qquad (2)$$

where q_{max} corresponds to the maximum capacity of K-nZVI to remove Cr(VI) and K_L is an equilibrium constant. From the linearization of equation (2) it was calculated that the maximum capacity q_{max} was equal to 20 mg/g.

Table 1. Experimental results for Cr(VI) removal by K-nZVI at 3 hours

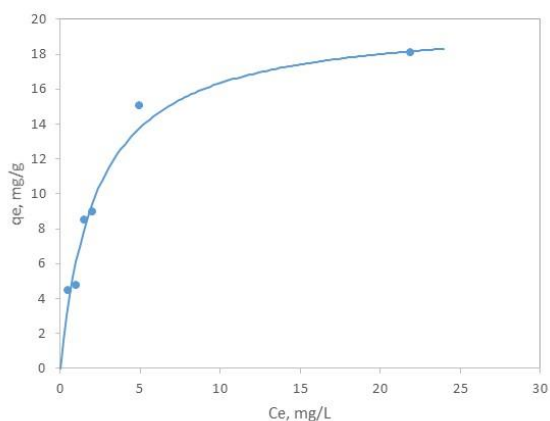| K-nZVI dose (M/V), g/L	Cr(VI) in solution mg/L		Cr load on K-nZVI, mg/g	Cr(VI) removal %
	Initial C_0	3 hours C_e	3 hours q_e	
1	5	0.49	4.51	90.2
1	10	1.52	8.48	84.8
1	20	4.96	15.04	75.2
1	40	21.9	18.09	45.2
2	20	2.18	8.91	89.1
4	20	0.98	4.76	95.1

Figure 1. K-nZVI loading in Cr with respect to the remaining concentration of Cr(VI) in the aqueous phase.
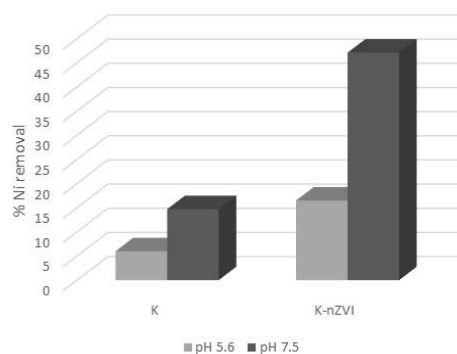

Figure 2. Removal of Ni with simple kaoline (K) and composite K-nZVI at pH 5.6 and 7.5.

The removal of Ni with simple kaolin (K) and composite K-nZVI was evaluated at two pH values 5.6 and 7.5 and the results are shown in Figure 2. As seen in the figure the removal of Ni is highly dependent on the pH of the aqueous solution, with better results at the slightly alkaline pH 7.5. It is also seen that the presence of n-ZVI greatly enhanced the removal capacity.

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