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Cr(VI) Removal by Green-Synthetized Iron-Based Nanoparticles: Effect of Cr(VI) Concentration and pH Condition on Adsorption Process

Irene Bavasso*, Nicola Verdone, Luca Di Palma

Department of Chemical Engineering Materials Environment, Sapienza University of Rome, Italy
irene.bavasso@uniroma1.it

The removal of hexavalent Chromium from aqueous solutions by adsorption method has been investigated. In this study, magnetic nanoparticles were used as adsorbent materials and their synthesis was performed by using two different ways including a classical ammonia synthesis (nMG) and a green approach by using fructose and NaOH (GnMG). The Cr(VI) removal tests demonstrated that the synthesis procedure adopted did not influence the results. The same adsorption kinetic was observed according to a pseudo-first order with 0.026 min^{-1} and 0.032 min^{-1} as kinetic constants respectively for GnMG and nMG. In the case of high Cr(VI) concentration (20 mg L^{-1}), the effect of nanoparticle dimension was relevant in which low nanoparticle size (44.1 nm) of nMG corresponded to a high adsorption capacity. The effect of pH on the adsorption process was investigated. Increasing the pH value to neutral condition (pH = 6) has a positive effect on the Cr(VI) removal. In contrast, the alkaline condition negatively affects the adsorption process by a reduction about 30 % of the total Cr(VI) obtained at pH= 6.

1. Introduction

The application of nanotechnology for the development of effective environmental processes started at the end of XX century, mainly through the application of iron-based nanoparticles for the removal of halogenated hydrocarbons and for the reduction of hexavalent chromium species (Cr(VI)) (Gueye et al., 2016). Cr(VI) still represents a serious environmental problem, in particular in the Mediterranean Area (Vilardi et al., 2018a). The Cr(VI) species are characterized by a remarkable mobility in the environment, because of their high solubility and low tendency to generate insoluble hydroxides in the classical pH and Eh range of water bodies and soils (Vilardi et al., 2017a). On the contrary, the trivalent species of Chromium are low soluble and mobile, and tend to form insoluble hydroxides that precipitate or co-precipitate in association with other metals, such as Fe and Al (Vilardi et al., 2017a). The fundamental difference among the two species is represented by their toxicity towards organisms and microorganisms: the Cr(VI) species are 2-3 orders of magnitude more toxic in comparison with the trivalent species, and are considered carcinogenic and mutagenic also for humans (Dashti et al., 2016). The most efficient and rapid technology for the removal of Cr(VI) from industrial polluted wastewaters is represented by a combination of chemical reduction, precipitation and adsorption processes. This Cr(VI) removal pathway can be successfully achieved through the employment of the iron-based nanoparticles (IBNs).

The use of IBNs for the removal of various inorganic species, such as nitrate and organic pollutants, such as phenols, through both redox and adsorption mechanisms, has already been developed and has demonstrated noticeable efficiency and remarkable kinetics (Vilardi et al., 2018b). In particular, nano-magnetite (nMG) particles are still the most employed iron-based nanoparticles in several applications, such as adsorption (Chiavola et al., 2016), in functionalized aggregates (Di Palma et al., 2015), photocatalysis and as pre-treatment for membrane processes (Stoller et al., 2017a). An important issue related to the use of IBNs is the synthesis processes, and more in detail the use of harmful reagents, such as NaBH4, NH4OH etc. that may enter the environment when the IBNs are used in real-site applications (Ju-Nam and Lead, 2008). A number of efforts that has been made by various researchers in the green chemistry processes have led to the development of

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environmentally friendly synthesis (Kumar, 2014). These particular syntheses are possible through the use of natural extracts that derived from the extraction of reducing compounds from agro-industrial solid waste, employed as reagents for the synthesis of metallic nanoparticles. The remaining solid waste can then be used in other processes such as the bio-adsorption of heavy metals (Vilardi et al., 2018a).

The main aims of the present work are as follows:

1) To develop an environmentally friendly synthesis path for the production of nMG, without using ammonia.
2) To compare the Cr(VI) removal efficiency obtained by means of green-synthetized nMG and classical nMG.

The experimental results were compared with those reported in literature for other classical iron nanoparticles and for bio-sorbents. A kinetic modelling of the experimental data was performed to estimate the kinetic constants that characterize the reduction/adsorption process.

2. Materials and Methods

2.1 Materials

All reagents were an analytical grade and purchased from Sigma Aldrich, in Milan. The solutions were prepared in deionized water. The following reagents were used in the experiments: NaOH, $C_6H_{12}O_6$, K_2Cr_2O7, $FeCl_3{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$, NH_4OH, Diphenylcarbazide, C_3H_6O, C_2H_6O, and H_2SO_4.

2.2 Synthesis

The nMG particles were synthetized in batch glass reactors, using a molar ratio of 2:1 among Fe(III) and Fe(II) species in aqueous solution and a molar ratio of 8:1 among NH_4OH and Fe(II) reagents. An aqueous solution of 0.1 M of $FeSO_4{\cdot}7H_2O$ and 0.2 M of $FeCl_3{\cdot}6H_2O$ was prepared in a reactor of 250 mL of volume (stirred at 500 rpm) and ammonia solution (10 M) was added dropwise until the required molar ratio was reached. The nMG particles were then magnetically separated, recovered, and washed with pure ethanol. The same procedure was followed to produce green nMG particles (GnMG), but instead of ammonia a basic solution (pH = 10) of fructose (1 M) was used. The nMG and GnMG particles were then characterized by Dynamic Light Scattering showing a mean dimension of 44.1 ± 3.2 nm and 89 ± 11.4 nm.

2.3 Experimental set-up and methods

The Cr(VI) removal tests were carried out using three different initial concentration of Cr(VI) (10 mg L^{-1}, 15 mg L^{-1}, and 20 mg L^{-1}) and fixing the initial concentration of nanoparticles (0.5 g L^{-1}). The tests were conducted at three different pH (3, 6, and 10) and at determined interval steps of 5 min a liquid sample was withdrawn from the reactors and the Cr(VI) concentration was measured in the liquid phase, after magnetic separation of the nanoparticles. The Cr(VI) concentration was determined using the Diphenylcarbazide method (EPA 7196A). The kinetic tests were stopped until the asymptotic value was reached (120 min). The equilibrium concentration of Cr(VI) on solid phase (q_e) was calculated by using the mass balance reported in the Equation (1):

$$q_e(t) = \frac{V_L}{m_{nMG}} \left[Cr(VI)_0 - Cr(VI)_t\right] \tag{1}$$

where V_L is the solution volume (L), m_{nMG} is the mass of nanoparticles (g) and $Cr(VI)_0$-$Cr(VI)_t$ (mg L^{-1}) is the difference of Cr(VI) concentration between the zero-time value (0) and at a generic interval time (t). The overall removal rate was calculated by using the Equation (2):

$$R(\%) = \frac{Cr(VI)_0 - Cr(VI)_f}{Cr(VI)_0}\ x\ 100 \tag{2}$$

Where $Cr(VI)_f$ identifies the concentration of Cr(VI) at the end of the treatment.

The kinetic data were then used to obtain the kinetic constants for the mechanisms of pseudo-first order, in gPROMS Version 3.4 environment (Winkel et al., 1995), in a multiple non-linear data regression procedure, optimizing the kinetic constant using all the data sets simultaneously. The model equation was that of the pseudo-first order, which is reported as follows:

$$\frac{Cr(VI)_t}{Cr(VI)_0} = \exp(-kt) \tag{3}$$

where k (min^{-1}) is the pseudo-first-order kinetic constant.

3. Results and Discussion

3.1 Effect of Cr(VI) concentration

Preliminary tests at selected Cr(VI) initial concentration were performed to establish a possible effect of nMG or GnMG on the adsorption process. In Figure 1, the adsorbed Cr(VI) concentration (q_e) on solid phase at 6 pH is reported and q_e is calculated according to the Eq. (1).

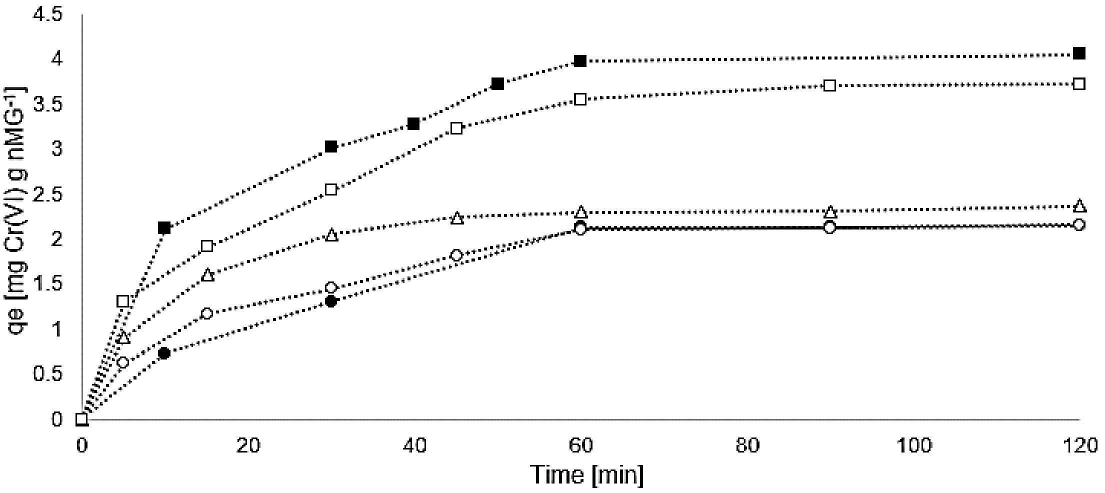

Figure 1: Cr (VI) adsorption on 0.5 mg L^{-1} of nMG (full symbol) or GnMG (empty symbol) at 10 mg L^{-1}(circle symbol), 15 mg L^{-1}(triangle symbol), and 20 mg L^{-1}(square symbol) as Cr (VI) initial concentration

The Cr(VI) concentration on nMG increased with the increasing of Cr(VI) initial concentration according to Equation (1) and an almost constant time value (60 min) was found to be necessary to achieve the maximum adsorption capacity. Only a slight difference between the sorption capacity of the two materials at high Cr(VI) concentration was observed. This was probably due to the lower mean dimension of nMG in comparison with GnMG that ensured a larger specific surface area. Table 1 shows the results of adsorption tests, which are summarized and compared to the results obtained in similar work using different adsorbent and bio-adsorbent.

Table 1: Cr(VI) removal % at different dosage of adsorbent. Comparison with other similar work with different nano-adsorbent and bio-adsorbent

Adsorbent	Adsorbent /Cr(VI)$_0$ [g_{ADS} $g_{Cr(VI)}^{-1}$]	*d* [nm]	*R*(%)	Reference
Biochar modified by ZnO	0.100	28.3 (ZnO)	96.00	Yu et al., 2018
Maghemite	0.040	15.00	52.24	Tahar et al., 2018
Coconut Shell	0.025	0.42- 1.70	65.28	Babel et al., 2004
Activated Carbon	0.025	0.50- 2.36	92.82	Babel et al., 2004
nMG	0.010	44.10	88.75	Present study
GnMG	0.010	89.00	88.75	Present study
nMG	0.020	44.10	82.71	Present study
GnMG	0.020	89.00	74.16	Present study

Good results in term of Cr(VI) were observed. The overall removal of Cr(VI) obtained by GnMG is similar to the overall removal observed by Babel and co-workers (2004) using activated carbon with lower concentration of adsorbent that our conditions. A kinetic study of adsorption process was made to complete the investigation. Figure 2 shows the multiple non-linear kinetic data regression of the two series of tests. Table 2 reports the optimized pseudo-first order kinetic constants.

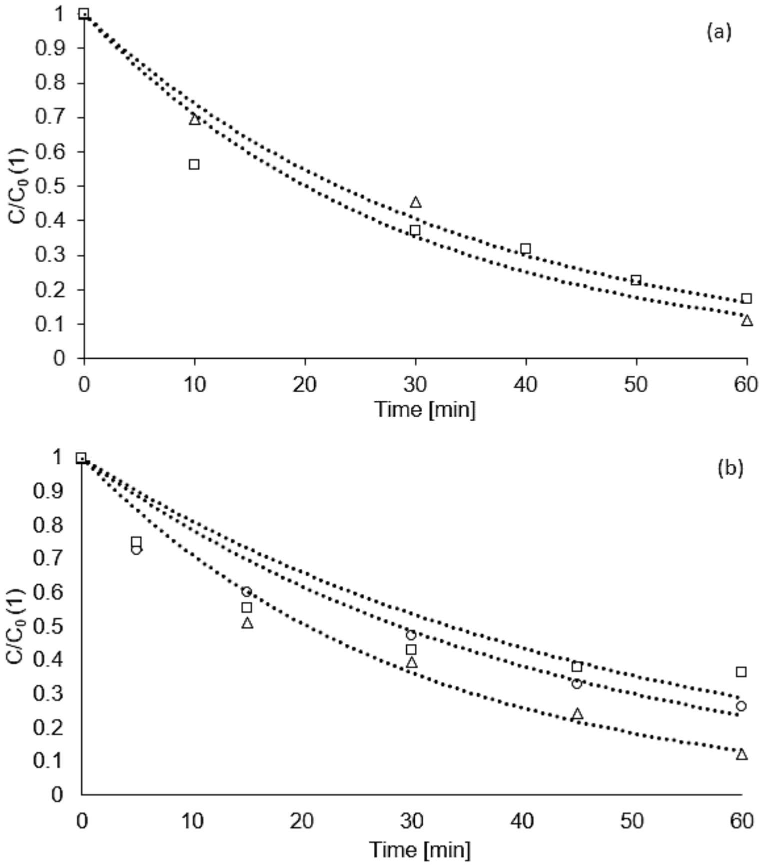

Figure 2: Kinetic data modelling of (a) nMG (square symbol 20 mg L^{-1} and triangle symbol 10 mg L^{-1}) and (b) GnMG (circle symbol 20 mg L^{-1}, square symbol 15 mg L^{-1} and triangle symbol 10 mg L^{-1})

The pseudo-first order kinetic model was able to well describe the experimental data, considering that the R^2 values were always in the range 0.95 - 0.98. The kinetic constants were obtained after the optimization of experimental data according to the pseudo-first order kinetic model, which were 0.026 min^{-1} and 0.032 min^{-1} for GnMG and nMG. The very slight difference among the kinetic constants demonstrated that the GnMG can be successfully used to achieve similar Cr(VI) removal efficiencies to the classical nMG particles.

3.2 Effect of pH

To evaluate the effect of pH on the adsorption process using GnMG, batch tests were performed at selected values of pH (3, 6 and 10) and results in term of Cr(VI) adsorbed (q_e) are reported in Figure 3. The overall removal rate (%) according to Equation (2) are summarized in Table 2.

Table 2: Overall removal R (%) of Cr(VI) at different initial concentration and different pH condition

Cr(VI)$_0$ [mg L^{-1}]	pH 3	*R* (%) pH 6	pH 10
10	90.67	89.60	77.07
15	69.20	79.20	57.84
20	77.68	77.40	76.82

The results show that in the case of the higher initial Cr(VI) concentration (20 mg L^{-1}), pH had no influence on the adsorption rate. Almost equal maximum Cr (VI) adsorption capacity (around 77 %) was observed in all the tests, as shown in Table 2. This effect suggested that a ratio Cr(VI)/GnMG of about 40 mg g^{-1} identified a condition, where the saturation of absorbent was reached and no further improvement on Cr(VI) removal was possible. For a concentration higher than 20 mg L^{-1} of Cr(VI), an addition of absorbent is required to obtain a comparable adsorption efficiency. For low Cr(VI) initial concentration, a positive effect of acid pH on adsorption process was observed. Furthermore, at a Cr(VI) concentration of 10 mg L^{-1} only a slight difference of Cr(VI) removal efficiency between pH 3 and 6 was observed, while at a Cr(VI) concentration of 15 mg L^{-1} an enhancement on Cr(VI) removal was observed at pH = 6. In general, an acidic pH led to better Cr(VI) removal results probably due to a possible occurrence of redox reaction between iron and Cr(VI) (López-Téllez et al., 2011). On the contrary, a decrease in Cr(VI) removal was observed from neutral pH condition to alkaline condition (pH = 10). In this last case, the adsorption process could be compromised by the formation of a passivation layer on magnetite nanoparticle (He and Traina, 2005). According to the previous authors, the Cr(VI) removal mechanism by means of nMG is based on a partial reduction/precipitation of Cr(VI) to Cr(III) and sorption of not reduced Cr(VI).

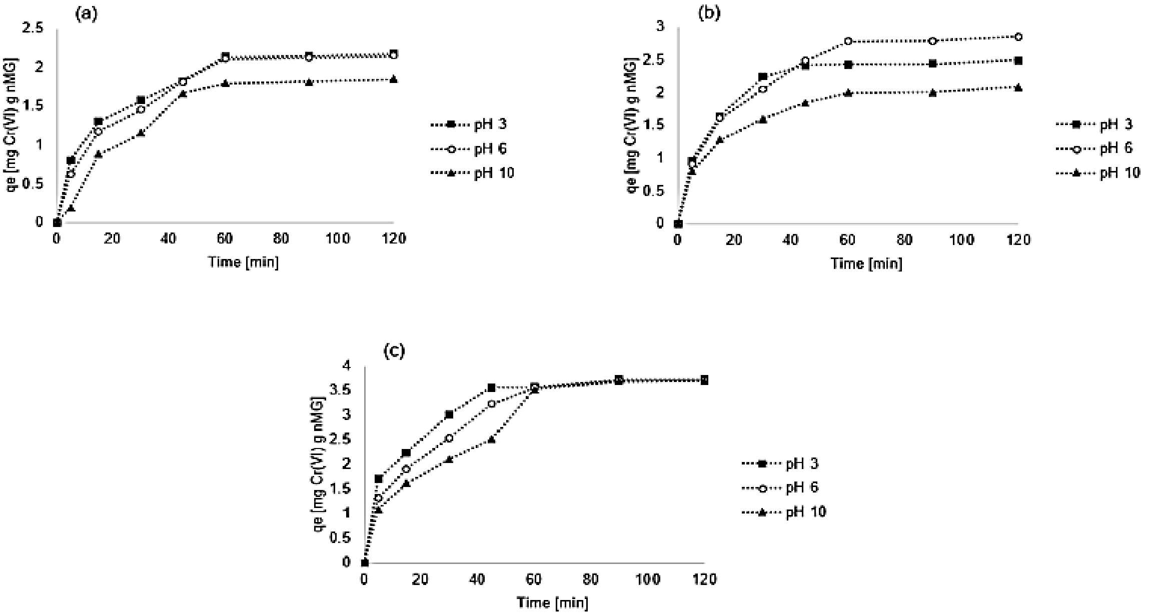

Figure 3: Effect of pH on Cr(VI) adsorption on GnMG at 10 mg L^{-1} (a), 15 mg L^{-1} (b) and 20 mg L^{-1} (c) as Cr(VI) initial concentration

4. Conclusions

The present work reports the use of magnetite nanoparticles for Cr(VI) removal from aqueous solutions. Different synthesis procedures including a classical ammonia synthesis (nMG) and a green synthesis (GnMG) by using fructose were studied. GnMG was successful in the removal of Cr(VI) with a sorption capacity about 2.10 mg Cr(VI) g^{-1}, 2.29 mg Cr(VI) g^{-1}, and 3.55 mg Cr(VI) g^{-1} respectively for 10 mg L^{-1}, 15 mg L^{-1}, and 20 mg L^{-1} as Cr(VI) initial concentration. These values were very similar to the equivalent ones of nMG. A pseudo-first order kinetic well described the experimental results: 0.026 min^{-1} and 0.032 min^{-1} as kinetic constant was found respectively for GnMG and nMG, showing appreciable removal kinetics in both cases. From 3 to 6 pH condition a positive effect on Cr(VI) removal was observed. A further increase on pH condition up to alkaline values, negatively affected the overall Cr(VI) removal due to the formation of a passivation layer on magnetite nanoparticles. The green magnetite nanoparticle showed good results in terms of Cr(VI) removal, mainly in acid environment and also at high Cr(VI) concentration (20 mg L^{-1}). It means that the environmentally friendly synthesis procedure allowed to produce a nano-material with analogous Cr(VI) removal capacity when compared with the nano-material produced by classical and more harmful synthesis.

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