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The influence of nitrate on the reduction of hexavalent chromium by zero-valent iron nanoparticles in polluted wastewater

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ABSTRACT

Hexavalent chromium, Cr(VI), still represents in several areas in Europe one of the groundwater pollutants of major concern, mainly due to its high toxicity, even enhanced by the synergic effect in the presence of other groundwater contaminants, such as nitrate. In this work, experimental tests of hexavalent chromium reduction in polluted groundwater in the presence of nitrate by nanoscale zero-valent iron (nZVI) particles are presented and discussed. The effect of nitrate on process mechanism was investigated and a kinetic model was proposed. nZVI produced by iron sulfate heptahydrate reduction with sodium borohydride was stabilized by carboxymethyl cellulose, and added to synthetic solutions at different nitrate contents. Results show that nitrate exerts an adverse effect on Cr(VI) reduction, depending on nZVI/Cr(VI) and Cr(VI)/NO_3^- ratio. Though hexavalent chromium reduction resulted slightly enhanced at low nitrate concentration (up to 1.5 nZVI/Cr(VI) molar ratio), as a consequence of the increase of the ionic strength of the solution, a significant decrease was observed at high nitrate level (up to a 25% at Cr(VI)/NO_3^- molar ratio equal to 1.2 with an nZVI/[Cr(VI) + NO_3^-] molar ratio equal to 1), due to the competitive effect in the reaction with nZVI. In both cases, experimental data were successfully fitted by a pseudo-first-order kinetic until iron surface passivation determined nanoparticles deactivation.

Keywords: Water treatment; Hexavalent chromium; Nitrate; Nanotechnologies; Zero-valent iron

1. Introduction

Low cost and ease to use features allow the application of zero-valent iron (ZVI) particles in environmental remediation, both in soil and groundwater treatment. However, chemical and physical properties, such as large particle size, low specific surface area and short lifetime, have often limited their practical use, and a remarkable efficiency only in the treatment of shallow groundwater plumes has been observed [1,2]. Nevertheless, in the last two decades the application of nanoscale zero-valent iron (nZVI) particles has focused the attention of researchers as a more flexible technology for polluted site remediation [3]. Larger specific surface area, high superficial activity and the capacity to remain in suspension for long time when injected as colloidal suspension into contaminated zones, increase the efficiency of the decontamination process when nZVI particles are used [4–6]. Usually, the preparation of nZVI particles by reducing Fe(II) or Fe(III) in an aqueous solution using a strong reducing agent ($LiBH_4$ and $NaBH_4$) appears as most suitable due to the limited use of environmentally harmful solvents and chemicals. However, the high surface area and reactivity of nZVI particles prepared according to traditional methods favor either a fast agglomeration or a quick reaction with the surrounding media, resulting in rapid loss in reactivity (passivation of the surface) and mobility [7,8]. Three common methods allow

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reducing these drawbacks (second catalytic metal doping [9,10], chemical stabilization [11,12] and supporting [13,14]), but the use of carboxymethyl cellulose (CMC) as stabilizer appears the widest applied alternative. In aqueous solution, Na^+ is released by CMC which, once adsorbed on to the surface of nZVI particles, forms a negative charged layer preventing agglomeration by induction of repulsive forces [15]. Furthermore, this organic stabilizer reduces the toxicity of nZVI particles toward living organisms as bacteria and fungi [16,17], limiting the release of highly toxic reactive oxygen species caused by iron corrosion [18–20].

The first use of nZVI particles was reported by Wang and Zhang [21], basing on the previous study of Glavee et al. [22]. As widely reported in the recent literature, nZVI particles have been proved to be significantly effective in the removal of a wide range of organic pollutants from polluted water and wastewater, including chlorinated solvents [23]; chlorinated pesticides [24]; organophosphates [25]; nitroamines [26]; nitroaromatics [27] and polyphenols [28] (in this last case the obtained results were significantly better than those obtained by conventional processes [29]). Several literature experiences have also demonstrated the effectiveness of nZVI in the removal of hazardous inorganic species, such as nitrate [30,31]; metalloids [32], heavy metals [33], including radioactive metals [34] as an alternative to conventional immobilization technologies [35,36]. In particular, Cr(VI) is a heavy metal which exhibits a high selectivity in the reaction with nZVI particles [37,38], as reported by Tsai [39] who ranked the removal efficiency of ZVI from top to bottom as: As > Cr > Cu > Hg > Pb > Zn > Cd > Ni. Moreover, heavy metals, and in particular Cr(VI), can react with nZVI particles according to different mechanisms, i.e., reduction, adsorption or co-precipitation [40]. The interest in hexavalent chromium as a priority environmental pollutant [41] arises from its wide distribution due to the extensive exploitation of chromium in several industrial activities. When Cr(VI), as chromate or dichromate anion, is reduced by nZVI particles, it precipitates as insoluble hydroxide or co-precipitates with Fe(III) in a mixed oxyhydroxide [42]. The reduction process is characterized by several parameters, such as pH, temperature, presence of dissolved oxygen, active surface area and stability of the nanoparticles, and presence and mobility of other ionic species. As an example of the last parameter influence, the co-presence of nitrate may strongly affect the adsorption/reduction of dichromate ions by nZVI particles: depending on the NO_3^- concentration, the removal rate of Cr(VI) in water may result increased or even decreased, while in some cases the complete inhibition of the reaction has been observed [1]. Moreover, the contemporary presence of chromates and nitrates in groundwater was observed in several agricultural contaminated land, in proximity of sites associated with metal plating, wood processing, leather tanning, metal corrosion inhibition and pigment production [43].

The simultaneous removal of chromates and nitrates in water by nZVI particles is not still fully investigated, and the purpose of this work is to study the effective influence of different concentrations of nitrate anion on Cr(VI) removal by colloidal CMC–nZVI particles, at different values of the initial contaminants concentration. In addition, a kinetic study was also reported.

2. Materials and methods

nZVI particles were synthesized by reduction of iron sulfate heptahydrate ($FeSO_4·7H_2O$) with sodium borohydride ($NaBH_4$). Carboxy methyl cellulose was used as dispersing agent in the ratio CMC/Fe^{2+} = 0.005 (mol/mol) according to previous studies [44]. This organic stabilizer, in addition to the aforementioned benefits, reduces also the corrosion of iron nanoparticles by water and residual dissolved oxygen which occurs according to the mechanism:

$$Fe^0_{(s)} + 2H_2O_{(l)} \rightarrow Fe^{2+} + H_{2(g)} + 2OH^- \quad (1)$$

$$2Fe^0_{(s)} + 4H^+ + O_{2(g)} \rightarrow 2Fe^{2+} + 2H_2O_{(l)} \quad (2)$$

In the synthesis procedure, the use of hydrated ferrous sulfate ($FeSO_4·7H_2O$) as starting salt in place of the commonly used ferric chloride ($FeCl_3$) presents two main advantages: (i) the reduction of ferrous ions needs a lesser amount of borohydride ion (BH_4^-) as a reducing agent and (ii) ferrous ions and CMC complexes are more stable than complexes formed with ferric ions [44]. All reagents were used without any purification, and all the solutions were prepared in deionized water. The synthesis was carried out in a 500-mL flask where nitrogen (N_2) was purged during the entire preparation. The selected procedure consisted of the preparation of 120 mL of a 0.04 M Fe^{2+}–CMC solution to which 120 mL of a solution 0.08 M of BH_4^- were added dropwise. No buffer systems were used during nanoparticles synthesis or during the experiments. Reaction mixture was shaken vigorously for an hour, up to the gas evolution (hydrogen) ceased. The reduction of ferrous ions follows the main reaction:

$$2BH_4^- + Fe(H_2O)^{2+} \rightarrow Fe^0_{(s)} + 2B(OH)_{3(s)} + 7H_{2(g)} \quad (3)$$

According to the neutral-alkaline pH measured (7.78) at the end of the synthesis. The molar ratio BH_4^-/Fe^{2+} was increased to 2.2 to promote the total reduction of ferrous iron, limited by the fast hydrolysis of sodium borohydride favored at acidic pH [45].

All reagents were of purity grade and were supplied by Sigma-Aldrich (Milano, Italy).

2.1. Experimental procedure

In this study, an aqueous model solution containing sodium nitrate ($NaNO_3$) and potassium dichromate ($K_2Cr_2O_7$) was used as polluted medium. A series of batch experiments were carried out to examine the nitrate and chromate removal from aqueous solutions using nZVI particles. All tests were performed on a shaker in a 250 mL conical flask at 25°C. Several test solutions were prepared, with different NO_3^- and Cr(VI) initial concentrations. Initially, a nitrate solution (58 mg/L of NO_3^-) and two dichromate solutions (58 and 98 mg/L of Cr(VI)) were separately tested to investigate the removal reaction kinetic of each contaminant alone, using four increasing concentrations of nanoparticles (0.15, 0.2, 0.3 and 0.5 g/L). Successively, three mixed nitrate-dichromate solutions (8 mg/L NO_3^- + 58 mg/L Cr(VI); 32 mg/L NO_3^- + 58 mg/L Cr(VI) and 58 mg/L NO_3^- + 58 mg/L

Cr(VI) with corresponding Cr(VI)/NO_3^- molar ratio equal to 8.6, 2.2 and 1.2, respectively) were tested using a stoichiometric amount of nZVI particles with respect to [Cr(VI) + NO_3^-] concentration. Nitrogen was purged inside the reactor during the treatment, and the reaction mixture was continuously shaken without any pH control. At selected time intervals (0, 1, 2, 3, 4, 5, 10, 15, 30, 45 and 60 min), a sample of 2 mL was withdrawn, 3 mL of a NaOH (2 M) solution were added to each sample and the diluted sample was filtered through a 0.45 μm Whatman membrane filter. Nitrates were measured by ion chromatography (Dionex ICS-1100), Cr(VI) concentration was determined using the 1,5-diphenylcarbazide colorimetric method at 540 nm with a detection limit of 0.05 μm [46] using a UV–visible spectrophotometry (T80+, PG Instruments, Ltd., Leicestershire, UK) whereas the concentration of nZVI was measured at 508 nm [47]. The mean diameter of the nanoparticles was detected by a nanosizer (NANOTRAC, measurement range 0.8 nm–6.5 μm, supplied by Microtrac Inc., PA, USA) and the average value of 88 ± 13 nm was measured. All the experiments were carried out in triplicates to ensure repeatability within a constant error equal to about 5%.

3. Results and discussion

3.1. Effect of nZVI particles concentration in the treatment of nitrate and chromate solution

Cr(VI) and NO_3^- removal efficiency at the end of the 60 min treatment are reported in Figs. 1 and 2, respectively, at the selected concentration of nZVI particles adopted in the tests.

Results reported in Fig. 1 show a slight increase in the Cr(VI) removal at increasing amount of nZVI, and decreasing initial pollutant concentration. Such behavior can be explained by an overload of the active sites caused by the high content of dichromate anions in the solution: similar phenomena have already been observed in trichloroethylene degradation by nZVI particles [44].

Considering nitrate removal efficiency, results reported in Fig. 2 show a nitrate removal higher than the corresponding increase obtained for the Cr(VI) removal at increasing nZVI particles concentration. However, a direct comparison between the two anions removal at a fixed nZVI particles concentration must take into account the actual molar concentration of all the species involved. In fact, according to the following reduction reactions [4], the stoichiometric ratio between reducing/oxidizing agents is different for the two chemical species:

$$3Fe^0_{(s)} + Cr_2O_7^{2-} + 7H_2O_{(1)} \rightarrow 3Fe^{2+} + 2Cr(OH)_{3(s)} + 8OH^- \quad (4)$$

$$4Fe^0_{(s)} + NO_3^- + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O_{(1)} \quad (5)$$

In particular, a stoichiometric molar ratio (nZVI/Cr(VI)) equal to 1.5 for the Cr(VI) reduction and a higher value (nZVI/NO_3^-), equal to 4, for the nitrate reduction can be identified. Accordingly, the stoichiometric amounts of nZVI particles for Cr(VI) and NO_3^-, depending on the initial concentration of 98 and 58 mg/L of Cr(VI) and NO_3^-, respectively, is about 0.15 g/L for Cr(VI) and 0.2 g/L for NO_3^-. Therefore, focusing on the efficiency of the treatment, nZVI particles appear to be more efficient toward hexavalent chromium than nitrate reduction. The tests carried out in the presence of nitrates were prolonged until an almost asymptotic value was reached (120 min).

As shown in Fig. 3, where NO_3^- removal efficiency values at 120 min are reported, the maximum nitrates removal obtained for the stoichiometric addition of nZVI particles was 43.4%, compared with the 97.9% obtained for the Cr(VI) removal.

3.2. Influence of nitrate on hexavalent chromium removal

The trends of Cr(VI) reduction (initial concentration of Cr(VI) equal to 58 mg/L) at different nZVI particles amounts

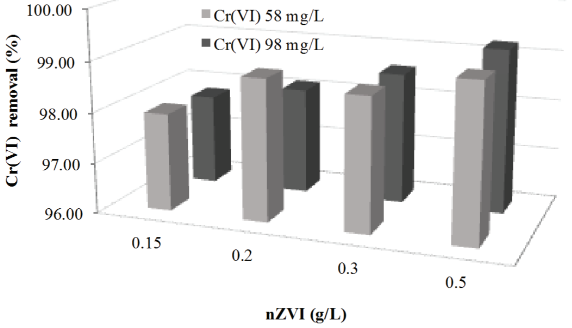

Fig. 1. Cr(VI) removal at selected nZVI particles concentrations (after 60 min).

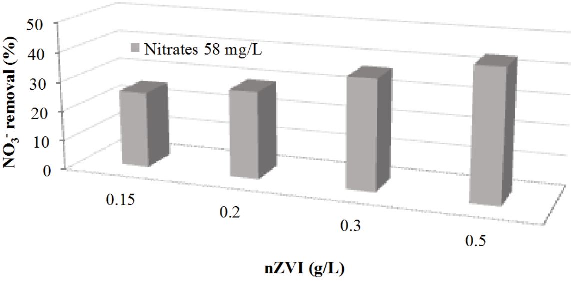

Fig. 2. NO_3^- removal at selected nZVI particles concentrations (after 60 min).

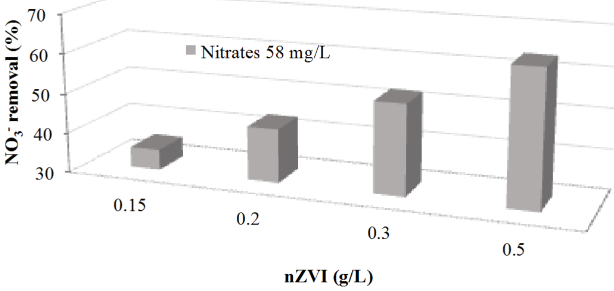

Fig. 3. NO_3^- removal at selected nZVI particles concentrations (after 120 min).

are reported in Fig. 4, adopting a logarithmic scale to improve the comprehensibility of the graphs. The shown profiles preclude the use of a simple pseudo-first-order law to model the kinetics in the whole time range.

The influence of nitrates was investigated performing three sets of experimental runs carried out in treating mixed synthetic solutions with different nitrate/dichromate ratios as specified above. In all the experiments, the nZVI particles concentration was set at the stoichiometric amount, accounting for the total content of the two oxidizing species (Fig. 5).

From the results reported in Fig. 5, the influence of the presence of nitrate anions on the Cr(VI) reduction can be clearly identified. According to a previous study [1] which considers the presence of co-existing anions in the treated solution, two main processes could occur: (i) an increase in the ionic strength of the solution and (ii) a competition between dichromate and nitrate anions for the active sites on the surface of nZVI particles. In the first set of test, due to the little amount of nitrate (8 mg/L), competition did not occur at a detectable extent, and the slight increase in the Cr(VI) removal (97.9%–98.4%) can be explained by an increase in the ionic strength of the solution [1]. On the contrary, in the second and third set of tests, a significant decrease in the Cr(VI) reduction occurred (from 97.9% to 92.4% and to 72.6% in the presence of 32 and 58 mg/L of nitrate, respectively) due to the large amount of competitive anions saturating the active sites onto the nZVI particles. However, trends in Figs. 4 and 5 clearly show similar profiles which allow a confident application of the pseudo-first-order kinetic model according to Eq. (6) in fitting the experimental data only in the very initial contact time:

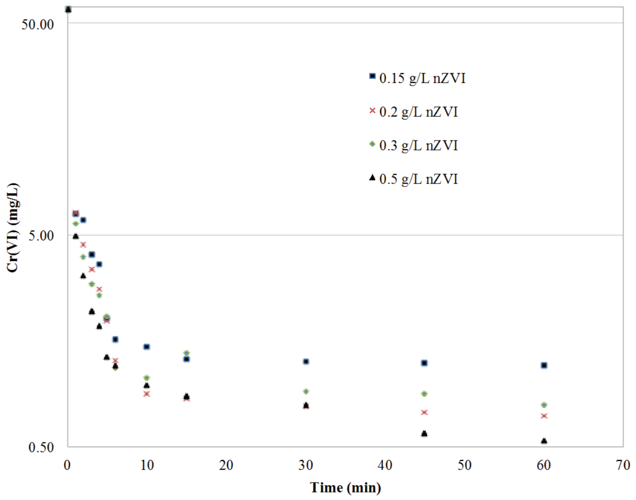

Fig. 4. Cr(VI) removal at selected nZVI particles concentrations.

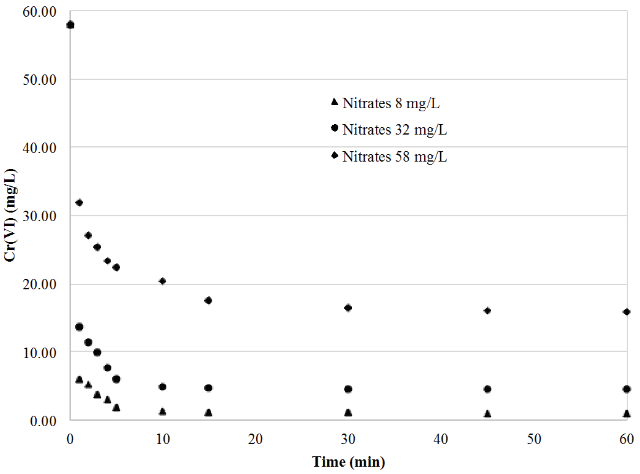

Fig. 5. Chromate removal in the presence of nitrate at nZVI/Cr(VI) = 1.5.

$$\ln[(\mathrm{Cr(VI)})] = \ln[\mathrm{Cr(VI)}_0] - k_{obs} \cdot t \qquad (6)$$

where $\mathrm{Cr(VI)}_0$ (mg/L) is the initial hexavalent chromium concentration, t (min) the contact time and k_{obs} (min^{-1}) the observed rate constant of the pseudo-first-order reduction kinetics. The results of the regression procedure are reported in Fig. 6.

The quite similar trends show that nitrates only affected the overall process efficiency, without providing any changing in the kinetic profile. In particular, the k_{obs} value initially increased, from 0.2757 to 0.2936 min^{-1} at a nitrate initial concentration equal to 8 mg/L, whereas, at higher initial nitrate concentration, the k_{obs} value started to decrease, due to the competitive mechanism, and a value of 0.0862 min^{-1} was calculated at the maximum initial nitrate concentration. The former phenomena is probably due to the low nitrate amount, with respect to the Cr(VI) one, which does not cause the occurrence of the competitive mechanism but, on the contrary, increases the ionic strength of the solution enhancing the electron transfer.

The competitive mechanism was confirmed by the simultaneous reduction of nitrate anions observed in the last two sets of experiments and reported in Fig. 7, where it is clearly shown that the nitrate reduction occurs by following the same trend of the Cr(VI) reduction. Contrary to what observed for the Cr(VI) reduction, the trends reported in Fig. 7 are furthermore in contrast with that detected in the nitrate alone reduction, shown in Fig. 8 for an initial nitrate concentration of 58 mg/L. In this latter case, as reported in a previous work [4], the reduction mechanism follows

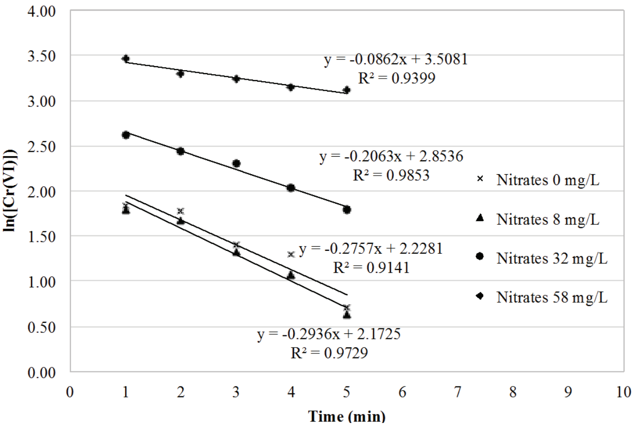

Fig. 6. Kinetics of Cr(VI) removal (first 5 min of treatment).

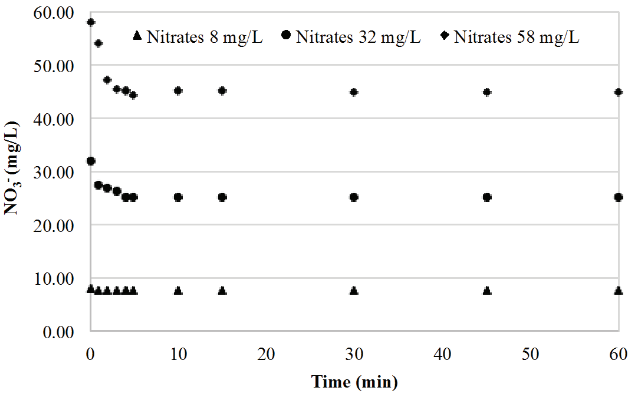

Fig. 7. Nitrate removal at fixed initial concentration of Cr(VI) (58 mg/L).

a pseudo-first-order kinetic described by Eq. (6), whose application is also reported in Fig. 8.

This different behavior may be explained by the fast passivation of the active surface of the nZVI particles due to the formation of the Fe(III) hydroxide, mixed Fe(III)–Cr(III) oxy-hydroxide and Cr(III) hydroxide which occurs during the reduction reaction of Cr(VI) [43]. This fast step is due to the quick reduction of Cr(VI), which, in presence of a significant content of nitrate, simultaneously occurred to the nitrate reduction. Thus, a competitive mechanism arises between the two chemical species (characterized by a similar redox potential E^0, 1.32 V for nitrate to ammonia [48] and 1.36 V for Cr(VI) to Cr(III) [49]) which leads to a partial reduction of the nitrate species and a higher reduction of Cr(VI). The result is a remarkable and fast passivation of the active surface of the reducing agent which inhibits the well-known continuous nitrate reduction characterized by a lower rate. Consequently, kinetics can be divided into three steps, each characterized by a different k_{obs} value, as reported in Fig. 8.

In Fig. 9, the nZVI consumption values measured during the competitive process are finally reported.

The kinetics of the nZVI consumption was well-fitted by a pseudo-first-order model. The three kinetic constant values are quite similar (0.0081, 0.008 and 0.0086 min^{-1}) whereas the R^2 values are always above 0.9. According to the following Eq. (7), the root mean square error (RMSE) values were calculated for the three data sets as:

$$\mathrm{RMSE} = \sqrt{\frac{\Sigma\left(\left[\mathrm{Fe}(0)\right]_{exp} - \left[\mathrm{Fe}(0)\right]_{cal}\right)^2}{n}} \tag{7}$$

where $[\mathrm{Fe}(0)]_{exp}$ and $[\mathrm{Fe}(0)]_{cal}$ are the experimental and calculated nZVI concentrations and n is the number of experimental data. The calculated RMSE values were 0.033, 0.034 and 0.051 for the experiments performed with a nitrates initial concentration equal to 8, 32 and 58 mg/L, respectively.

4. Conclusions

In this study, the effectiveness of nZVI particles as reducing agent for dichromate, nitrate and both species were investigated. Considering the stoichiometric amount of reducing agent for both cases, in Cr(VI) reduction the use of nZVI granted a remarkable efficiency which overcame 97% after 60 min of treatment, whereas nitrate reduction reached 43.3% after 120 min of treatment. As already reported, the nitrate reduction follows a pseudo-first-order kinetics, whereas the mechanism of dichromate reduction seems to be more complex. It proceeds initially very quickly, reducing almost the whole amount of Cr(VI) in the first minutes, then slowing down to an asymptotic value when the total passivation of the active surface of the nanoparticles occurs. In the first part of this trend, it is possible to well-fit the experimental data through a pseudo-first-order kinetics, both in the experiments considering dichromate alone and in co-presence of nitrate. In the latter case, the reduction kinetic of Cr(VI) suffers a worsening or an enhancement depending on the concentration and physicochemical characteristics of the other anion (NO_3^-). In particular, it was observed that a small concentration of nitrate (8 mg/L) produced a slight increase in the Cr(VI) reduction (from 97.9% to 98.4% at 1.5 Fe^0/Cr(VI)

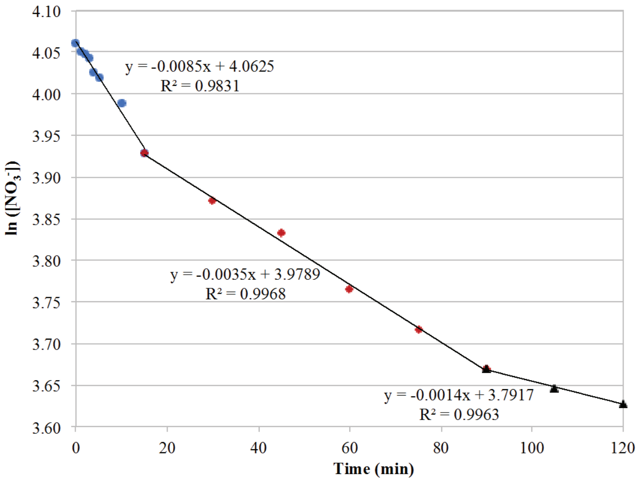

Fig. 8. Kinetics of nitrate removal at fixed concentration of nZVI particles (0.2 g/L).

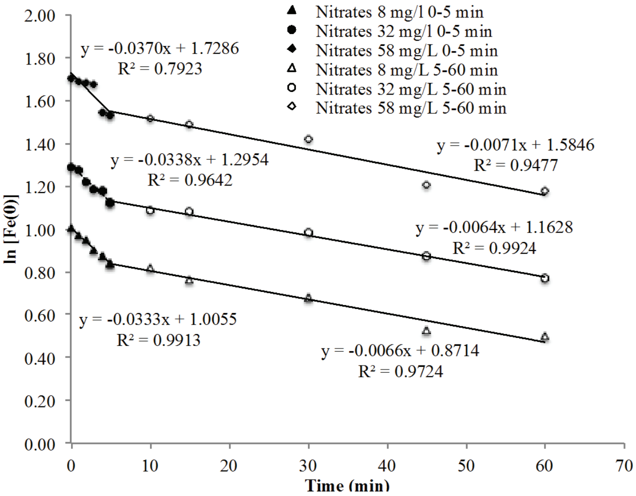

Fig. 9. Kinetics of nZVI consumption (nZVI/[Cr(VI) + NO_3^-] stoichiometric ratio).

molar ratio) due to the increase of the ionic strength of the solution. On the contrary, a higher initial nitrate concentration caused the establishment of a competitive mechanism for the active sites of the reducing agent by the two oxidizing species, which produced a decrease in the efficiency of the Cr(VI) reduction (in the presence of 32 mg/L of nitrate it decreased from 97.9% to 92.4%, while in the presence of 58 mg/L of nitrate it decreased down to 72.6%). Considering the reduction of nitrate with the co-existence of dichromate anions, it was possible to observe the significant variation of the kinetic trend, which altered from an evident pseudo-first order to a more complex mechanism. The kinetic study focusing on the consumption of nZVI during the competitive reduction of the two oxidizing species seems to confirm that the reaction mechanism follows properly a pseudo-first-order kinetics.

The reported study allows to state, in any case, the selectivity of nZVI for the dichromate reduction, which shows a remarkable efficiency also in the presence of the same initial concentration of another active oxidizing species as NO_3^-.

In conclusion, colloidal CMC–nZVI particles proved to be a fast and efficient agent in reducing hexavalent chromium, but their effectiveness strongly depend on the characteristics of the external medium, the characteristics of the nanoparticles and the co-existence of other oxidizing species.

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