

Competitive Reaction Modelling in Aqueous Systems: the Case of Contemporary Reduction of Dichromates and Nitrates by nZVI

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In various Countries, Cr(VI) still represents one of the groundwater pollutant of major concern, mainly due to its high toxicity, furthermore enhanced by the synergic effect in presence of other contaminants. As widely reported in the recent literature, nanoscale zero valent iron particles (nZVI-p) have been proved to be particularly effective in the removal of a wide range of contaminants from polluted waters. In this work, experimental tests of hexavalent chromium reduction in polluted groundwater in the presence of nitrate by nZVI-p are presented and discussed. The effect of different nitrate amounts on Cr(VI) reduction mechanism was investigated and the obtained results were successfully interpreted by the proposed kinetic model. nZVI-p produced by the classical borohydride reduction method were added in to synthetic solutions with the initial concentration of Cr(VI) set at 93, 62 and 31 mg L⁻¹ and different nitrate contents in the range 10-100 mg L⁻¹. According to the experimental results, nitrate showed an adverse effect on Cr(VI) reduction, depending on the nZVI/Cr(VI) and Cr(VI)/NO₃⁻ ratio. The proposed kinetic model soundly grasps the competitive nature of the Cr(VI) reduction process when other chemical species are present in the treated solution.

1. Introduction

The increasing water demand and the necessity of sustainable technologies and solutions to a vast range of environmental challenges led to the development of useful nano-materials, characterized by peculiar physico-chemical properties (Bavasso et al., 2016). The remarkable nZVI-p characteristics, i.e. large specific surface area, high superficial activity and the capacity to remain in suspension for long time when injected as colloidal suspension into contaminated zones, let this nanomaterial be suitable for the in-site treatment technology (Gueye et al., 2016). Traditionally, nanomaterials synthesis is performed in batch systems (Genova et al., 2015; Genova et al., 2016) and concerning nZVI-p synthesis, it has been performed by reducing Fe(II) or Fe(III) in an aqueous solution by a strong reducing agent (LiBH₄, NaBH₄) and still appears as most suitable because of the limited use of environmentally harmful solvents and chemicals and faster than the "green" synthesis path, employing natural extracts as reducing agents. However, the high reactivity of nZVI-p favours either a fast agglomeration and a quick reaction with the surrounding media, resulting in rapid loss in reactivity (passivation of the surface) and mobility (Liu et al. 2015). Among the three common methods allow reducing these drawbacks (second catalytic metal doping (Muradova et al. 2016) and chemical stabilization (Di Palma et al. 2015)), the use of a steric stabilizer like the carboxymethyl cellulose (CMC) appears the widest applied alternative. nZVI-p have been proved to be significantly effective in the removal of a wide range of inorganic and organic pollutants from polluted water and wastewater, including: chlorinated solvents (He et al. 2010), polyphenols (Lopes et al. 2015) with significantly better results than those obtained by conventional processes (Stoller et al. 2016), hazardous inorganic species such as nitrates (Vilardi and Di Palma 2017; Vilardi et al., 2017a) and heavy metals such as uranium and hexavalent chromium (Di Palma et al. 2015). In the last two cases nZVI-p treatment granted more remarkable results, with respect to other processes (Marsili et al. 2005; Marsili et al., 2007; Di Palma and Verdone, 2009; Lagiopoulos et al. 2017; Vilardi et al., 2017b). The interest in hexavalent chromium as a priority environmental pollutant arises from its wide distribution due to the extensive exploitation of chromium in several industrial activities (Dermatas et al. 2017). The Cr(VI) reduction to Cr(III) is

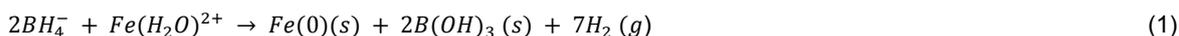
the most suitable process for the removal of hexavalent chromium from wastewaters and groundwater. In fact, Cr(III) species are essential nutrients for the lipid metabolism of several mammals and its toxicity is not significant if compared to that of Cr(VI) species (Dermatas et al. 2015). Moreover, the Cr(III) species are less soluble than Cr(VI) ones and easily precipitate or co-precipitate in the liquid medium. The reduction process is influenced by several parameters, as pH, temperature, presence of dissolved oxygen, active surface area and stability of the nanoparticles, and presence and mobility of other ionic species. Concerning the last parameter influence, the NO_3^- co-presence may strongly affect the adsorption/reduction of dichromate ions by nZVI-p, as already observed by the same authors (Vilardi et al., 2017c). The purpose of this work consists in the development of a simple competitive model capable of predicting the nZVI-p consumption taking into account the initial concentration of the chemical species and the theoretical stoichiometry of the parallel reactions (competitive reduction of nitrates and Cr(VI) by nZVI-p). The parameters of the model were evaluated through the experimental nZVI-p reduction data regression, adopting a non-linear fitting methodology.

2. Materials and Methods

2.1 Experimental

The nZVI-p production followed the classical boro-hydride reduction method, using iron sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) as iron(II) source and carboxy methyl cellulose as dispersing agent according to previous studies (Vilardi et al., 2017c). This organic stabilizer, in addition to the aforementioned benefits, reduces also the corrosion of iron nanoparticles by water and residual dissolved oxygen.

The synthesis was carried out by means of a Spinning Disk Reactor, to ensure higher treatment efficiency (Vilardi et al., 2017a). The reduction of ferrous ions follows the main reaction:



according to the neutral-alkaline pH measured (7.78) at the end of the synthesis. All reagents were used without any purification and were supplied by Sigma Aldrich (Milano, Italy). All the solutions were prepared in deionized water (DI). The produced nZVI-p were employed in the reduction experiments loading a small excess respect to the stoichiometric value, adopting as model pollutants in aqueous solutions sodium nitrate (NaNO_3) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). The tests were performed on an orbital shaker in a 250 mL conical flask at 25°C. To maintain the reaction volume constant each time step two identical samples were withdrawn from two equal reactors, the former was used for the measures, the latter was poured in the first reactor. Firstly, three Cr(VI) solutions (1.8, 1.2 and 0.6 mM) and as many NO_3^- solutions (1.5, 1 and 0.5 mM) were tested loading a stoichiometric amount of nZVI-p (Vilardi et al., 2017b), according to the following chemical reactions (eq. 2 and 3):



And monitoring the nitrate and Cr(VI) concentration over the reaction time (the measures were performed at 5, 10, 15, 20, 25, 30, 45, 60, 75, 90, 105 and 120 minutes). The competitive mechanism was then analysed monitoring the nZVI-p consumption in the simultaneous reduction of Cr(VI) and nitrates fixing the initial concentration of Cr(VI) (1.8 mM) and varying the nitrates concentration (1.5, 1 and 0.5 mM). The analysis procedure adopted was the same for both the series of experiments: after each time step a sample of 5 mL was withdrawn and filtered through a Whatman filter (220 nm). 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 (EPA 7196) using a UV-visible spectrophotometry (T80+, PG Instruments, Ltd.), and the nZVI-p concentration was measured at 508 nm (Saleh et al., 2008). All the experiments were carried out in duplicate to ensure repeatability within a constant error equal to about 8%.

2.2 Kinetic Model of single reduction

A simple scheme was considered to solve analytically the rate equations of Cr(VI) and NO_3^- reduction, alone. Considering the reactions reported in equations (2) and (3) as second order reactions, with the following kinetic rate expressions:

$$\frac{d[Cr(VI)]}{dt} = -k_1[Fe(0)][Cr(VI)] \quad (4)$$

$$\frac{d[NO_3^-]}{dt} = -k_2[Fe(0)][NO_3^-] \quad (5)$$

where k_1 and k_2 [$L \text{ mmol}^{-1} \text{ min}^{-1}$] are the kinetic constants of eqs. (2) and (3), respectively. In the hypothesis that the reaction volume does not vary in the reaction progress, an analytical solution expressing the actual species concentration can be easily derived. To show the procedure, focusing only on Cr(VI) reduction and for the sake of simplification utilizing the chemical symbols to express concentrations, the actual Fe concentration results as:

$$Fe = (Fe_0 - 1.5(Cr_0 - Cr)) \quad (6)$$

where the subscript 0 indicates the initial concentration of the chemical species. The substitution of eq. (6) in eq. (4) yields:

$$\frac{dCr}{dt} = -k_1Cr(Fe_0 - 1.5(Cr_0 - Cr)) \quad (7)$$

By some algebraic passages and defining the following constants, $a = -1.5k_1$ and $b = k_1Fe_0 - 1.5k_1Cr_0$, by simple algebra, eq. (7) reads as:

$$\frac{dCr}{dt} = aCr - bCr^2 \quad (8)$$

and through a partial fraction decomposition, the preceding equation assumes the form:

$$dt = \left(\frac{1}{aCr} + \frac{b}{a(a-bCr)} \right) dCr \quad (9)$$

Eq. (9) can be easily integrated when the following initial conditions are set:

$$\begin{cases} t = 0, Cr(VI) = Cr_0 \\ t = t, Cr(VI) = Cr \end{cases} \quad (10)$$

yielding:

$$\frac{1}{a}(\ln(Cr) + \ln(a - bCr) - \ln(Cr_0) - \ln(a - bCr_0)) = t \quad (11)$$

and finally obtaining:

$$bCr^2 - aCr + Cr_0(a - bCr_0) \exp(at) = 0 \quad (12)$$

From eq. (12) two solutions can be derived, but only the positive one has a physical significance and was adopted to fit the experimental data:

$$Cr = \frac{a + \sqrt{a^2 - 4bCr_0(a - bCr_0) \exp(at)}}{2b} \quad (13)$$

Substituting the values of the constants a and b , eq. (13) yields:

$$Cr = \frac{-1.5k_1 + \sqrt{(-1.5k_1)^2 - 4Cr_0((-1.5k_1Cr_0 + k_1Fe_0)(-1.5k_1 + (1.5k_1Cr_0 - k_1Fe_0))Cr_0) \exp(-1.5k_1t)}}{2(1.5k_1Cr_0 - k_1Fe_0)} \quad (14)$$

To develop the explicit relationships expressing the actual concentration of nitrates, the same procedure can be applied to eq. (5), yielding:

$$N = \frac{-4k_2 + \sqrt{(-4k_2)^2 - 4N_0((-4k_2N_0 + k_2Fe_0)(-4k_2 + (4k_2N_0 - k_2Fe_0)N_0) \exp(-4k_2t))}}{2(4k_2N_0 - k_2Fe_0)} \quad (15)$$

k_1 and k_2 were obtained by multiple non-linear fitting of experimental Cr(VI)/NO₃⁻ reduction data, using eq. (14) and (15), adopting the `scipy.optimize.curve_fit` method in Python software (ver. 3.6.1). The regressed values, reported in Table 1, were subsequently used as initial values for the competitive model parameters estimation.

2.3 Competitive Kinetic Model

In this case, eqs. (2) and (3) were considered as parallel reactions. Since the experimental results highlight a progressive depletion of the Fe(0) content when Cr(VI) and NO₃⁻ reached a plateau, the possible Fe(0) oxidation due to the presence of dissolved O₂ and to the Fe(0) corrosion carried out by H₂O should be considered in the model:





These phenomena were lumped in the material balance of Fe(0) by the introduction of the third kinetic constant k_3 [s⁻¹]:

$$\frac{dFe}{dt} = -1.5k_1CrFe - 4k_2NFe - k_3Fe \quad (18)$$

The kinetic constant values were calculated through the parameter estimation module available in the gPROMSTM (ver.3.2.0) environment, numerically solving eqs. (4), (5) and (18) in an iterative procedure.

3. Results and Discussion

3.1 Modelling Results

Figure 1 (a, b) shows the single reduction model results, as a function of the initial oxidant species concentration.

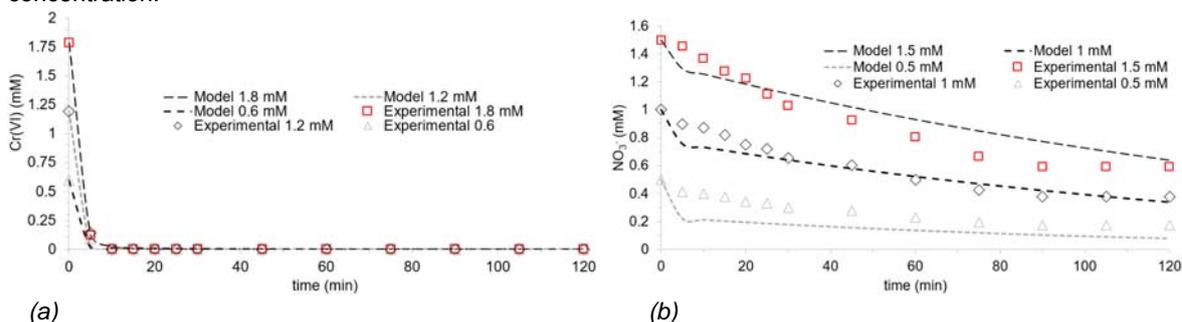


Figure 1: Cr(VI) reduction model (a) and NO₃⁻ reduction model (b) results.

The Cr(VI) reduction experimental data (Figure 1a) were well-fitted by the model and the remarkable reduction velocity is well represented. On the contrary, the nitrates reduction data fitting adopting the same model resulted less accurate (Figure 1b). A more complex model will be necessary to take into account the various phenomena (external-diffusion, intraparticle-diffusion, adsorption, ...) caused the slower kinetics, with respect to that characterized the Cr(VI) reduction process. As far as the competitive model is concerned, the data-fitting results are reported in Figure 2 (a, b) and Figure 3.

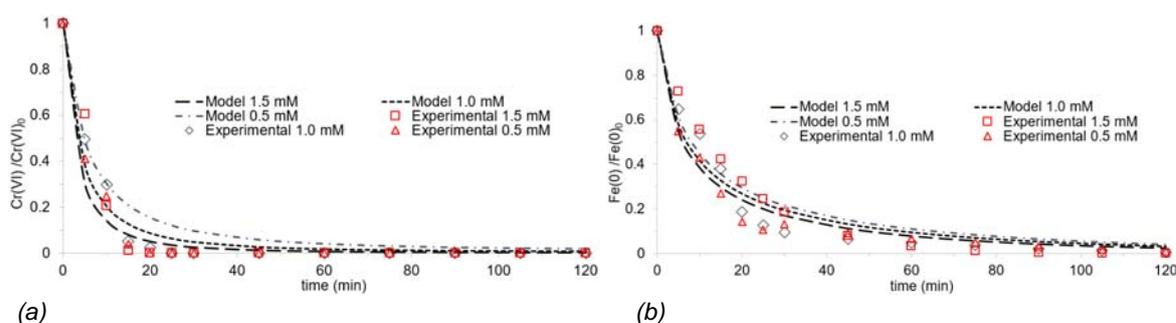


Figure 2: competitive model results of Cr(VI) reduction (a) and Fe(0) consumption (b), in function of nitrates initial concentration (1.5, 1.0 and 0.5 mM).

The competitive model is suitable to represent the fast Cr(VI) reduction kinetics, which was observed also in the simultaneous reduction experiments. The presence of [NO₃]₀ does not influence the Cr(VI) reduction efficiency nor the overall kinetic trend. In all the tests, the initial Fe(0) concentration was set larger than the stoichiometric amount, but no significant Fe(0) residual concentrations were measured. This implies that besides the two oxidants (Cr(VI) and nitrate), further reducible species were present in the solution. Indeed, as reported in Figure 3, the maximum nitrate reduction efficiency was about 80%. This behavior indicates that the slower nitrates reduction kinetics (see Table 1) let the other species (oxygen and water) be reduced by Fe(0), which in turn is oxidized and deactivated. The proposed competitive model well represented the overall phenomenon.

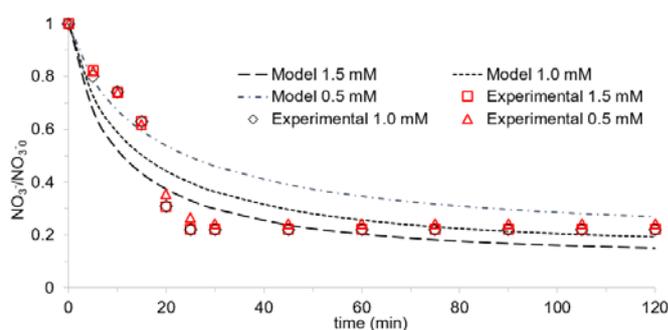


Figure 3: competitive model results of nitrates reduction fixing the initial Cr(VI) concentration to 1.8 mM.

Table 1: kinetic parameters obtained by model data fitting (Unit of measure defined in the text).

		k_1	k_2	k_3	Cr(VI)/NO ₃ ⁻ initial concentration	R ²
Single model	[Cr(VI)]	0.227	-	-	1.8 / 0	0.997
					1.2 / 0	0.984
					0.6 / 0	0.982
	[NO ₃ ⁻]	-	0.007	-	0 / 1.5	0.945
					0 / 1	0.892
Competitive model	[Cr(VI)]	0.037	0.012	0.066	0 / 0.5	0.826
					1.8 / 1.5	0.907
					1.8 / 1	0.963
	[NO ₃ ⁻]	0.037	0.012	0.066	1.8 / 0.5	0.906
					1.8 / 1.5	0.953
					1.8 / 1	0.959
	[Fe(0)]	0.037	0.012	0.066	1.8 / 0.5	0.792
					1.8 / 1.5	0.923
					1.8 / 1	0.949
					1.8 / 0.5	0.924

As expected, in the regression procedure, single-reduction model returns the highest R² values, independently from the chemical species initial concentration. The single Cr(VI) reduction data fitting returned higher kinetic constants than those obtained in the application of the competitive-model. This result is caused by the contemporary presence of nitrates, which tend to compete for the Fe(0) active-sites. The faster Cr(VI) reduction kinetics, with respect to nitrates ones, is well represented by the k_1 value, larger than k_2 and k_3 in the simultaneous reduction processes.

4. Conclusions

The reported research discussed two simple model capable to well represent the Cr(VI) and nitrates reduction kinetics using nZVI-p as reducing agent. The first model was derived adopting a second-order reaction scheme for the two single reduction processes and the problem was solved analytically. On the contrary, the second model consisted in an ODE system numerically integrated. To take into account also the possible nZVI-p deactivation by dissolved oxygen and water, in the latter model a further contribution for the Fe(0) consumption was introduced in the equation rate. Both model demonstrated to be suitable to represent the kinetics of both the processes. In detail, the correlation factor values, always larger than 0.9, showed the remarkable fitting goodness with the experimental Cr(VI) reduction data, while the nitrate reduction process seemed to be more complex and a more itemized model is necessary. The kinetic constant values obtained from the experimental data fitting when the competitive model was adopted are in good agreement with the observed phenomena.

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