

Removal of Nitrate and Hexavalent Chromium from Groundwater Using Zerovalent Iron – A Laboratory Study

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Abstract. Groundwater contamination by inorganic pollutants such as heavy metals, chromium and nitrate has recently begun to attract widespread interests because of significant threat to human health. Nitrate and chromate are most frequently detected contaminants in groundwater. In this paper, we describe a series of laboratory experiments which quantify the rate of chromium (Cr^{6+}) and nitrate reduction by Fe^0 . The main goal of these experiments was to determine the removal efficiency of chromium (Cr^{6+}) and nitrate ions using iron. The results indicate that in the presence of zero valence iron Cr^{6+} reduces to Cr^{3+} , and NO_3^- to NH_4^+ .

Keywords: nitrate, chromium, zero valent iron, groundwater, reduction.

INTRODUCTION

In the current political context, the farmer must balance trade offs between productivity and the environmental impacts of farming practices adopted. The increasing emphasis on the effect of agriculture on water quality and other forms of environmental degradation is due to the EC Nitrates Directive (Directive 91/676/EEC), which limits the peak concentration of nitrates in watercourses. As a consequence, European agricultural support measures are increasingly including cross-compliance elements, and thus farmers will be required to respect environmental criteria in order to be able to benefit from support payments (Stout W .L., *et al.*, 1997).

New agricultural techniques application, based on the newest scientific knowledge in the field of technologies, especially on the ecological feasible ones, is a major challenge for sustainable agriculture. For that, it is very important to elaborate, but also to use in practice some good agriculture practice. These represent an assembly of technical and scientific knowledge for farmers. If every farmer learns how to use correctly this information, then it will be possible to obtain good results regarding crops, to protect the environment, on short or long term.

Groundwater contamination by inorganic pollutants such as heavy metals, chromium and nitrate has recently begun to attract widespread interests because of significant threat to human health. Nitrate and chromium are most frequently detected contaminants in groundwater. Nitrate levels have been increasing due to increased usage of nitrogen based fertilizers, changes in land-use patterns from pasture to arable, and increased recycling of domestic wastewater in low-land Rivers (J. Bohdziewicz, *et al.*, 1999). Nitrate at the concentrations greater than 10 mg/l can be fatal to infants under 6 months of age and pregnant women. In infants body, nitrate is reduced to nitrite, which combines with hemoglobin in the

blood to form met hemoglobin and leads to a commonly known as blue baby syndrome. The US EPA and WHO established a maximum contamination level of 10mg/l nitrate as a guideline (K. Baek, *et al.*, 2004). The raw wastewater contains a great deal of organic nitrogen and ammonia. These compounds comprise a large portion of the total nitrogen found in the water sample. Over a period of time, these forms in an aerobic environment would be transformed to nitrate-N. The nitrate ion is the most oxidized form of nitrogen and is chemically unreactive in dilute aqueous solutions (Benefield L. D., *et al.*, 1982). The zerovalent metals due to their electron donating tendency can degrade several chemicals including the anions through reduction. This property of metals has attracted considerable attention of environmental chemical engineers involved in developing the contamination remediation techniques.

The behavior of nitrate in the presence of metallic compounds was observed by Servant *et al.* (1992) (Servant *et al.*, 1992, Modrogan C., *et al.* 2007, Modrogan C., *et al.*, 2010). The nitrate in water was reduced with iron, aluminum and stainless steel and in the process was converted into nitrite, ammonia and then into nitrogen. The extensive use of chromium in metallurgic, leather tanning, electroplating, electricity generation and other industries resulted in the release of chromium into surface water and groundwater in numerous areas. Chromium can be acutely toxic to both plants and animals. To develop effective remediation plans for contaminated sites, we must understand the processes which are governing the transport and fate of chromium in the environment. Since both the mobility and toxicity of Cr depend on its oxidation state, redox reactions involving Cr are extremely important in determining its fate in the environment and its risk to human health (Gillham, R.W. *et al.*, 1994). The aim of this paper was to study the kinetic of nitrate ions (NO_3^-) and chromium (Cr^{6+}) removal from water, in the presence of iron as function of water pH and temperature (Michael J. *et al.*, 2002).

MATERIALS AND METHODS

All aqueous solutions were prepared with nano-pure water. All commercially available chemicals and minerals were used as received. Industrial iron grains were used in the tests. The iron used in this experiment was used as scraping generated from iron processing in industrial activities.

The iron scraping was firstly cutted into smaller slices and then was treated with sodium hydroxide solution and after that with fluorhydric and acetic acid in order to be properly used for the following experiments. The KNO_3 was used as NO_3^- source, and as chromium source was used potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$).

Experimental methods

The batch tests under acidic-basic conditions were conducted in a pH-stat. The pH-stat was made from a 150-ml triangle flask capped with a rubber stopper and placed on a magnetic stirrer. Two holes were punched on the stopper, one with the exact size to hold a pH microelectrode, and the other as the port to add chlorhydric acid into the solution. A stirrer bar, suspended with a thread and operating at 300 rpm, was used to completely mix the test solution. Because of the magnetic effect, iron grains were attracted with each other to form numerous chains with one end attaching to the bar. The chains were separated from each other because of the repulsive magnetic force. Therefore, the iron grains were exposed to the solution, which would make the external mass transport resistant be negligible as the stirrer bar rotated at 300 rpm. The pH of the solution was continuously monitored with a calibrated pH probe and adjusted to maintain within a specific range by adding HCl with a 50 ml

dispenser. Control tests using uncoated Fe⁰ without adding nitrate were conducted to investigate the effects of nitrate and the black coating on the reactivity of iron. The test procedure was as follows: 50 ml water was added into the reactor, followed by pH adjustment with HCl or NaOH to a desired pH value. After iron grains was added. The pH control was initiated upon the addition of iron. The concentrations of chromium (Cr⁶⁺) total dissolved Fe and pH were measured in the course of the experiment. The pH range is 2.5–12. Initial chromium concentration ranged from 5 to 30 mg/l. The concentration of Cr (VI) was determined spectrophotometrically with diphenylcarbazide at 540 nm and nitrate was determined spectrophotometrically with fenoldisulfonic acid at 410 nm using UV-VIS spectrophotometer.

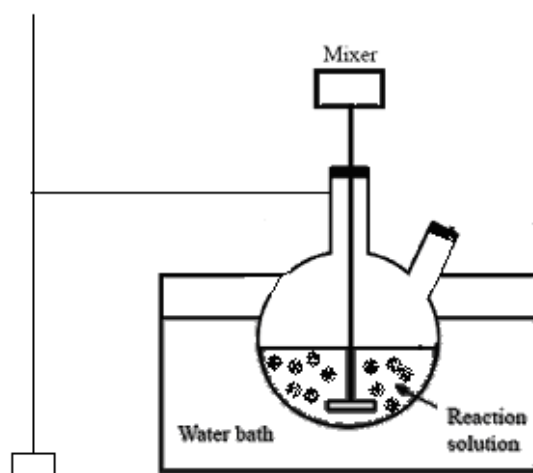
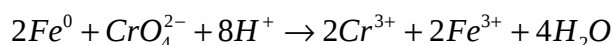
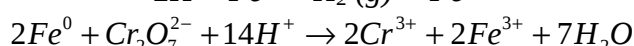
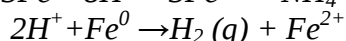
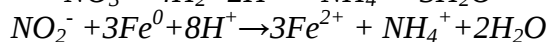
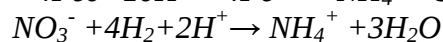
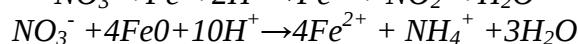
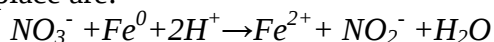


Fig. 1. Experimental set-up

Reactions that take place are:



RESULTS AND DISCUSSION

In this study, we conducted a series of laboratory experiments in order to quantify the rate of chromium (Cr⁶⁺) and nitrate reduction by iron. The main goals of the experiments were to determine the removal efficiency as a function of time, chromium (Cr⁶⁺) concentration, and Fe⁰ quality and to develop an empirical rate for Cr⁶⁺/Fe⁰ reactions.

The kinetics of nitrate and Cr (VI) reduction by one type of iron metal (Fe⁰) were studied in batch reactors for a range of Fe⁰ surface area concentrations and solution pH values (2.5–12.0). Unlike Cr (VI), Fe⁰ surface area concentration had little effect on rates of nitrate reduction. The rates of nitrate and Cr (VI) reduction by Fe⁰ decreased with increasing pH. Buffer character had minimal effects on reduction rates, indicating that pH was primarily responsible for the differences appeared in the rate values. At high pH values, Cr (VI)

reduction was observed after a short period of time, and negligible nitrite reduction was observed over 24 h.

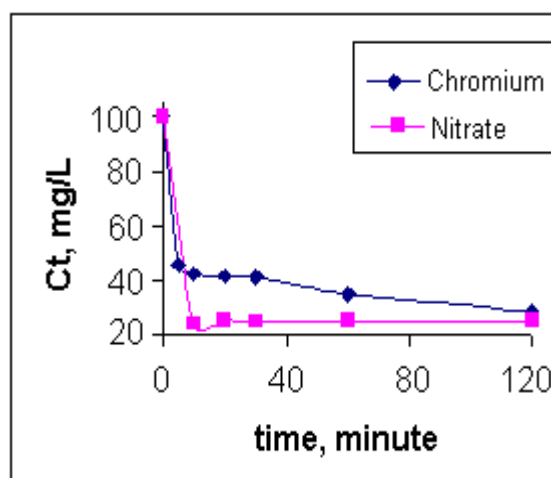


Fig. 2 Nitrate and chromium ions removal using iron

Experimental data regarding the kinetics of nitrate ion and chromium (Cr^{6+}) retention are presented in Fig. 1, under the form of integrated kinetic curves which represent the variation of ion's concentration in solution during the experiments.

The comparative kinetic data presented in Fig. 1 highlight the fact that reduction kinetic is different for the two ions studied, in the sense that, in similar conditions, nitrate ion concentration in solution decrease is more pronounced compared with chromium.

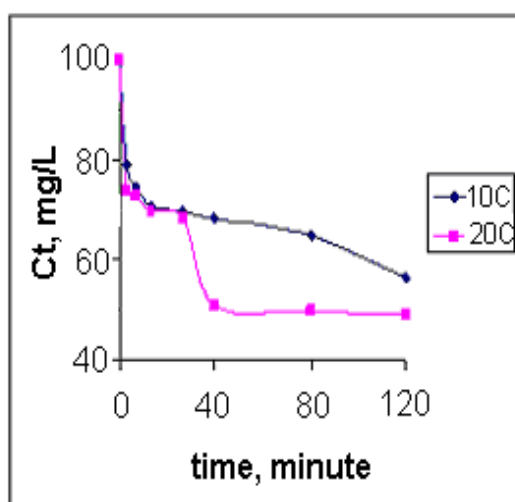


Fig. 3 Temperature influence on nitrate ion reduction in Fe^0 -solution KNO_3 system at $\text{pH}=2,5$, and different temperatures (10°C și 20°C), $C_i = 100$ mg/l with zero valent iron

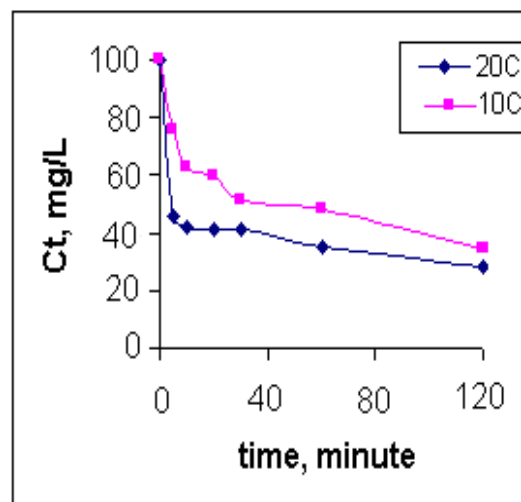


Fig. 4 Temperature influence on chromium reduction in Fe^0 -solution KCrO_7 system at $\text{pH}=2,5$, and different temperatures (10°C și 20°C), $C_i = 100$ mg/l with zero valent iron

In the set of experiments presented in figure 3 were evaluated the effects of temperature on NO_3^- reduction with Fe^0 . In order to establish the influence of this parameter, the temperature was varied in the domain $10\text{-}20^\circ\text{C}$. The reaction temperature was maintained

constant by using an incubator. By analysing the data it can be observed that in the first 20 minutes the curves have a similar behaviour.

After 30 minutes time of contactation, the NO_3^- removal efficiency at 20°C drops faster compared with the behaviour observed at 10°C when the removal efficiency decrease is lower. It can be observed from figure 4 that in the first 40 minutes of contact, Cr(VI) is removed fast, the concentration from solution being reduced from 100 mg/l to 41.4 mg/L. Once the time passes, Cr(VI) concentration in water slowly decreases from 66 mg/L to 40 mg/L. The temperature has small influence on Cr(VI) removal from water, at 20°C the concentration decreases after 120 minutes contact time, until 28,32 mg/L, while at 10 °C the concentration drops at 34.56 mg/L.

The most interesting phenomena besides NO_3^- reduction observed during the tests done at low pH value (2,5) was the generation at few minutes after the beginning of the process of a distinctive black material which started to coat the Fe^0 granule along with continuous hydrogen bubbles generation. This fact indicates the possible generation in the system of a certain iron based compound.

The influence of pH value on nitrate and chromium removal from water

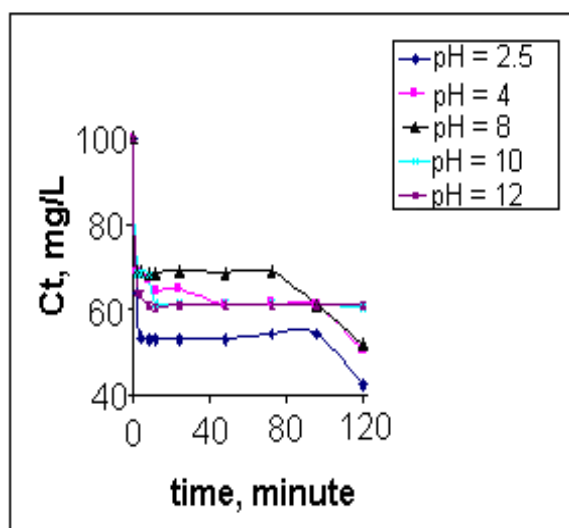


Fig. 5. The influence of pH value on nitrate reduction kinetic study using iron

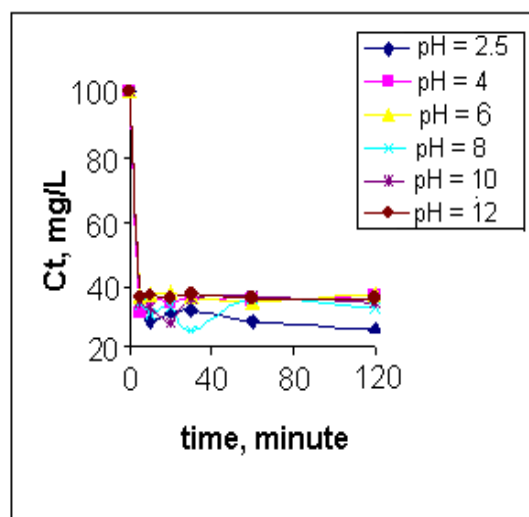


Fig. 6. The influence of pH value on chromium reduction kinetic study using iron

Fig. 5 and 6 highlight the optimal working conditions from the point of view of pH value at which iron is the most reactive in order to ensure an efficient nitrate and chromium reduction from water. The experimental data represented in Fig. 5 reveal the pH influence on NO_3^- removal. During the experiments, the NO_3^- concentration was maintained constant at 100 mg/l. At the beginning of the experiments, the initial pH value of the solution was adjusted to the desired value as follows: 2,5 4, 8, 10, 12 using HCl or NaOH. During the process, the pH value variation wasn't monitored. From data analysis we can conclude that because at pH =2.5 the removal efficiency obtained was around 50- 60% (for 100 mg/l initial concentration), while at pH = 8 the obtained removal efficiency was 30-40 %, NO_3^- reduction in the presence of Fe^0 gives better results at acidic pH values.

The experimental data set presented in figure 6 reveals the pH effects concerning the reduction of chromium with Fe^0 , the pH was varied in the range 2.5-12. The initial working concentration was 100 mg/l, while the residual concentration obtained at pH = 2.5 was 28.32 mg/l.

In the first test, pH was adjusted and maintained constant at 2.5. Immediately after, 1 g Fe^0 was added in nitrate or chromium containing solution. Six samples were collected over the test period (120 min). In addition to monitoring the nitrogen species, the cation and anion charge balance of the solution in the reactor was performed to determine the reactions involved. The anions in the solution might consist of NO_3^- , NH_4^+ , and Cl^- with OH^- being negligible at pH = 2.5.

The ammonium ion might exist as an intermediate product of nitrate reduction. The chloride ion was introduced by adding HCl. The cations consist of K^+ , H^+ , NH_4^+ , Fe^{2+} , and Fe^{3+} . The NH_4^+ could be present as a product of NO_3^- reduction, while Fe^{2+} and Fe^{3+} were the products of iron corrosion and/or dissolution. The amount of K^+ introduced by adding KNO_3 , was unlikely to be involved in reaction, and therefore, could maintain its initial concentration over the whole test period.

As shown in Fig. 5, the following aspects were observed in the first test: almost half of nitrates, 100 mg/l as measured, were transformed into ammonium efficiently and completely within 5 minutes. Since the Cl^- was introduced only by adding HCl and a steady pH of 2.5 was controlled in the pH-stat, the accumulated acid consumption over time can be represented by the accumulated Cl^- addition. After nitrate reduction, the acid consumption rate slowed down, but was still slightly higher than that in the control. Thus, the test results indicate that nitrate will stimulate acid consumption. The total cation charges at anytime were well balanced with the corresponding anion charges.

It was obvious that the presence of H^+ greatly enhanced the nitrate reduction. Ahn *et al.* (2001) suggested that both the initial pH of the solution and the change of pH during reactions played very important roles in the reduction. As shown in Fig. 6, the Cr (VI) removal efficiency increased significantly with decreasing pH, mainly because in acid condition, the accelerated corrosion of Fe^0 enhanced the reaction rate. In the initial five minutes, the plots below pH 4 decreased rapidly, indicating that the Fe^0 were still high reactivity. In contrast, the pH>8 plots decreased gently because of the form of $\text{Fe}(\text{OH})_3$ during high pH value. The almost horizontal segment of the plots after sixty minutes was caused by Fe^0 oxidation.

Reduction of Cr (VI) by Fe^0 as reducing agent was studied using potassium dichromate solution as the model contaminant. The concentration of Fe^0 had significant effect on the reduction of Cr (VI). The reaction occurred in broad pH value scale and the reaction efficiency increased significantly with decreasing initial pH. The starch-stabilized Fe^0 exhibited higher removal efficiency because starch is a good dispersant and could prevent Fe^0 agglomeration. Electrochemical analysis of the reaction process showed that $\text{Cr}(\text{OH})_3$ should be the final and dominant product of Cr (VI). The remediation of areas polluted with Cr (VI) was widely researched before. This study indicated that Fe^0 , especially the one which was starch-stabilized, can yield to higher removal efficiency in the remediation of Cr (VI)-contaminated soils and groundwater.

CONCLUSIONS

Our team was also involved in developing a new technique for nitrate removal using Fe^0 metal under ordinary laboratory conditions and in the absence of a pH buffer in particular.

The results of the preliminary experiments indicate that almost complete removal of the nitrate ion has occurred.

The remediation of Cr (VI) contaminated sites was widely researched before. This study indicated that Fe^0 , especially those which were starch-stabilized, can yield to higher removal efficiency in the remediation of Cr (VI)-contaminated soils and groundwater. The remediation of Cr (VI) was widely researched before. This study indicated that Fe^0 , especially those which were starch-stabilized, can yield to higher removal efficiency in the remediation of Cr (VI)-contaminated soils and groundwater. The formation rate and composition of the black film depends on the system pH and the presence of nitrate or chromium. Without nitrate or chromium, no black coating is formed on iron (Fe^0) grains. The presence of the black film enhances nitrate reduction and iron acidic corrosion rather than reduce the reactivity of Fe^0 .

Nitrate and chromium (Cr^{6+}) reduction from water using zero valence iron represents a cheap partial waste water treatment alternative. In the case of acid waters, the removal efficiency is higher compared with the case of neutral or alkaline wastewaters.

From comparative point of view regarding nitrates and chromium (Cr^{6+}) reduction a similarity was observed. So, nitrates and chromium (Cr^{6+}) concentrations are reduced with pH increase and are raised with temperature. From sorption rate point of view we observed a difference, due to the fact that the rate value is smaller for nitrates and higher for chromium (Cr^{6+}).

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