E: Remediation Concepts & Technologies

PRETREATMENT OF ZERO-VALENT IRON FOR REACTIVE PERMEABLE BARRIERS IN CHROMIUM (VI) REMEDIATION

A. Vega de la Fuente[1,2], A. Silva[1], G. Carvalho[1], C. Delerue-Matos[1], A. Fiúza[2]

[1] REQUIMTE, Instituto Superior de Engenharia do Porto,
Rua Dr. Bernardino de Almeida, 4200-072 Porto (Portugal)
alf@isep.ipp.pt **Phone:** +351 228 340 500
[2] CIGAR, University of Porto, Rua Dr. Roberto Frias, S/N, 4200-072 Porto (Portugal)

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I Introduction

Environmental contamination by heavy metals is a subject of great concern in many sites all over the world. Chromium is identified as one of the major pollutants detected in groundwater and soils. It can be detected in all the environmental compartments, with concentrations between 0,1 µg/m^3 in the air and 4 g/kg in soils (Merian, 1985). Its biochemical functions and effects depend on the oxidation state: it occurs in the environment speciazed either as Cr^{3+} or Cr^{6+}; natural chromium is practically always present in the tri-valent state; therefore, hexavalent chromium in the environment has anthropologic origins. It is usually associated with stainless steel and alloys, leather processing, pigments, metal plating and wood processing industries. The higher oxidation state Cr^{6+} is far more toxic, carcinogenic, and mobile in the ground water than the reduced Cr^{3+} compounds (Puls, 1997).

Permeable Reactive Barriers (PRBs) are passive systems of groundwater treatment that remove contaminants when the water flows through an appropriate porous treatment medium, under a natural hydraulic gradient. The barrier, which can be placed in the path of a contaminated groundwater plume in various possible configurations, contains substances to remove pollutants from the plume passively resulting in a low cost operation when compared with other remediation technologies (FRTR, 2002). This technology emerged in mid 1990s with the use of granular zero-valent iron as a reactive medium for treatment of groundwater contaminated with halogenated organic compounds (VOCs), such as trichloroethylene (TCE) On the other hand, it seems to be suitable for a series of heavy metals occurring in anionic form well (Cr^{6+}, As^{6+}, As^{3+} and Se^{6+}) (Blowes, et al., 1999), (Wilkin, et al., 2003).

In recent years, researchers demonstrated that Cr^{+6} can be effective reduced by iron. The net reactions of Cr^{+6} reduction with zero valent iron and co-precipitation of Cr^{+3} and Fe^{+2} are (Blowes, et al., 1997) (Lee, et al., 2003):

$$Cr_2O_7^{2-}{}_{(aq)} + 2Fe^{0}{}_{(s)} + 14H^{+}{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 2Fe^{3+}{}_{(aq)} + 7H_2 0 \tag{1}$$

$$(1-x)Fe^{3+}{}_{(aq)} + (x)Cr^{3+}{}_{(aq)} + 2H_2O \rightarrow Cr_xFe_{(1-x)}OOH_{(s)} + 3H^{+} \tag{2}$$

The zero-valent iron not only effectively reduces mobility and bioavailability of Cr (Kumpienea, et al., 2006) but it is also used in PRBs as an effective reductant for Cr^{+6} (Powell, et al., 1995);

(Deng, et al., 1996), (Puls, et al., 1999). The iron used in these applications is available from a variety of commercial sources, having different forms and size distributions, and small variations in the chemical composition. Obviously, these parameters will influence the process of remediation inside the barrier (Baciocch, et al., 2003), and they must be taken into consideration in its design and construction.

The state of the iron which is going to be used in the construction of the barrier is a parameter that should be studied, since iron properties as reductant can be altered (Lin, et al., 2005) due to several reasons related with its storage and delay of its application. The objectives of these batch experimental studies are: a) Compare the performance of different types of zero-valent iron to remediate Cr^{6+} and b) Determinate the effects of iron pre-treatment in Cr^{6+} remediation process (effectiveness and kinetics).

II Material and Method

II.I Materials

For type of iron were used for batch experiments: **a)** Commercial iron (bulk) 0,3 mm – 0,6 mm a low carbon iron spheres; **b)** Iron metal filings Laboratory (Reagent Product Code**:** I/0850/60 CAS Number: 7439-89-6 Manufacturer: Fisher Scientific), **c)** Iron metal fine filings Laboratory Reagent (Product Code: I/0850/63 CAS Number: 7439-89-6 Manufacturer: Fisher Scientific) and **d)** pure 99,98 % pure iron chips (CAS Number: 7439-89-6, Manufacturer: Sigma-Aldrich).

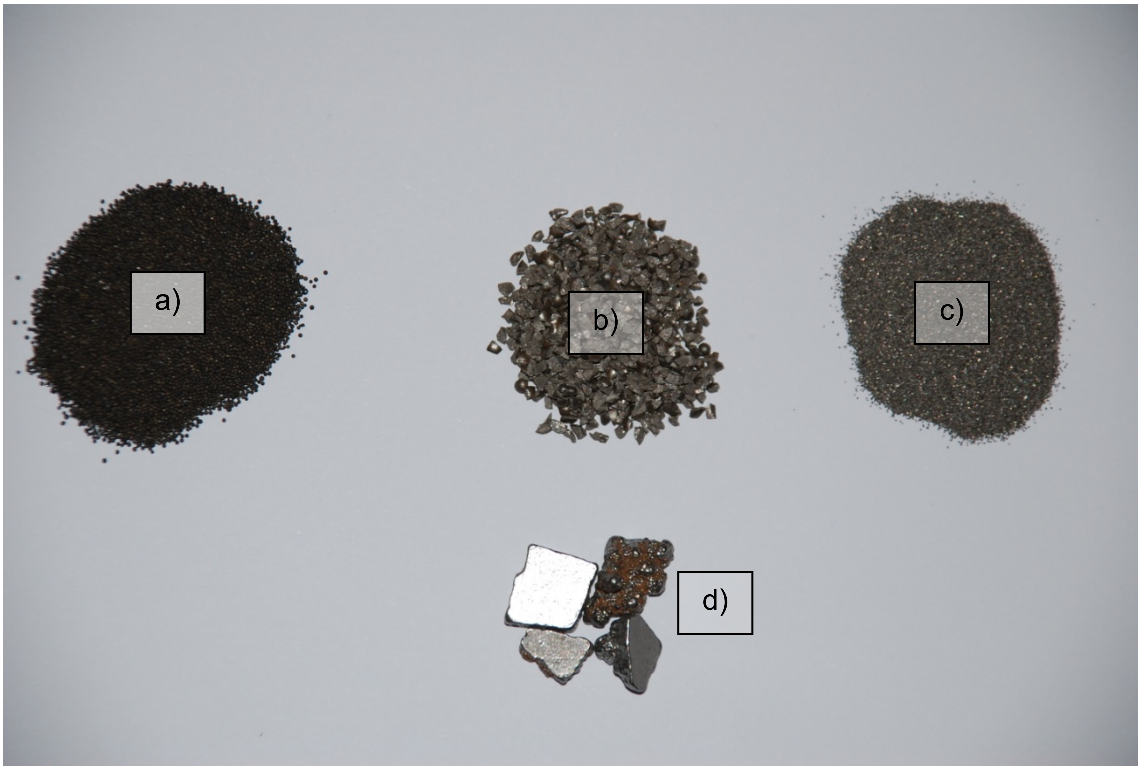

Figure 1 Types of iron used: a) Commercial iron, b) Lab iron fillings, c) Fine lab iron fillings d) Pure Iron chips

Hexavalent chromium stock solutions (500 mg/l) were prepared by dissolving 0,1415 g of Merck analytical grade $K_2Cr_2O_7$ in 100 ml of deionised water with conductivity less than 0.1 S/cm; the desired initial concentrations of Cr^{+6} were prepared by diluting the stock solution.

The washing liquids were prepared by dilution of p.a. grade reagents. HCl, NaOH, HNO_3 and H_2SO_4 were used to pre-treat the different types of iron.

II.II Method

One gram of iron of a), b) and c) iron types were washed with 0,02N, 0,06N and 0,2N solutions of NaOH, HNO_3 and H_2SO_4. The iron samples were soaked, at least three times in the solution, and the excess of liquid was removed with pure acetone. Batch experiments were conducted in 500ml Erlenmeyer, containing 100 ml of Cr (VI) solution, and 1.0 g of washed iron. Batch experiments with all types of iron without pre-treatment were also performed. At last, d) iron was tested without treatment and with the solution that leaded to better results after washing pre-treatment were done to establish the differences between both alternatives.

Five milliliters samples were collected periodically and the Cr^{+6} concentration was measured by the diphenylcarbazide colorimetric method (Standards Methods, 3500). After 15 minutes the purple color was completely developed and the samples were analyzed in a simple beam Cary Varyan 50 Conc. spectrophotometer. The absorbance was measured at 540 nm in 1cm pathway plastic cell.

III Results and Discussion

Preliminary tests were done using a commercial bulk granular iron without any previous treatment; different masses of iron were put in contact with a 10 mg/L solution of Cr^{+6} and after 2.5 h almost no decrease in the chromium concentration was achieved.

This result indicates that the iron surface doesn't have the ability to causes the chromium reduction, so several different pre-treatment procedures were tested. Iron was washed with water, sodium hydroxide and different regular acids. The evaluation of iron samples pre-treatment was determined calculating the percentage of Cr^{+6} removals in different time periods.

III.I Iron without pre-treatment

Batch experiences were conducted, in the first place, to determinate the effectiveness of the irons a), b) and c) to remove Cr^{+6} without any kind of pre-treatment. It was used 10 ppm as initial concentration, in open air flasks without agitation. The results are summarized in Table 1.

	Chromium removal (%)	
	20 min.	60 min.
Iron a)	2.10	4.16
Iron b)	3.21	11.52
Iron c)r	13.26	21.61

Table 1. Chromium removal achieved with iron whit no pre-treatment

Commercial iron a), without pre-treatment, presents very low performances as chromium reductant. Laboratory reagents irons b) and c) present better results. The comparison data with different types of iron showed that the increasing of the specific surface area related to the decreasing particle size distribution may signify that external area plays an important role in the removal process.

III.II Iron washed with sodium hydroxide.

Batch experiments were perform to establish the ability of basic solutions to improve the iron behaviour in the iron chromium reaction; it was studied iron washed with 0.02N, 0.06N and 0.2N NaOH solutions (Table 2).

	Chromium removal %					
NaOH (N)	0.02		0.06		0.2	
Time (min.)	20	60	20	60	20	60
Iron a)	6.80	8.98	9.08	9.99	9.27	10.71
Iron b)	6.89	16.71	8.30	17.89	11.31	16.79
Iron c)	36.77	57.26	29.121	50.987	18.03	39.73

Table 2– Chromium removal % after iron pre-treatment whit sodium hydroxide

It is evident that removal rates are better than the ones obtained without pre-treatment. Irons a) and b) shows a slight improve in their reduction ability that is practically independent of the sodium hydroxide concentration. The iron c) presents an inverse trend - when NaOH concentration increase, the removal rate decreases. This fact is probable due to an inefficient removal of the washing liquid, since the reaction is more effective with neutral or slightly acid pH (Gheju, et al., 2006).

III.III Iron washed with nitric acid

Batch experiments were perform to establish the ability of acid solutions to improve the iron behaviour in the iron chromium reaction; it was studied iron washed with 0.02N, 0.06N and 0.2N $NHNO_3$ solutions (Table 3).

	Chromium removal %					
HNO_3 (N)	0.02		0.06		0.2	
Time (min.)	20	60	20	60	20	60
Iron a)	8.32	7.11	8.94	10.10	14.99	15.32
Iron b)	4.28	7.31	9.75	14.21	11.04	9.06*
Iron c)	9.28	11.57	11.25	14.72	26.56	36.60

Table 3. Chromium removal % after iron pre-treatment whit nitric acid

All the three kind of irons improve their behavior when the concentration of acid solution increased. The c) type iron showed better performance.

III.IV Iron washed with sulfuric acid

Same batch experiments were perform with 0.02N, 0.06N and 0.2N solutions of H_2SO_4 and iron a), b) and c). Results are present in Figure 1, Figure 2, and Figure 3. They show that sulfuric acid seems to be the best tested pre-treatment. With a 0,2 N solution, a 100% removal of chromium was achieve within an hour, The iron with better performance is the type c), characterized by a smaller size distribution and bigger specific area.
Other acids was tested (HCl and H_3PO_4); they have, in general, the same behavior but their performance to remove chromium was less than attained by sulfuric acid.

III.V Iron d) study

Batch experiments were perform with 99.9% pure iron chips to investigate the effect of pre-treatment with sulfuric acid when it is compared with the absence of treatment. The objective was to verify if the pre-treatment is recommended in all situations, even with a lab pure iron reagent.

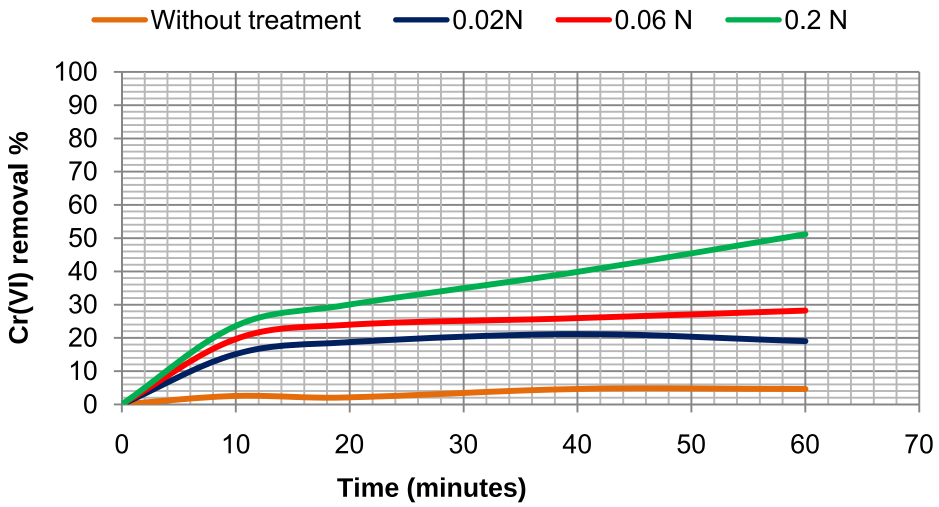

Figure 2. Chromium hexavalent removal rates after iron Type a) were pre treated whith 0.02, 0.06, 0.2 N sulphuric acid

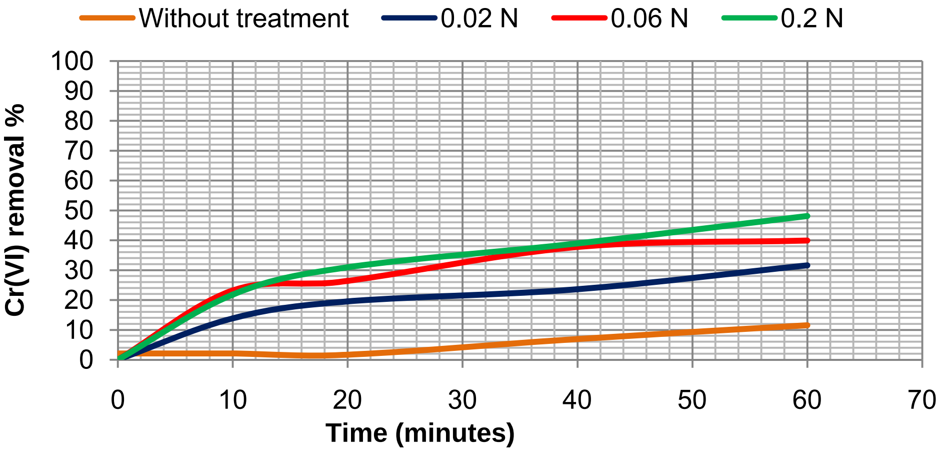

Figure 3. Chromium hexavalent removal rates after iron Type b) were pre treated whith 0.02, 0.06, 0.2 N sulphuric acid

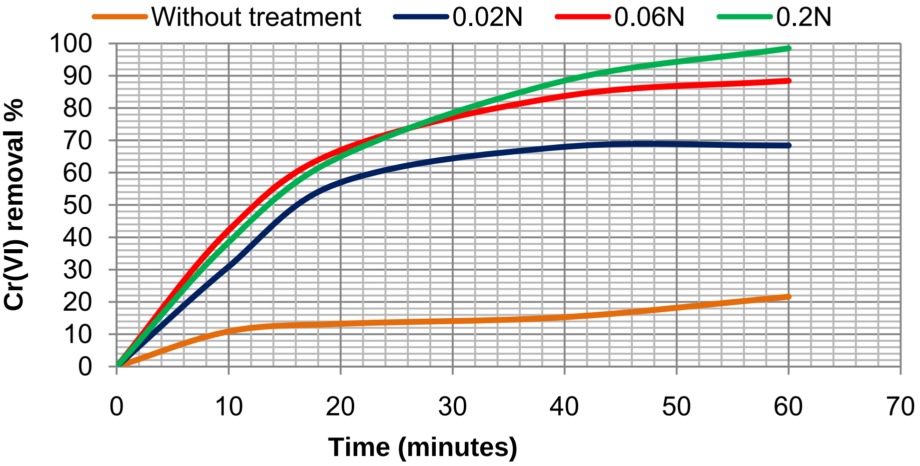

Figure 4. Chromium hexavalent removal rates after iron type c) were pre treated whith 0.02, 0.06, 0.2 N sulphuric acid

Initial concentration of 50 ppm was established to begin de experiment which lasted for a longer period of time (Figure 4).

The pre-treatment of iron with sulfuric acid, even when it is almost pure, increase the rate of chromium reduction.

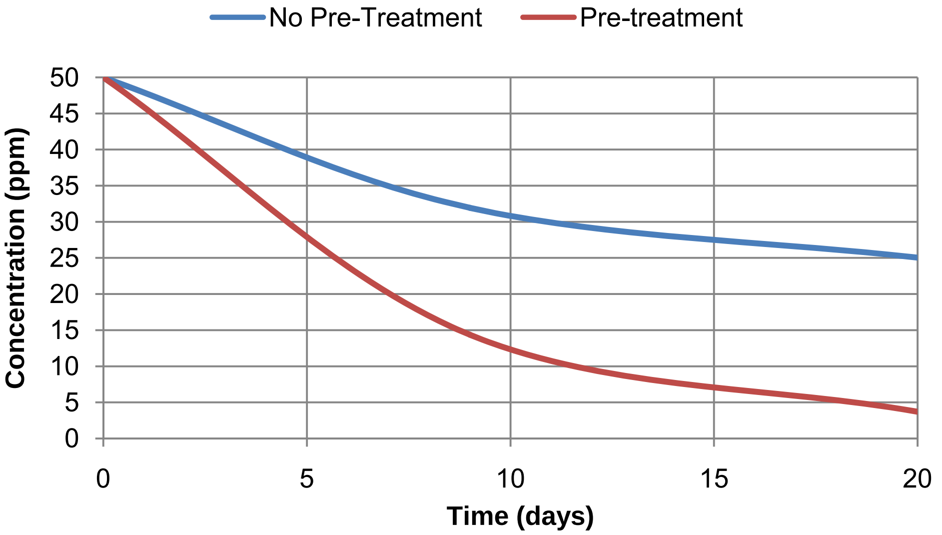

Figure 5. Chromium hexavalent removal rates of iron Type d) without any pre-treatment and washed with 0.2 N sulphuric acid

IV Conclusions

An acid pre-treatment of iron is recommended in order to improve the reduction of Cr^{+6} with zero-valent iron. The results with all type of irons tested were conclusive, and the gains in term of kinetics have great significance. Sulfuric acid was revealed as the best washing agent among all the chemicals tested. The state of iron, as a consequence of probable surface chemical alterations due to long-time storing should be considerate to establish the necessity of a pre-treatment before construction of PRBs.

One of the most important parameters to design permeable reactive barriers is the kinetics of the reaction between the contaminants and the active filling reagent. This principle applies to chromium-iron processes as well. Engineers establish the minimum residence time to decontaminate groundwater in the barriers using the characteristic of the iron evidenced in laboratory testing.

Problems can appear when iron, due to long time storing, has modified its reducing capacity and it doesn't acts as it was supposed. Storage conditions before application can compromise the effectiveness of a remediation system since phenomena as surface deactivation, corrosion, oxidation of the surface of iron particles can occur.

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