Treatment of Cr(VI) polluted wastewater by use of scrap iron, a cheap and locally available alternative electron source

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Abstract The reduction of Cr(VI) by use of a cheap and locally available industrial waste, scrap iron, was investigated in continuous system. The experimental results showed that, at the beginning of the column experiment, Cr(VI) was not detected in column effluent, which means that it was completely reduced. The greater the pH of column influent, the lower the time period before the breakthrough of hexavalent chromium in column effluent, excepting pH = 2.0 when the increased contribution of H^+ ions to the corrosion of scrap iron leads to a rapid decrease in time of the scrap iron mass. After Cr(VI) breakthrough, its concentration in column effluent continuously increased in time until a steady-state value was observed. The behavior of Cr(III), Fe(II) and Fe(III) in column effluent was found to be, with minor exceptions, similar: the concentrations decreased, more or less rapid, in column effluent, until a steady-state value was observed. Experiments performed in this work confirmed the possibility of treating Cr(VI) polluted wastewater by using scrap iron as reducing agent.

Keywords: hexavalent chromium, toxic metals, scrap iron, reduction, wastewater treatment.

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1. Introduction

Environmental pollution has been accepted for a long time as an undesired side effect of civilization and progress. Metals environmental contaminants are particularly problematic because, unlike most organic contaminants, they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain [1]. Although numerous metals are important micronutrients, being responsible for biochemical, immunological and physiological activities of the living organisms, some of them, especially heavy metals, can negatively affect, even in low doses, the health of living organisms [2]. Oxidation states of chromium range from (–IV) to (+VI), but only the (+III) and (+VI) states are stable under most natural environments [3]. Hexavalent chromium is the most stable form under oxidizing conditions, whereas trivalent chromium is the most stable form under reducing conditions. Chromium usually exists in aqueous systems in both trivalent and hexavalent

forms, which are characterized by different toxicity and chemical behavior. Cr(VI) is known to be toxic to humans, animals, plants and microorganisms, and to have a significant solubility and mobility [4-6]. Cr(III), on the other hand, is less toxic and less mobile, because it readily precipitates as $Cr(OH)_3$ [7] or as mixed Fe(III)-Cr(III) (oxy)hydroxides [8] under alkaline or even slightly acidic conditions. While chromium concentrations in non-polluted fresh waters should vary from 0.1 to 0.5 ppm, contamination of ground and surface waters with levels as high as 80 ppm has been observed in industrial areas, due to improper waste disposal and leakages from industries like paint and pigment manufacturing, refractory, leather tanning, chrome plating, textile, wood preserving [4, 9]. It is obviously that removal of Cr(VI) is an essential pollution abatement process that should be applied to wastewaters contaminated with this heavy metal, prior to discharging them into the natural water bodies. Chemical reduction to Cr(III) followed by precipitation is the most used technique for the

decontamination of wastewaters polluted with Cr(VI) compounds. The reducing agents commonly used are ferrous sulphate, sulphur dioxide and sodium sulphites. The major drawback of this conventional treatment method is the high cost of chemicals used for the reduction purposes. In last years there has been great interest in using zerovalent iron as electron donor for the Cr(VI) reduction process [8, 10, 11]. The aim of this work was to examine the use of scrap iron, a cheap and locally available industrial waste, for the continuous reduction of hexavalent chromium in flow-through columns.

2. Experimental

Column experiments conducted in this study were performed by using iron shavings, characterized in our previous study [12]. Hexavalent chromium stock solutions (1g/L) were prepared by dissolving 2.829 g $K_2Cr_2O_7$ in 1000 mL of distilled deionised water. Synthetic hexavalent chromium wastewater of the desired initial concentration (10 mg/L) was prepared by diluting the stock solution. H_2SO_4 was used for adjusting pH of the feed solution. All chemicals used were of AR grade.

Column flow-through reduction experiments were conducted at room temperature (24^oC) by passing synthetic Cr(VI) polluted wastewater (10 mg/L) through a glass column (inner diameter: 2.00 cm; height: 12.00 cm) with a porous plate at the bottom, packed with 30 g scrap iron (scrap iron volume: 18.84 cm^3), from the bottom to the top, by using a Unipan peristaltic pump, with a pumping rate of 0.3 L/hour (hydraulic contact time = 2.60 minutes). To remove traces of chromium and iron, the column was soaked in HCl 35% and washed with distilled deionised water before each experiment. Column effluent samples were withdrawn at regular time intervals and Fe(II), Fe(total), Cr(VI) and Cr(total) concentration were determined. The effect of feed solution pH on the on the Cr and Fe species concentration in the treated effluent was studied over the pH range of 2.0 - 7.3.

Cr and Fe aqueous species were determined by colorimetric methods [13], using a Jasco V 530 spectrophotometer. Cr(VI) concentrations were determined by the 1,5-diphenylcarbazide method. Cr(total) was determined by oxidizing any trivalent chromium with potassium permanganate, followed

by analysis as Cr(VI). Cr(III) was determined from the difference between total and hexavalent chromium. Fe(II) concentrations were determined by the 1,10-phenanthroline method; Fe(total) was determined by reduction of any Fe(III) to Fe(II) with hydroxylamine hydrochloride followed by analysis as Fe(II). Fe(III) was determined from the difference between total and bivalent iron. The pH of solutions was measured using an Inolab pH-meter.

3. Results and Discussions

3.1. Cr(VI) concentrations in the column effluent

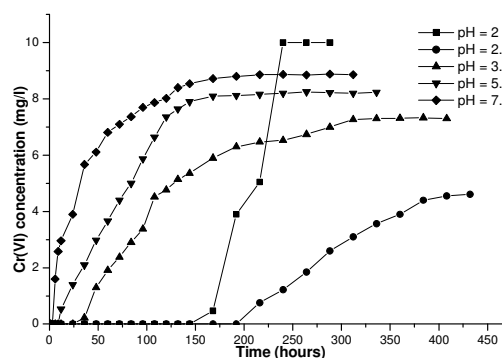Cr(VI) concentrations in column effluent, as a function of elapsed time and pH, are presented in Fig. 1.

Fig.1. Cr(VI) concentration in column effluent vs. time, at different feed solution pH

The results show that Cr(VI) reduction by Fe(0) is comparable with a column ion exchange process. It can be seen that, during the first hours of the column experiment, Cr(VI) was completely reduced. After some time (the greater the pH, the lower the time period), hexavalent chromium breakthrough in column effluent occurs, and, from this moment, Cr(VI) concentration in column effluent increases in time, until a steady-state concentration, lower than 10 mg/L, was observed. The steady-state Cr(VI) concentration in column effluent decreased with decreasing the initial pH of Cr(VI) solution up to 2.5. The breakthrough of Cr(VI) followed by the increase of its concentration is due to co-precipitation of simple and/or mixed Fe(III)-Cr(III) (oxy)hydroxides on filling surface, which block the access of Cr(VI) to the iron surface and leads to a decrease in Cr(VI) reduction rate. The time period

during Cr(VI) was not detected in column effluent increased with decreasing pH. But, we also noticed one exception from this rule: at pH = 2.0 hexavalent chromium concentration in column effluent was zero for a shorter time than at pH 2.5. In the same time, no steady-state Cr(VI) concentration in column effluent was observed at pH 2.0. This behavior is due to the increased contribution of H^+ ions to the corrosion of scrap iron, which leads to a rapid decrease in time of the scrap iron mass.

3.2. Cr(III) concentrations in the column effluent

Cr(III) concentrations in column effluent, as a function of elapsed time and pH, are presented in Fig.2. The results show that, over the pH range of 2.5 - 7.3, Cr(III) concentration in column effluent slowly decreased in time during the experiment until a steady-state concentration was observed.
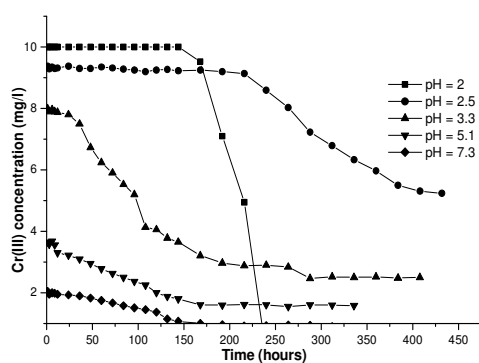

Fig.2. Cr(III) concentration in column effluent vs. time, at different feed solution pH

The decrease of Cr(III) concentration has the same explanation like the increase of Cr(VI) concentration in column effluent: the co-precipitation of mixed Fe(III) - Cr(III) (oxy) hydroxides on the scrap iron surface. The steady-state Cr(III) concentration in column effluent decreased with increasing the initial pH of Cr(VI) solution up to 2.5. At pH = 2.0 Cr(III) concentration in column effluent decreased very rapid from 10 mg/L to 0 mg/L, and no steady-state Cr(III) concentration was observed.

3.3. Cr(total) concentrations in column effluent

Cr(total) concentrations in column effluent, as a function of elapsed time and pH, are presented in

Fig. 3. The results show that, over the pH range of 2.5 - 7.3 two steady-state Cr(total) concentrations in column effluent were observed.
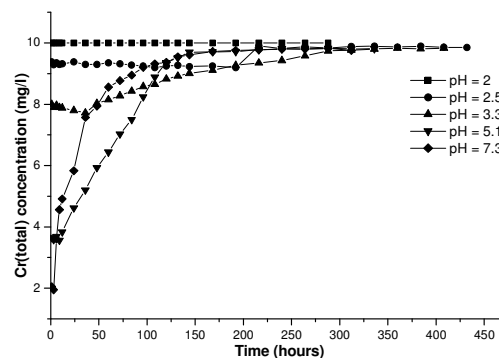

Fig.3. Cr(total) concentration in column effluent vs. time, at different feed solution pH

The first steady-state concentration was observed at the beginning of the column experiment and its duration increased with decreasing pH. Afterwards, Cr(total) concentrations in column effluent increased in time during the experiment until a second steady-state concentration was observed. Both first and second steady-state Cr(total) concentration in column effluent increased with decreasing the initial pH of Cr(VI) solution. Instead, at pH = 2.0, no steady-state Cr(total) concentration was observed. At this low pH, for the entire period of the experiment, Cr(total) concentration in column effluent was constant and equal with the value of Cr(VI) in column influent (10 mg/L). This means that, at pH = 2.0, no precipitation of mixed Fe(III)-Cr(III) (oxy)hydroxides occurs on the scrap iron surface.

3.4. Fe(II) concentrations in the column effluent

Fe(II) concentrations in column effluent, as a function of elapsed time and pH, are presented in Fig. 4. It can be seen that, for the entire experiment duration, at pH = 7.3, Fe(II) was not identified in column effluent. This means that, at pH = 7.3, all Fe(II) formed due to reduction of hexavalent chromium with zerovalent iron was either oxidized to Fe(III), or precipitated inside the column. Over the pH range of 2.5 - 5.1 the results show a continuously decrease of Fe(II) concentration in

column effluent until a steady-state concentration was observed. The decrease of Fe(II) concentration was caused by the decrease in time of scrap iron corrosion rate, but also by a increased contribution of Fe(II) to the Cr(VI) reduction. It can also be seen that the initial Fe(II) concentration (after one hour) in column effluent increased with increasing the initial pH of Cr(VI) solution.
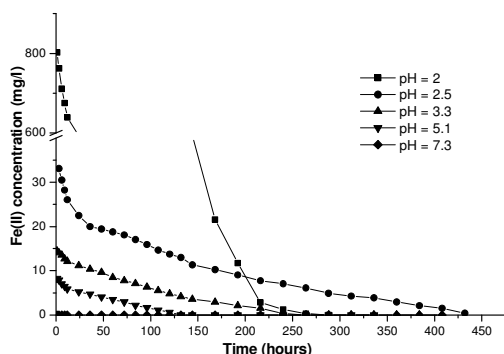

Fig.4. Fe(II) concentration in column effluent vs. time, at different feed solution pH

3.5. Fe(III) concentrations in column effluent

Fe(III) concentrations in column effluent, as a function of elapsed time and pH, are presented in Fig. 5. It can be seen that, for the entire experiment duration, at pH = 7.3, Fe(III) was not identified in column effluent.
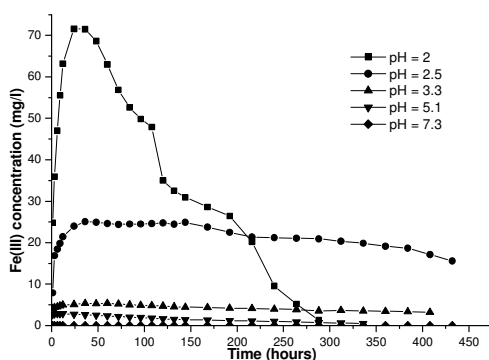

Fig.5. Fe(III) concentration in column effluent vs. time, at different feed solution pH

This means that, at pH = 7.3, all Fe(III) formed due to the oxidation of Fe(II) precipitated inside the

column. The results also show that, over the pH range of 2.5 - 5.1, Fe(III) concentration in column effluent slowly increased in time during the first hours of the experiment until maximum concentration was observed. After that, the Fe(III) concentration in column effluent slowly decreased in time until a steady-state concentration was observed. The initial increase of Fe(III) concentration is due to a faster rate of Cr(VI) reduction process during the first hours of the experiment. Afterwards, the rate of Cr(VI) reduction decreases in time, due to passivation of the scrap iron surface, which leads to a decrease of Fe(III) concentration in column effluent.

3.6. Fe(total) concentrations in the column effluent

Fe (total) concentrations in column effluent, as a function of elapsed time and pH, are presented in Fig. 6. Because for the entire experiment duration, at pH = 7.3, Fe(II) and Fe(III) were not identified in column effluent, it is obvious that Fe(total) will also not be present at this pH. Over the pH range of 2.5 - 5.1 the results show a continuously decrease of Fe(total) concentration in column effluent until a steady-state concentration was observed. The decrease of Fe(total) concentration was caused by the decrease in time of scrap iron corrosion rate. Initial Fe(total) concentration (after one hour) in column effluent increased with increasing the initial pH of Cr(VI) solution. By comparing figures 4-6 it can also be seen that the major component of Fe(total) was Fe(II).
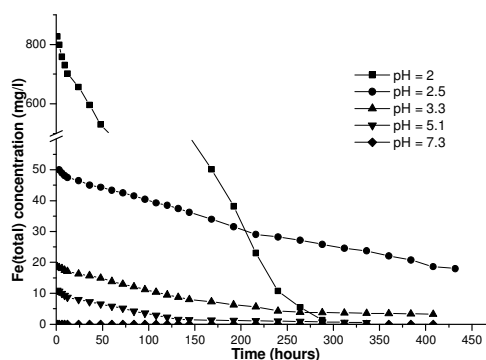

Fig.6. Fe(total) concentration in column effluent vs. time, at different feed solution pH

4. Conclusions

Long-term column experiments performed in this work confirmed the possibility of treating Cr(VI) polluted wastewaters by using scrap iron as reducing agent. The experimental results indicate that pH of Cr(VI) solution significantly affects the reduction capacity of scrap iron. The concentration of Cr and Fe species in the column effluent was found to be also directly dependent on the concentration of hydrogen ions in initial Cr(VI) solution.

At the beginning of the column experiment Cr(VI) was not detected in column effluent, which means that it was completely reduced. The greater the pH, the lower the time period before the breakthrough of hexavalent chromium in column effluent. At pH = 2.0 (and probably at pH values lower than that) this rule was no more valid, due to the increased contribution of H^+ ions to the corrosion of scrap iron, which leads to a rapid decrease in time of the scrap iron mass. After Cr(VI) breakthrough, its concentration in column effluent continuously increased in time until a steady-state value was observed. The behavior of Cr(III), Fe(II) and Fe(III) in column effluent was found to be, with some exceptions, similar: the concentrations decreased, more or less rapid, in column effluent until a steady-state value was observed. The breakthrough of Cr(VI) followed by the increase of its concentration, and the decrease of Cr(III), Fe(II) and Fe(III) concentration in column effluent are due to co-precipitation of mixed Fe(III) - Cr(III) (oxy) hydroxides on Fe(0) surface, which block the access of Cr(VI) to the iron surface and leads to a decrease in Cr(VI) reduction rate.

5. Acknowledgments

6. References

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[1]. R. Shrivastava, R.K. Upreti and U.C. Chaturvedi, FEMS Immunology and Medical Microbiology **38,** 65 (2003).

[2]. S.E. Manahan, *Fundamentals of environmental chemistry*, Lewis Publishers, Chelsea, 1993.

[3]. F.A. Cotton, G. Wilkinson, C.A. Murillo and M. Bochmann, *Advanced inorganic chemistry*, John Wiley & Sons, Inc., 1999.

[4]. D.E. Kimbrough, Y. Cohen and A.M. Winer, Critical Reviews in Environmental Science and Technology **29**, 1 (1999).

[5]. J. Barnhart, Journal of Soil Contamination **6**, 561 (1997).

[6]. M. Gheju, *Chromium and the environment*, „Politehnica" Publishing House, Timisoara, 2005.

[7]. D. Rai, B.M. Sass and D.A. Moore, Inorganic Chemistry **26**, 345 (1987).

[8]. D.W. Blowes, C.J. Ptacek, S.G. Benner, C.W.T. McRae, T.A. Bennett and R.W. Puls, Journal of Contaminat Hydrology 45, 123 (2000).

[9]. C. Cervantes, J.C. Garcia, S. Devars, F.G. Corona, H.L. Tavera, J.G. Guzman and R. Moreno-Sanchez, FEMS Immunology and Medical Microbiology **25**, 335 (2001).

[10]. R.W. Puls, D.W. Blowes and R.W. Gillham, Journal of Hazardous Materials **68**, 109 (1999).

[11]. R.W. Puls, C.J. Paul and R.M. Powell, Applied Geochemistry **14**, 989 (1999).

[12]. M. Gheju and A. Iovi, Kinetics of hexavalent chromium reduction by scrap iron, Journal of Hazardous Materials **135B**, 66 (2006).

[13]. APHA, AWWA, WEF, *Standard methods for the examination of water and wastewater, 21th Edition*, United Book Press, Inc., Baltimore, MdD, 2005.