

Cr(VI) reduction in aqueous solutions by siderite

Mehmet Erdem^{a,*}, Faruk Gür^b, Fikret Tümen^b

^a Department of Environmental Engineering, Institute of Natural and Applied Science, University of Firat, 23279 Elazığ, Turkey

^b Department of Chemical Engineering, Firat University, 23279 Elazığ, Turkey

Received 23 March 2004; accepted 21 June 2004

Available online 31 July 2004

Abstract

Hexavalent chromium is a common and toxic pollutant in soils and wastewaters. Reduction of the mobile Cr(VI) to less mobile and less toxic Cr(III) is a solution for decontamination of industrial effluents. In this study, the reduction of hexavalent chromium in aqueous solutions by siderite was investigated. The influences of amount of acid, contact time, siderite dosage, initial Cr(VI) concentration, temperature and particle size of siderite have been tested in batch runs. The process was found to be acid, temperature and concentration dependent. The amount of acid is the most effective parameter affecting the Cr(VI) reduction since carbonaceous gangue minerals consume acid by side reactions. The highest Cr(VI) reduction efficiency (100%) occurred in the 50 mg/l Cr(VI) solution containing two times acid with respect to stoichiometric amount of Cr(VI) and at the conditions of siderite dosage 20 g/l, contact time 120 min and temperature 25 °C. Reduction efficiency increased with increase in temperature and decrease in particle size. The reduction capacity of siderite was found to be 17 mg-Cr(VI)/g.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Hexavalent chromium; Reduction; Heavy metal; Siderite

1. Introduction

Chromium is usually encountered in the environment in the oxidation states of (III) and (VI) and is released by effluents discharged from electroplating, leather tanning, chemical manufacturing, cooling systems etc. Since the hexavalent chromium is a very soluble and mobile species, highly toxic and susceptible to be mutagen and carcinogen, it is considered as a priority pollutant for soils and natural waters. In contrast, trivalent chromium, having a limited hydroxide solubility and lower toxicity, is generally regarded as less dangerous pollutant. As a consequence of the dramatic differences in physical and chemical properties of two chromium types and benign character of Cr(III), the reduction of Cr(VI) alone may be considered as a satisfactory solution. However, subsequent Cr(OH)₃ precipitation is a complementary step of conventional chromium removal process.

The reducing agents commonly used for hexavalent chromium are sulphur dioxide, sodium sulphites and ferrous sulphate [1–5]. Zero- and divalent iron are evaluated to be efficient reductants for technical removal processes and possibly for a subsurface soil remediation material as well [6–10]. A number of iron based reductants such as ferrous ion [11–17], ferrous-ions derived from hematite and biotite [18], various types of metallic iron [19–26], iron sulphide and pyrite [27–30], iron silicate slag [31], green rust [32] have been studied for the reduction of hexavalent chromium.

The lowering of detoxification cost of wastewater containing hexavalent chromium requires the application of low-cost materials. Finding the cost effective reductants requires further investigation in the use of natural materials such as cheap iron(II) bearing minerals. The use of siderite as a reductant for Cr(VI) removal from aqueous solution has not been systematically investigated before. The objective of this study is to assess the feasibility of using siderite as a low-cost material for Cr(VI) removal. For this purpose, batch experiments were conducted to study the main parameters such as acid concentration, contact time, initial Cr(VI) concentration, re-

* Corresponding author. Tel.: +90 424 2370000; fax: +90 424 2415526.
E-mail address: merdem@firat.edu.tr (M. Erdem).

ductant dosage, temperature and particle size of siderite on the reduction of Cr(VI).

2. Materials and methods

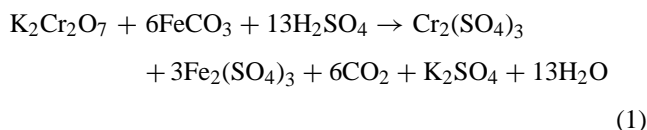
2.1. Materials

Siderite used in the study was provided from an iron mine, Malatya (Turkey). After crushing, the visible impurities were removed by hand and then the sample was ground and sieved to obtain various fractions. The material fractionated was stored in a tightly closed jar throughout the study. The fraction of <44 μm was used in the study except for experiments where the effect of particle size was investigated.

A stock solution of Cr(VI) (10 g/l) was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ (Merck, 4862) in distilled water. The working solutions were prepared by diluting the stock solution with distilled water. Sulphuric acid was used to provide the acidity required for the reduction of Cr(VI). Other reagents used in this study were of analytical grade.

2.2. Experimental procedure

The experiments were carried out by using an orbital flask shaker (Selecta Rotabit Shaker) equipped with a temperature controller. 100 ml Cr(VI) solutions of desired concentration were combined with varying amounts of siderite in a 250 ml flasks. The reaction mixtures were shaken at 200 rpm at different temperature for contact times ranging from 5 to 120 min. The amount of sulphuric acid to be added to the working solutions was calculated with respect to stoichiometric amount of Cr(VI) present in the solutions, by considering Eq. (1). In addition, to determine reduction capacity of the siderite, a 20 g siderite sample was successively treated with 1000 ml of Cr(VI) solutions (50 mg-Cr(VI)/l) the acid content of which is 2 stoichiometric amounts at 25 °C for different contact times until the reduction efficiency of siderite dropped at lower value than 10%.



At the end of predetermined contact period, reaction mixture was filtered and then the final pH of the filtrates was measured. After the Cr(VI) analysis was performed, the filtrates were acidified with 1 ml of HNO_3 solution to prevent the precipitation and analysed for total chromium and iron.

The experiments were performed in duplicate and mean values were taken into account.

2.3. Methods of analysis

Mineralogical composition of siderite used in the study was determined by X-ray diffractometer (Shimadzu XRD-

6000). Chemical analysis of siderite was done by XRF spectrophotometer (Philips PW-2404).

For the determination of Fe(II) content of siderite, a sample of 0.15 g was dissolved in a solution containing 20 ml of 25% (v/v) HCl and 15 ml of 10^{-2} M $\text{K}_2\text{Cr}_2\text{O}_7$ in a carbon dioxide atmosphere to avoid oxidation to Fe(III). The excess of $\text{K}_2\text{Cr}_2\text{O}_7$ was determined by titration using a standard ferrous ammonium sulphate ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) solution.

In the reduction study, the concentration of Cr(VI) in the solutions was determined colorimetrically with 1.5-diphenyl carbazide method [33] by using UV-1201V Model Shimadzu Spectrophotometer. The concentrations of total chromium and iron in the solutions were determined by atomic absorption spectrophotometer (Perkin–Elmer, 370).

The solution pH was measured using a Mettler Delta 350 pH meter.

3. Results and discussion

3.1. Characterization of Siderite

The chemical and mineralogical compositions of the siderite are presented in Table 1. As seen, siderite contains 52.45% Fe, 3.02% Mn, 4.75% Ca and 4.26% Mg as major elements. Varying amounts of other minor elements such as Al, Zn, Si and S take place in the material. It was found that the Fe(II) content of siderite is 38.19%, which may correspond to 79.11% as FeCO_3 in weight. XRD analysis of the sample shows that it is composed mainly of siderite and secondary of dolomite and hematite.

3.2. Effects of acid concentration and contact time

In some studies dealing with Cr(VI) reduction, it has been reported that the Cr(VI) reduction efficiency of reducing agent depends largely on amount of acid and reduction reaction rapidly occurs at low pHs [3,5,21,27,29]. Starting from these results, 50 mg/l Cr(VI) solution containing stoichiometric amount of acid was mixed with siderite in the dosage of 20 g/l and a preliminary study was performed depending on

Table 1
Chemical and mineralogical compositions of siderite

Chemical composition		Mineralogical composition	
Constituent	w/w (%)	Mineral	Formula
Fe	52.45	Siderite	FeCO_3
Mn	3.02	Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Ca	4.75	Hematite	Fe_2O_3
Mg	4.26		
Al	0.39		
Zn	0.04		
Si	1.07		
S	300 mg/kg		
Cr, Pb, Ni, Zr, Cu, Sr	UDL ^a		

^a UDL: under detection limits.

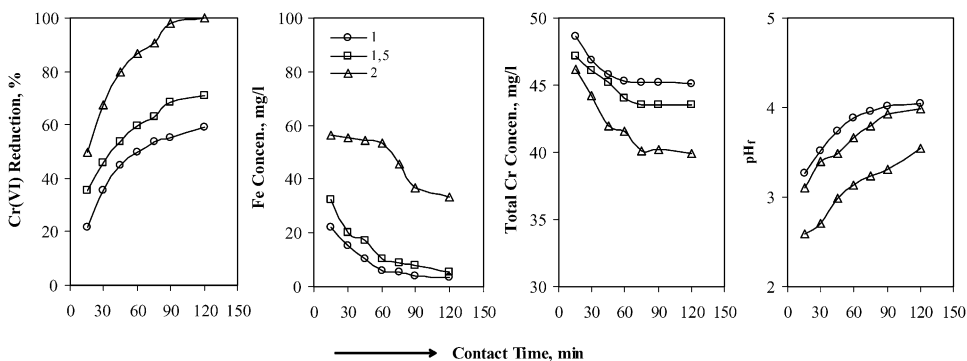
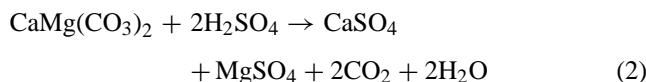


Fig. 1. Effects of acid concentration and contact time on the Cr(VI) reduction (siderite dosage: 20 g/l; initial Cr(VI) concentration: 50 mg/l; temperature: 25 °C).

contact time. The results show that the maximum Cr(VI) reduction yield of 62.18% could be obtained at the end of the contact period of 150 min. In order to obtain more effective reduction yields, Cr(VI) solutions containing 1, 1.5 and 2 stoichiometric amount of acid were prepared and systematic Cr(VI) reduction experiments were performed.

Fig. 1 shows Cr(VI) reduction percentage, concentration of iron released from siderite, total chromium concentration and final pH variations as a function of contact time and amount of acid. The Cr(VI) reduction yield increases by contact time and amount of acid. In the solutions containing 1.0 and 1.5 stoichiometric acid, Cr(VI) could not be completely reduced at the end of the contact period of 120 min. This situation is, to a large extent, related to the amount of alkaline components in the material. Because, siderite used in the study contains Ca and Mg in the form of dolomite, consumes acid by neutralization (Eq. (2)). During the reduction process, Cr(VI) reduction and neutralization simultaneously take place and acid is consumed in these two reactions. However, Cr(VI) reduction is almost completed within 120 min in the presence of 2.0 stoichiometric amount of acid.



As seen from Fig. 1, the concentration of iron dissolved from siderite increases with acid concentration. But, it decreases with increasing contact time. This situation may be attributed to an increase in the final pH of the solutions, which is suitable to precipitate iron(III) ions in the solution by hydrolyze.

3.3. Effect of siderite dosage

In order to determine the effect of the amount of siderite on the Cr(VI) reduction, siderite dosage was taken in the range of 5–30 g/l and reduction experiments were performed for various contact times. With increasing the siderite dosage from 5 to 30 g/l, the reduction percentage of Cr(VI) increases. But, siderite dosages less than 15 g/l are insufficient to complete reduction of Cr(VI) within 120 min (Fig. 2). The reduction percentage values for dosages of 20, 25 and 30 are close to each other. Therefore, it can be noted that a further increase in siderite dosage higher than 20 g/l has a negligible effect on the Cr(VI) reduction. Final pH of the solutions measured at the high siderite dosages shows that the acid consumption rate is rather high. At the higher than 10 g/l siderite dosages, solution pH increasing up to 4.7 causes to precipitate the ferric ions as ferric hydroxide. This situation can be clearly seen from the decreasing iron concentration values (Fig. 2). The concentration of total chromium in the treated solutions shows a decreasing trend with increasing contact time and

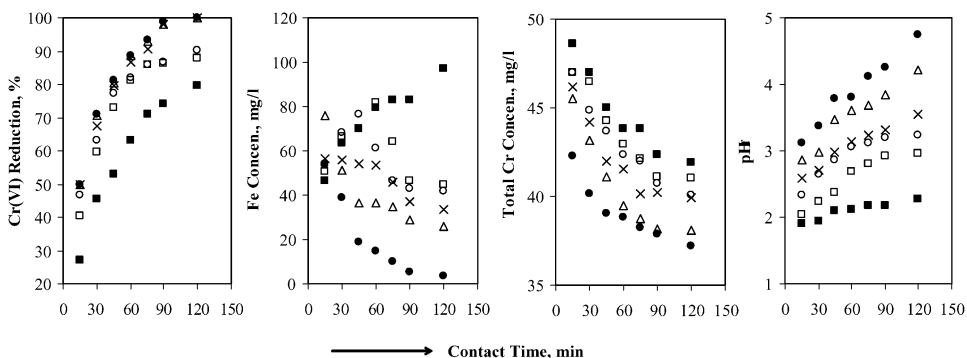


Fig. 2. Effect of siderite dosage on the Cr(VI) reduction depending on contact time (acid concentration: 2 stoichiometric amount; initial Cr(VI) concentration: 50 mg/l; temperature: 25 °C) ((■) 5 g/l; (□) 10 g/l; (○) 15 g/l; (×) 20 g/l; (△) 25 g/l; (●) 30 g/l).

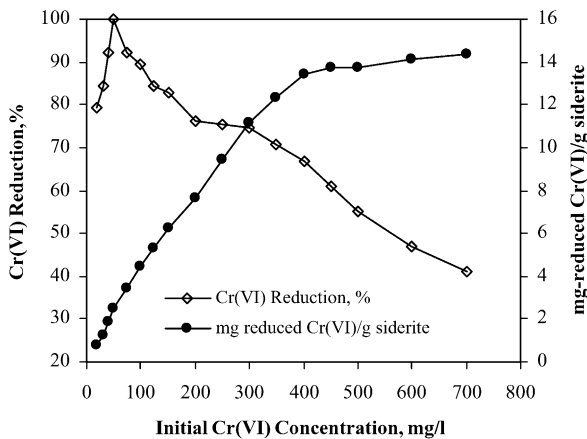


Fig. 3. Effect of initial Cr(VI) concentration on the Cr(VI) reduction (siderite dosage: 20 g/l; acid concentration: 2 stoichiometric amount; contact time: 120 min; temperature: 25 °C).

dosage. This decreasing may be due to adsorption onto both siderite and ferric hydroxide formed.

3.4. Effect of initial Cr(VI) concentration

The effect of initial Cr(VI) concentration on the reduction yield was investigated by treating 2 g of siderite with 100 ml Cr(VI) solution having different initial concentrations in the range of 20–700 mg-Cr(VI)/l. The results obtained are presented in Fig. 3. The maximum reduction efficiency (100%) was obtained only for 50 mg/l within 120 min of contact time. The reduction percentages for Cr(VI) solutions having initial concentration values higher and lower than 50 mg/l declined. However, the amount of the Cr(VI) reduced per gram of siderite increases with increasing the initial concentration. Since amount of acid added to the solution was determined with respect to the Cr(VI) content of the solution, for the solution containing lower Cr(VI), it can be said that the acidity of the medium is insufficient. It is evident that alkaline constituent of the material such as dolomite concurrently consumes acid. On the contrary, when the solutions having high Cr(VI) concentrations was used, this time, siderite dosage may become insufficient within selected contact time.

As process parameters were optimized for 50 mg/l initial Cr(VI) concentration and most effective reduction yield was obtained for this concentration, further experiments were carried out with the solution having 50 mg/l initial Cr(VI) concentration.

3.5. Effect of temperature

Fig. 4 shows Cr(VI) reduction percentage, concentration of iron released from siderite, total chromium concentration and final pH variations as a function of contact time and temperature. As seen, reduction percentage of the Cr(VI) increases by increasing temperature of the solution. In this case, the contact time required to complete Cr(VI) reduction shortens. For example, while all the Cr(VI) ions in the solution are reduced at 25 °C at the end of contact period of 120 min, each raise of 10 °C in the temperature shortens the contact time required about 30 min for a complete reduction. It can be concluded that the reduction process of Cr(VI) by the siderite is endothermic.

While the concentrations of total chromium and iron in the solutions decrease with increasing temperature and contact time, the final pH of the solutions increases.

3.6. Effect of particle size

The influence of particle size on the Cr(VI) reduction was determined for 11 siderite particle size ranges from 1200–600 μm (16–30 mesh) to <44 μm (<325 mesh) by treating the 50 mg/l Cr(VI) solutions containing 2 stoichiometric amount of acid with siderite in the dosage of 20 g/l at 25 °C for a contact time of 120 min. Cr(VI) reduction efficiency increases with decreasing in particle size of siderite (Fig. 5). The reduction percentage of Cr(VI) increases from 78 to 100% with the decrease of siderite particle size ranging from 1000–500 to 75–53 μm (16–30 to 200–270 mesh), thereafter reduction efficiency increases slightly. Under the investigated experimental conditions, particles smaller than 200 mesh (<75 μm) is sufficient to reduce all Cr(VI) ions in a relatively short contact time.

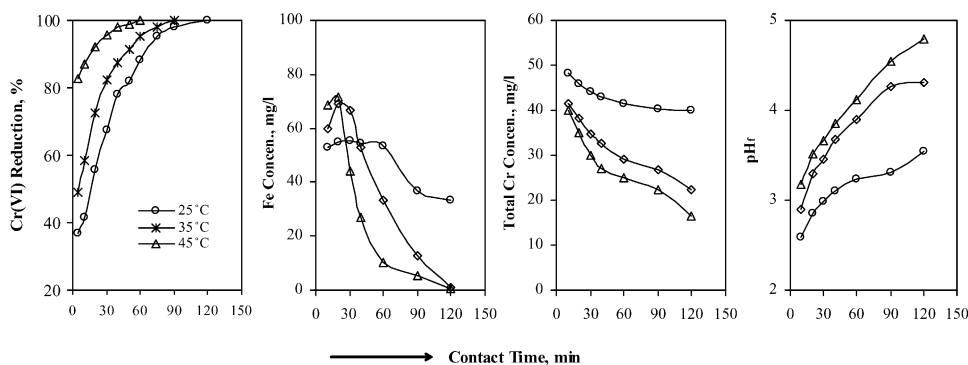


Fig. 4. The variation of Cr(VI) reduction percentage with temperature and contact time (siderite dosage: 20 g/l; initial Cr(VI) concentration: 50 mg/l; acid concentration: 2 stoichiometric amount).

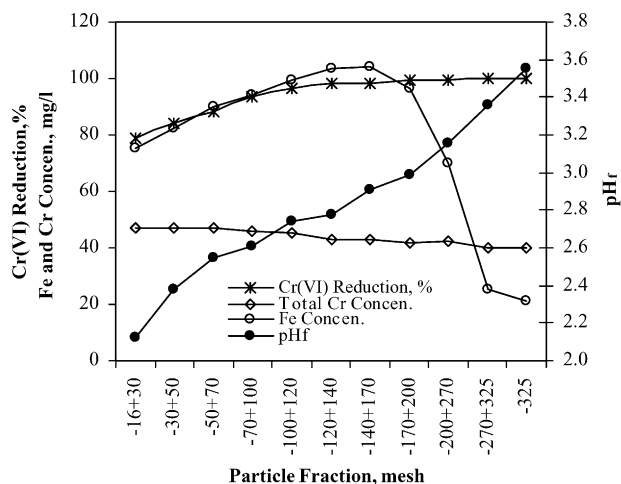


Fig. 5. Effect of particle size on the Cr(VI) reduction (siderite dosage: 20 g/l; initial Cr(VI) concentration: 50 mg/l; acid concentration: 2 stoichiometric amount; contact time: 120 min; temperature: 25 °C).

On the other hand, iron content of reduced solutions increases with decreasing particle size up to the fraction of 140–170 mesh, thereafter a decrease is observed probably due to the increase in pH. At pHs higher than 2, formed ferric ions can precipitate as Fe(OH)₃ by hydrolysing. Dark brown colour of solid separated confirms this phenomenon. However, reduced iron content may be evaluated as an advantage for the reduction process, since Fe(III) and Cr(III) will be removed by precipitation in subsequent step of treatment.

3.7. Reduction capacity of siderite

To determine the reduction capacity of siderite, a certain amount of siderite was subjected to successive reduction experiments. For this purpose, a 20 g of siderite and one liter of 50 mg/l Cr(VI) solution containing 2 stoichiometric amount of H₂SO₄ was mixed. The mixture was shaken at 200 rpm for contact time ranging from 15 to 120 min. At the end of predetermined contact time, a 10 ml aliquot was withdrawn and immediately filtered and analysed for Cr(VI). At the end of each 120 min, to provide same Cr(VI) concentration value

(50 mg/l) and acid content (2 stoichiometric amount), adequate volume of acidic stock Cr(VI) solution was added to the mixture and same procedure was repeated until the reduction efficiency of siderite dropped at lower value than 10%. The results obtained are shown in Fig. 6.

In the first two reduction steps, Cr(VI) ions in the solution are completely reduced. Thereafter, the Cr(VI) reduction yield of siderite decreases. At the end of the 8th reduction step, it falls up to 8.96%. When the cumulative amount of Cr(VI) reduced is calculated, it is found that the Cr(VI) reduction capacity of the siderite is about 17 mg-Cr(VI)/g siderite. In spite of the fact that theoretical reduction capacity of the siderite used is 236 mg-Cr(VI)/g (Eq. (2)), the observed reduction capacity of the siderite is very low. This can be attributed to alkaline components of the siderite. In our previous studies, related to Cr(VI) reduction by pyrite [27], copper smelter slag [31] and synthetic iron sulphide [29], the Cr(VI) reduction capacities of these materials were found to be 42.5, 76.5 and 238 mg-Cr(VI)/g at similar conditions, respectively.

4. Conclusion

Taking into consideration results obtained from this study where the effects of acid concentration, siderite dosage, initial Cr(VI) concentration, temperature and particle size on the Cr(VI) reduction in the aqueous solution by using siderite was investigated, the following conclusions may be drawn.

The Cr(VI) reduction efficiency of the siderite was found to be strongly depended on acid content of the solution. The maximum Cr(VI) reduction yield for 50 mg/l initial concentration is obtained in the presence of 20 g/l siderite for 120 min when 2 stoichiometric amount of acid is used with respect to Cr(VI).

By the increasing temperature, the Cr(VI) reduction yield increases and the contact time required for a complete reduction shortens.

The reduction percentage of Cr(VI) increases with the decreasing in siderite particle size. The siderite fractions smaller than 200 mesh is sufficient to reduce all Cr(VI) ions

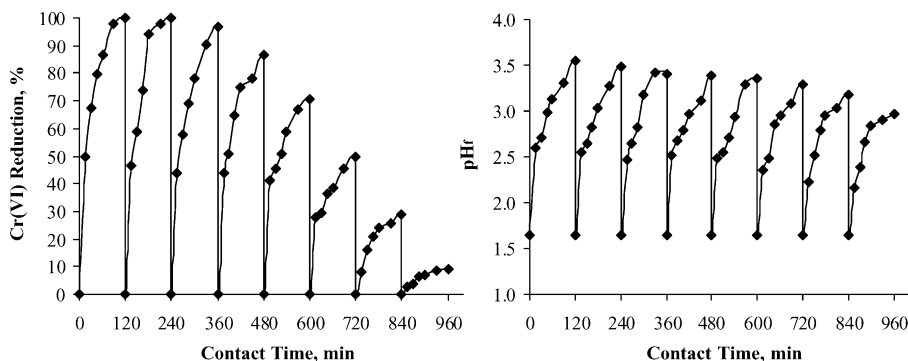


Fig. 6. The results of the successive experiments carried out to determine the reduction capacity of siderite (siderite dosage: 20 g/l; initial Cr(VI) concentration: 50 mg/l; acid concentration: 2 stoichiometric amount; temperature: 25 °C).

in the solution at the conditions of initial Cr(VI) concentration: 50 mg/l; amount of acid: 2 stoichiometric; contact time: 120 min; adsorbent dosage: 20 g/l and temperature: 25 °C.

The reduction capacity of siderite was calculated as about 17 mg-Cr(VI)/g siderite.

The experimental results shows that the Cr(VI) in aqueous solution can be reduced by using siderite. This reduction process may be applied to metal plating wastewater containing Cr(VI) and high amounts of acid.

Acknowledgements

This study was supported by the Research Foundation of Fratt University under project no FBAP-678.ü

References

- [1] M. Sittig, Pollutant Removal Handbook, Noyes Data Co., New Jersey, 1973.
- [2] J.W. Patterson, Wastewater Treatment Technology, Ann Arbor Inc., New York, 1975.
- [3] K.H. Lanouette, Heavy metal removal, Chem. Eng. Deskbook Issue (1977).
- [4] A.V. Bridgwater, C.J. Mumford, Waste Recycling and Pollution Control Handbook, London, George Godwin Limited, 1979.
- [5] W.W. Eckenfelder, Industrial Water Pollution Control, second ed., McGraw Hill, New York, 1989.
- [6] I.J. Buerge, S.J. Hug, Kinetics and pH dependence of chromium(VI) reduction by iron(II), Environ. Sci. Technol. 31 (1997) 1426–1432.
- [7] R.M. Powell, R.W. Puls, Proton generation by dissolution of intrinsic or augmented aluminosilicate minerals for in situ contaminant remediation by zero-valence-state iron, Environ. Sci. Technol. 31 (1997) 2244–2251.
- [8] D.W. Blowes, C.J. Ptacek, J.L. Jambor, In-situ remediation of Cr(VI)-contaminated groundwater using permeable reactive walls: laboratory studies, Environ. Sci. Technol. 31 (1997) 3348–3357.
- [9] A.R. Pratt, D.W. Blowes, C.J. Ptacek, Products of chromate reduction on proposed subsurface remediation material, Environ. Sci. Technol. 31 (1997) 2492–2498.
- [10] R.M. Powell, R.W. Puls, S.K. Hightower, D.A. Sabatini, Coupled iron corrosion and chromate reduction: mechanisms for subsurface remediation, Environ. Sci. Technol. 29 (1995) 1913–1922.
- [11] J.N. Anderson, B.A. Bolto, L. Powlowski, A method for chromate removal from cooling tower blowdown water, Nucl. Chem. Waste Manage. 5 (1984) 125–129.
- [12] L.E. Eary, D. Rai, Chromate removal from aqueous wastes by reducing with ferrous ion, Environ. Sci. Technol. 22 (1988) 972–977.
- [13] S.E. Fendorf, G. Li, Kinetics of chromate reduction by ferrous iron, Environ. Sci. Technol. 30 (1996) 1614–1617.
- [14] I.J. Buerge, S.J. Hug, Influence of mineral surfaces on chromium(VI) reduction by iron(II), Environ. Sci. Technol. 33 (1999) 4285–4291.
- [15] D.L. Sedlak, P.G. Chan, Reduction of hexavalent chromium by ferrous iron, Geochim. Cosmochim. Acta 61 (1997) 2185–2192.
- [16] M. Pettine, L. D'Ottone, L. Campanella, F.J. Millero, R. Passino, The reduction of chromium(IV) by iron(II) in aqueous solutions, Geochim. Cosmochim. Acta 62 (1998) 1509–1519.
- [17] M.A. Schlautman, I. Han, Effects of pH and dissolved oxygen on the reduction of hexavalent chromium by dissolved ferrous iron in poorly buffered aqueous systems, Water Res. 35 (2001) 1534–1546.
- [18] L.E. Eary, D. Rai, Kinetics of chromate reduction by ferrous-ions derived from hematite and biotite at 25 °C, Am. J. Sci. 289 (1989) 180–213.
- [19] L.E. Lancy, Treatment of spent cooling waters. US Patent 3294680 (1966).
- [20] J.P. Gould, The kinetics of hexavalent chromium reduction by metallic iron, Water Res. 16 (1982) 871–877.
- [21] A. Özer, H.S. Altundoğan, M. Erdem, F. Tümen, A study on the Cr(VI) removal from aqueous solutions by steel wool, Environ. Pollu. 97 (1997) 107–112.
- [22] M.S.E. Abdo, G.H. Sedahmed, A new technique for removing hexavalent chromium from waste water and energy generation via galvanic reduction with scrap iron, Energ. Conver. Manage. 39 (1998) 943–951.
- [23] T. Astrup, S.L.S. Stipp, T.H. Christensen, Immobilization of chromate from coal fly ash leachate using an attenuating barrier containing zero valent iron, Environ. Sci. Technol. 34 (2000) 4163–4168.
- [24] N. Melitas, O. Chuffe-Moscoco, J. Farrell, Kinetics of soluble chromium removal from contaminated water by zerovalent iron media: corrosion inhibition and passive oxide effects, Environ. Sci. Technol. 35 (2001) 3948–3953.
- [25] M.J. Alowitz, M.M. Scherer, Kinetics of nitrate, nitrite, and Cr(VI) reduction by iron metal, Environ. Sci. Technol. 36 (2002) 299–306.
- [26] T. Lee, H. Lim, Y. Lee, J.-W. Park, Use of waste iron metal for removal of Cr(VI) from water, Chemosphere 53 (2003) 479–485.
- [27] M. Erdem, F. Tümen, Cr(VI) reduction in aqueous solutions by using pyrite, Tr. J. Eng. Environ. Sci. 20 (1996) 363–369 (in Turkish).
- [28] R.R. Patterson, S. Fendorf, M. Fendorf, Reduction of hexavalent chromium by amorphous iron sulphide, Environ. Sci. Technol. 31 (1997) 2039–2044.
- [29] M. Erdem, H.S. Altundoğan, A. Özer, F. Tümen, Cr(VI) reduction in aqueous solutions by using synthetic iron sulphide, Environ. Technol. 22 (2001) 1213–1222.
- [30] A.I. Zouboulis, K.A. Kydros, K.A. Matis, Removal of hexavalent chromium anions from solutions by pyrite fines, Water Res. 29 (1995) 1755–1760.
- [31] B. Kiyak, A. Özer, A. Altundoğan, M. Erdem, F. Tümen, Cr(VI) reduction in aqueous solutions by using copper smelter slag, Waste Manage. 19 (1999) 333–338.
- [32] A.G.B. Williams, M.M. Scherer, Kinetics of Cr(VI) reduction by carbonate green rust, Environ. Sci. Technol. 35 (2001) 3488–3494.
- [33] APHA, Standard Methods for the Examination of Water and Wastewater, 17th ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA, 1989.