

Reduction of Cr(VI) by hydrazine in solution saturated with KHCO_3

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Abstract

Cr(VI) that exists in many industrial wastes is considered highly toxic. One of the most common ways to dispose of these wastes is to reduce Cr(VI) to Cr(III), which is less toxic and can be easily removed or fixed. Reduction of Cr(VI) by hydrazine in aqueous solutions saturated with potassium bicarbonate was studied in this paper. The content of Cr(VI), molar ratio of hydrazine to Cr(VI) and reaction temperature were 200–1000 ppm, 2:1–10:1 and 25–70 °C, respectively. Results showed that the overall reaction was third-order, i.e. first-order with respect to hydrazine and second-order with respect to Cr(VI). The apparent empirical activation energy was 75.6 kJ mol⁻¹. The reaction kinetics could be interpreted by a three-step mechanism. Effect of the oxygen in the solution on the reduction of Cr(VI) was negligible.

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Keywords: Hexavalent chromium; Hydrazine; Reduction; Lye

1. Introduction

The production process of chromate is a typical heavy pollution source. Traditional production process of chromate produces a large amount of harmful wastes. Among those wastes, solid residue containing Cr(VI) is the most harmful because there is no effective ways to treat it [1,2]. To solve the problem, some researchers [3–6] tried, based on the conception of “green chemistry” or “cleaner production” to develop a new process to delete the pollution from the very beginning of the production. Li et al. [7] invented the “cleaner production process of chromate”, which uses liquid oxidation instead of the kiln roasting. The schematic diagram of the process is shown in Fig. 1.

With potassium hydroxide as reaction medium and through liquid oxidation and a series of separation steps, the main components of chromite ore, Cr, Fe, Al, Mg and Si, can be separated effectively. Therefore, no solid residue comes out. It can be found from Fig. 1 that the solution of potassium bicarbonate, which contains Cr(VI), is a by-product of the process. How to use and/or treat the lye is one of the

key factors affecting the profits of the process. One of the choices is to reduce and remove the Cr(VI) to produce commercial potassium carbonate. Quite a few methods for the removal of Cr(VI) can be found in the literatures [8–22], such as biosorption, ion exchange, solvent extraction, nanofiltration, micelle-enhanced ultra filtration, adsorption with inorganic sorbent materials, reduction and precipitation and so on. However, none of them can be directly used to this purpose due to two critical requirements. First, the method must be effective to concentrated lye. Second, it has not to introduce other ions, such as SO_4^{2-} and Cl^- , which are difficulty to separate, into the lye. Cheng et al. [2] described a method that uses ferrous pentacarbonyl, which is an acute poison, to reduce Cr(VI). Reduction of Cr(VI) by hydrazine in aqueous solutions saturated with potassium bicarbonate was studied in this paper.

2. Experimental

2.1. Materials and set-up

All the materials—potassium bicarbonate, potassium dichromate and hydrazine hydrate, were of reagent grade.

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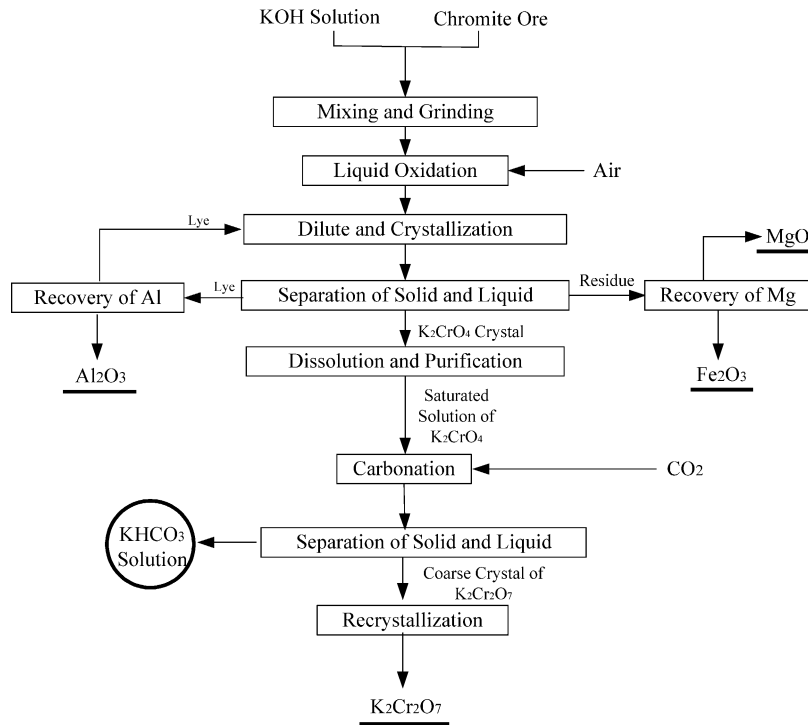


Fig. 1. Schematic diagram of cleaner production process of chromates.

The reduction was carried out in a conical flask immersed in a water-bath of constant temperature.

2.2. Procedures

Stock solutions of Cr(VI) and hydrazine were prepared, respectively, by dissolving potassium dichromate in distilled water and by diluting the solution of hydrazine hydrate with distilled water. Potassium bicarbonate and distilled water were mixed to be saturated solution in a conical flask placed in a thermostat. The solutions of Cr(VI) and hydrazine, according to predetermined molar ratio, were added into the lye while stirring. Samples were taken at time intervals. Cr(VI) concentrations were measured using a spectrophotometer (Model 722S, Leng Guang Teck., Shanghai, China) at $\lambda = 372$ nm, according to the method proposed by Oumedjbeur and Thomas [23].

3. Results and discussion

3.1. Effect of amount of hydrazine added on reduction of Cr(VI)

The effect of the molar ratios of hydrazine to Cr(VI) on the reduction of Cr(VI) is shown in Figs. 2–5. Fig. 2 shows the results at 60 °C and initial Cr(VI) 1000 ppm. It can be found that most of the Cr(VI) was reduced in the first half an hour. Reduction extents increase with increasing amounts of hydrazine. Cr(VI) can be reduced almost completely in

half an hour when the molar ratio of hydrazine to Cr(VI) reaches 10:1. When the molar ratio of hydrazine to Cr(VI) is less than 4:1; however, Cr(VI) cannot be reduced completely even if reaction time reaches 3 h. Figs. 3–5 shows the results of different temperatures and different initial concentrations of Cr(VI). Similarly, Cr(VI) cannot be reduced fully when the molar ratios of hydrazine to Cr(VI) are 2:1 and 3:1. Theoretically, the reduction reaction takes place as follows:

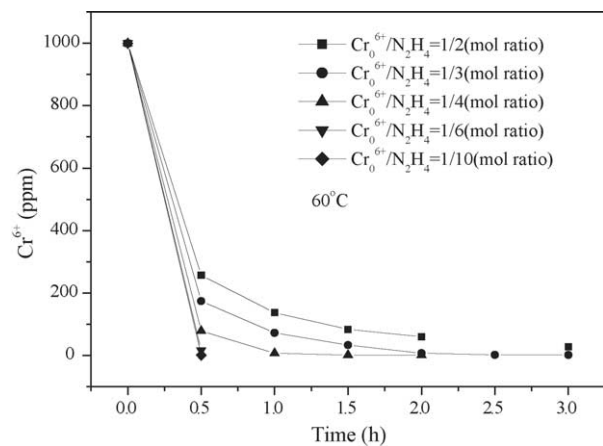
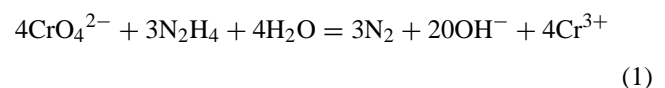


Fig. 2. Effect of the molar ratio of $\text{Cr}^{6+}/\text{N}_2\text{H}_4$ on the reduction of Cr^{6+} (60 °C, $\text{Cr}_0^{6+} = 1000$ ppm).

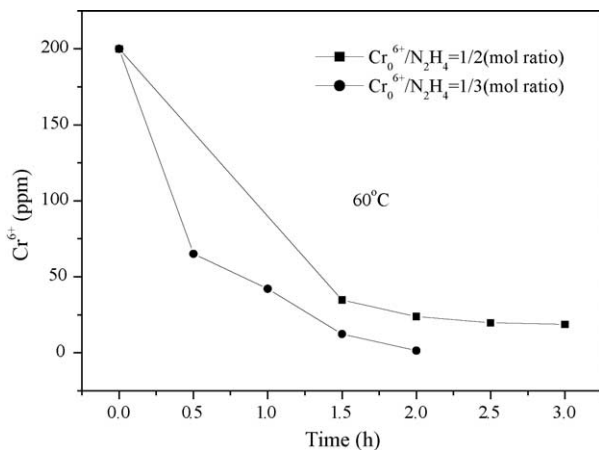


Fig. 3. Effect of the molar ratio of Cr⁶⁺/N₂H₄ on the reduction of Cr⁶⁺ (60 °C, Cr₀⁶⁺ = 200 ppm).

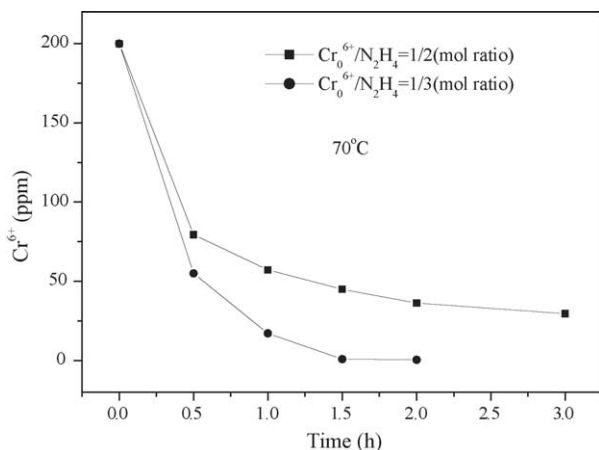


Fig. 4. Effect of the molar ratio of Cr⁶⁺/N₂H₄ on the reduction of Cr⁶⁺ (70 °C, Cr₀⁶⁺ = 200 ppm).

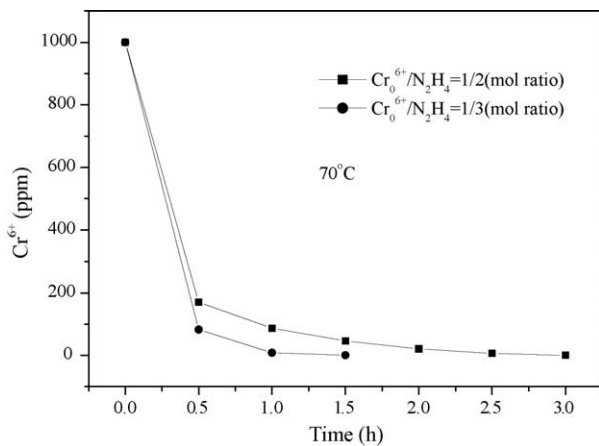


Fig. 5. Effect of the molar ratio of Cr⁶⁺/N₂H₄ on the reduction of Cr⁶⁺ (70 °C, Cr₀⁶⁺ = 1000 ppm).

Reduction of 1 mol Cr(VI) only needs 0.75 mol hydrazine. Why Cr(VI) cannot be reduced completely even the molar ratio of hydrazine to Cr(VI) reaches 3:1 to 4:1? There are two presumable causes: (1) the oxygen dissolved in the solutions consumed a part of the hydrazine and (2) time is not long enough for the reduction to reach completion. Although we did not measure the oxygen dissolved in the solutions, in term of the data provided by Schlautman and Han [24] and O'Brien and Woodbridge [25], it could not be more than 10 ppm. Comparing to the Cr(VI) in the solutions, reductant consumed by the oxygen was negligible. Therefore, the oxygen dissolved in the solutions should not affect the reduction of Cr(VI) substantially.

To investigate the effect of oxygen on the reaction, the following procedures were adopted: at the beginning, hydrazine was added in the solution in a proportion of 10 mol hydrazine per mol Cr(VI); after half an hour of reaction, hydrazine and Cr(VI) were added in a lower molar ratio. We postulated that the oxygen in the solution would be consumed in the first half an hour; therefore, hydrazine required for the reduction in the later stages would decrease and using lower molar ratios might obtain the same results as those of the beginning. The results are shown in Figs. 6–8. It can be found that the results are only partially consistent with the assumption. At 60 °C and after 0.5 h (Fig. 8), 1 mol hydrazine can reduce 1 mol Cr(VI). However, at 25 and 40 °C (Figs. 6 and 7), to ensure the reduction of Cr(VI) to be completion, the amounts of the hydrazine added still must exceed the stoichiometric ratio. This indirectly shows that it is kinetic factors, not the dissolved oxygen, which determines the reduction extent of Cr(VI).

3.2. Effect of temperature on reduction of Cr(VI)

The effect of temperature on the reduction of Cr(VI) can also be found in Figs. 2–8. It can be seen that higher temperatures favor the reduction of Cr(VI). Fig. 9 demonstrates that more clearly. Because potassium bicarbonate begins decomposing at 65 °C in water, pH of the solution rises with the

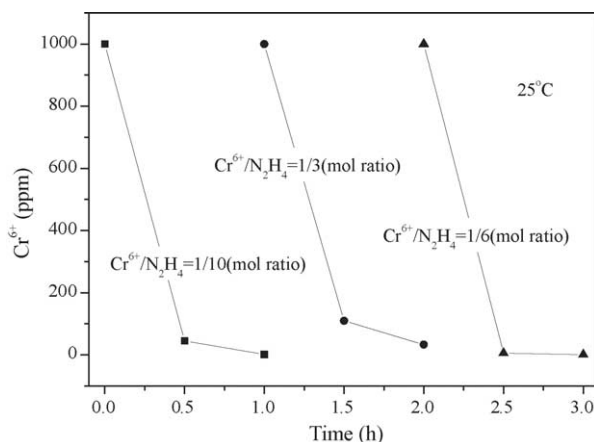


Fig. 6. Reduction results of Cr⁶⁺ in steps (25 °C, Cr₀⁶⁺ = 1000 ppm).

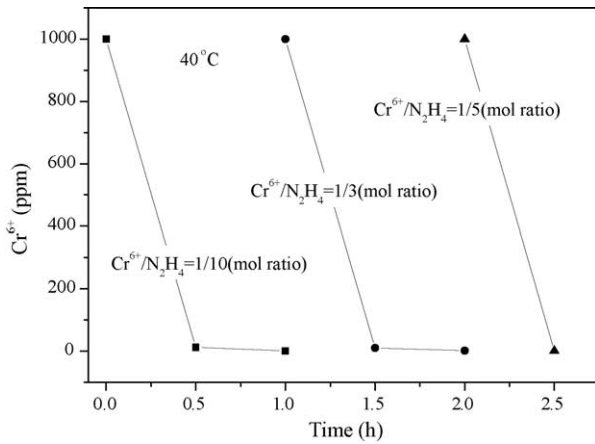


Fig. 7. Reduction results of Cr⁶⁺ in steps (40 °C, Cr₀⁶⁺ = 1000 ppm).

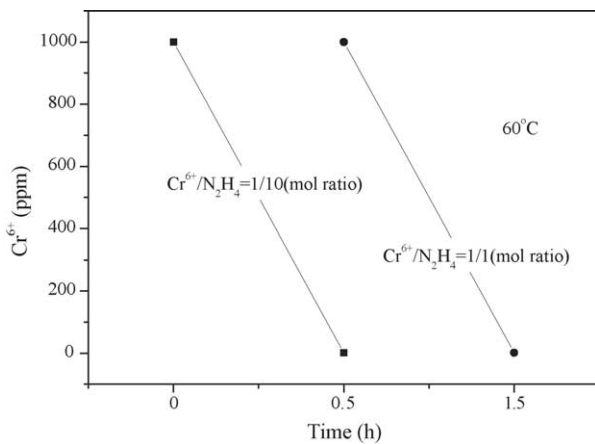


Fig. 8. Reduction results of Cr⁶⁺ in steps (60 °C, Cr₀⁶⁺ = 1000 ppm).

decomposition of potassium bicarbonate and efficacy of the reduction is poor above pH 10 [26], the investigation of the effect of temperature was conducted at no more than 70 °C. Obviously, molar ratio is more important than temperature.

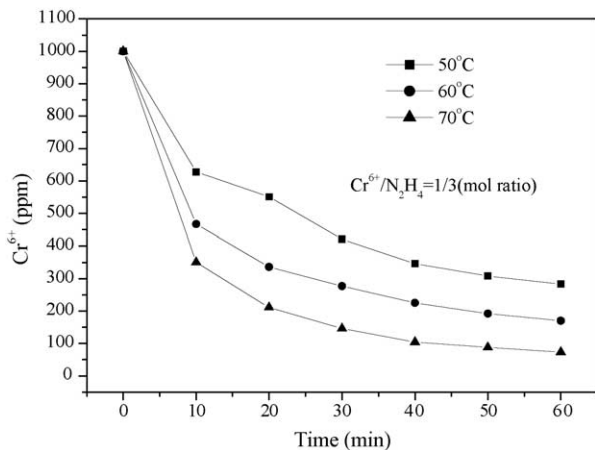
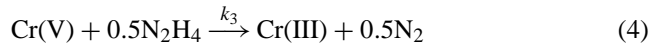
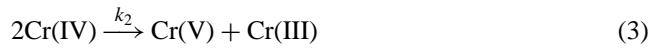
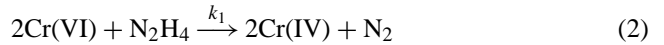


Fig. 9. Effect of temperature on the reduction of Cr⁶⁺ (Cr₀⁶⁺ = 1000 ppm).

With enough hydrazine, Cr(VI) can be reduced completely at 40 °C even a lower temperature.

3.3. Reduction kinetics

From the review of Beattie and Haight [20], reduction mechanism of Cr(VI) by hydrazine may be expressed as



First step is attributed to be rate determining and the following rate expression is obtained:

$$r = -\frac{dC_A}{dt} = k_1 C_A^2 C_B \quad (5)$$

where C_A and C_B represent the concentrations of Cr(VI) and hydrazine, respectively. If the reaction took place as Eq. (1) indicates, C_A and C_B would have the following relationship:

$$C_B = C_{B0} - \frac{3}{4}(C_{A0} - C_A) = \frac{3}{4} \left(\frac{4}{3}C_{B0} - C_{A0} + C_A \right) \quad (6)$$

where C_{A0} and C_{B0} are the initial concentrations of Cr(VI) and hydrazine in the solution, respectively. Using Eq. (6) to replace C_B in Eq. (5) gets:

$$-\frac{dC_A}{dt} = \frac{3}{4}k_1 C_A^2 \left(\frac{4}{3}C_{B0} - C_{A0} + C_A \right) \quad (7)$$

Integrating Eq. (7) gets the following equation:

$$Y = k_1 t \quad (8)$$

where

$$Y = \frac{4}{3b^2} \left[b \left(\frac{1}{C_A} - \frac{1}{C_{A0}} \right) + \ln \frac{C_A(b + C_{A0})}{C_{A0}(b + C_A)} \right]$$

$$b = \frac{4}{3}C_{B0} - C_{A0}$$

Using Eq. (8) to fit the data in Fig. 9, the result is shown in Fig. 10. It can be found that Eq. (8) may interpret the data very well. Obtained values of k_1 are 0.05 L² mmol⁻² min⁻¹ (50 °C), 0.10 L² mmol⁻² min⁻¹ (60 °C) and 0.26 L² mmol⁻² min⁻¹ (70 °C). Fendorf and Li [17] obtained a rate constant $56.3 \pm 3.7 \text{ L}^{0.6} \text{ mmol}^{-0.6} \text{ min}^{-1}$ for the reduction of Cr(VI) by Fe(II). Considering that reduction of Cr(VI) by Fe(II) is much faster than that by hydrazine, these k_1 values are reasonable. The empirical activation energy of the reaction was estimated based on the values of k_1 . The result is shown in Fig. 11, which gave an empirical activation energy 75.6 kJ mol⁻¹.

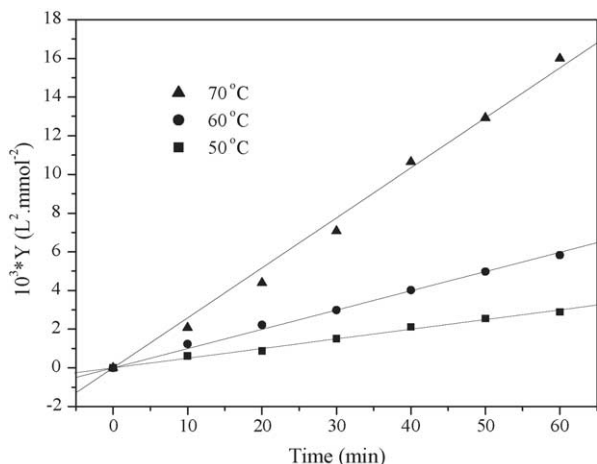


Fig. 10. Fitting results of the data of Fig. 9 by Eq. (8).

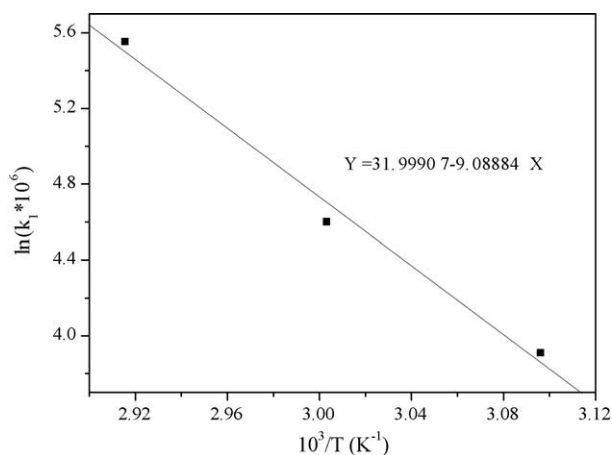
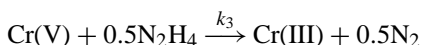
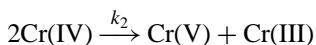
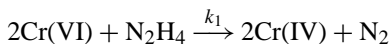


Fig. 11. Recovery of apparent activation energy.

4. Conclusions

Cr(VI) in aqueous solutions saturated with potassium bicarbonate can be reduced by hydrazine. The molar ratio of hydrazine to Cr(VI) is a key factor affecting the reduction extent. A higher temperature benefits the reduction as well. Effect of the oxygen in the solution is negligible. The reaction mechanism can be represented by



First step was considered to be rate determining and rate equation can be expressed as

$$r = -\frac{dC_A}{dt} = k_1 C_A^2 C_B$$

The apparent empirical activation energy was calculated to be 75.6 kJ mol^{-1} .

References

- [1] Y. Ding, Z. Ji, Production and Application of Chromium Compounds, Chemical Industry Press, Beijing, 2003, p. 272 (in Chinese).
- [2] S. Cheng, Y. Ding, C. Yang, Production Processes of Chromium Salts, Chemical Industry Press, Beijing, 1988, p. 390 (in Chinese).
- [3] Y. Zhang, Z. Li, T. Qi, Z. Wang, S. Zheng, Green chemistry of chromate cleaner production, Chin. J. Chem. 17 (1999) 258–266.
- [4] R. Drope, Process for the decomposition of chrome ore by alkaline oxidation, US Patent 5,547,646 (1996).
- [5] A.K. Tripathy, H.S. Ray, P.K. Pattnayak, Kinetics of roasting of chromium oxide with sodium nitrate flux, Metall. Mater. Trans. B 26 (1995) 449–452.
- [6] C. Arslan, G. Orhan, Investigation of chrome(VI) oxide production from chromite concentrate by alkaline fusion, Int. J. Miner. Process. 50 (1997) 87–96.
- [7] Z. Li, Y. Zhang, S. Zheng, T. Qi, H. Li, H. Xu, Z. Wang, Method for the production of chromates, World Patent Application PCT/CN03/00199, 2003-03-19.
- [8] T. Wang, Z. Li, Removal of chromium from water and wastewater, Environ. Sci. Technol. 26 (2003) 85 (in Chinese).
- [9] G.S. Gupta, Y.C. Sharma, Environmental management of textile and metallic industrial effluents, J. Colloid Interface Sci. 168 (1994) 118.
- [10] Fiorucci, C. Louis, Johnson, E. Michael, Use of selected catalyzed hydrazine compositions to reduce hexavalent chromium [(VI)], US Patent 4,367,213 (1983).
- [11] Jackson, R. John, Pitzer, L. Charles, Method for the removal of chromium compounds from aqueous solutions, US Patent 5,211,853 (1993).
- [12] T. Aoki, M. Munemori, Reduction of chromium(VI) by iron(II) hydroxide in alkaline solution, Bull. Chem. Soc. Jpn. 55 (1982) 730.
- [13] L.E. Eary, D. Rai, Chromate removal from aqueous wastes by reduction with ferrous ion, Environ. Sci. Technol. 22 (1988) 972.
- [14] B. Hua, B. Deng, Influences of water vapor on Cr(VI) reduction by gaseous hydrogen sulfide, Environ. Sci. Technol. 37 (2003) 4771.
- [15] M. Pettine, L. Campanella, F.J. Millero, Reduction of hexavalent chromium by H_2O_2 in acidic solutions, Environ. Sci. Technol. 36 (2002) 901–907.
- [16] C. Kim, Q. Zhou, B. Deng, E.C. Thornton, H. Xu, Chromium(VI) reduction by hydrogen sulfide in aqueous media: stoichiometry and kinetics, Environ. Sci. Technol. 35 (2001) 2219–2225.
- [17] S.E. Fendorf, G. Li, Kinetics of chromate reduction by ferrous iron, Environ. Sci. Technol. 30 (1996) 1614–1617.
- [18] I.J. Buerge, S.J. Hug, Kinetics and pH dependence of chromium(VI) reduction by iron(II), Environ. Sci. Technol. 31 (1997) 1426–1432.
- [19] C. Seigneur, E. Constantinou, Chemical kinetics mechanism for atmospheric chromium, Environ. Sci. Technol. 29 (1995) 222–231.
- [20] J.K. Beattie, G.P. Haight Jr., Chromium(VI) oxidations of inorganic substrates, Prog. Inorg. Chem. 17 (1972) 93–145.
- [21] K. Pohlandt-Schwandt, T. Salthammer, R. Marutzky, Reduction of soluble chromate in wood ash by formaldehyde, Biomass Bioenergy 22 (2002) 139.
- [22] M. Erdem, H.S. Altundogan, A. Ozer, F. Tumen, Cr(VI) reduction in aqueous solutions by using synthetic iron sulphide, Environ. Technol. 22 (2001) 1213–1222.
- [23] A. Oumedjbeur, O. Thomas, Dosage rapide du chrome(VI) dans les eaux naturelles, Analysis 17 (1989) 221.
- [24] 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 system, Water Res. 35 (2001) 1534–1546.
- [25] P. O'Brien, N. Woodbridge, A study of the kinetics of the reduction of chromate by ascorbate under aerobic and anaerobic conditions, Polyhedron 16 (1997) 2081–2086.
- [26] T. Wang, Study on a novel method and its process for manufacturing soda ash from sodium sulfate, Ph.D. Thesis, Institute of Process Engineering, Chinese Academy of Sciences, 2004 (in Chinese).