

Cr(VI) REDUCTION IN AQUEOUS SOLUTIONS BY USING SYNTHETIC IRON SULPHIDE

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ABSTRACT

This study was carried out to reduce Cr(VI) in aqueous solutions by using synthetic iron sulphide. For that purpose, the effects of acid content, contact time, initial Cr(VI) concentration, temperature of the solution, particle size and dosage of iron sulphide on the Cr(VI) reduction were investigated. Reduction extent of Cr(VI) is, to a great extent, dependent on the amount of acid. The Cr(VI) in the solution containing two times the H_2SO_4 with respect to stoichiometric amount of Cr(VI) was completely reduced within 45 min by using 2.5 g litre^{-1} iron sulphide at 25°C . The reduction efficiency of Cr(VI) was increased with temperature of solution. The variation in particle size of iron sulphide did not affect the reduction yield of Cr(VI). The total reduction capacity of synthetic iron sulphide was found to be $237.6\text{ mg Cr(VI) g}^{-1}$. The results related to shrinking particle model showed that the reduction reaction was chemically controlled and activation energy for the process was calculated as 38.4 kJ mol^{-1} .

Keywords: Cr(VI) reduction, Synthetic iron sulphide, Shrinking particle model

INTRODUCTION

Cr(VI) compounds known as chromates and dichromates enter waters from many industrial processes such as leather tanning, electroplating, metal cleaning, alloy preparation etc [1]. Cr(VI) is a strong oxidant. It is more hazardous to living organisms with respect to the other chromium species [1,2]. For that reason, industrial wastewaters containing hexavalent chromium must be treated before discharging into the environment to lower its concentration below the allowable limits described by various water quality criteria for surface waters. Although Cr(III) ions can be directly removed from wastewaters by precipitating in the form of Cr(III) hydroxide, direct precipitation of anionic Cr(VI) species present in wastewaters is not practical. The conventional treatment method for the removal of Cr(VI) from aqueous wastes involves reduction of Cr(VI) to Cr(III) and a subsequent adjustment of pH to near neutral conditions to precipitate the Cr(III) ions formed. The most common reducing agents used are sulphur dioxide, sodium sulphites and ferrous sulphate [1,3,4]. Beside the ferrous sulphate, various iron bearing materials such as ferrous salts [5-7], pyrite [8], metallic iron [9], steel wool [10] and copper smelter slag [11] have been studied for the reduction of Cr(VI). In this

connection, the use of synthetic iron sulphide (SIS) containing Fe(II) and sulphide, both are reductants, seems to be possible for reduction of Cr(VI) in aqueous solutions. For this purpose, synthetic iron sulphide (SIS) consisting mainly of ferrous sulphide was used in this study.

In this paper, the results relating to the effects of acid concentration, the dosage and particle size of SIS, initial Cr(VI) concentration and solution temperature on Cr(VI) reduction are reported. In addition, the applicability of Cr(VI) reduction mechanisms to the heterogen rate expressions was investigated.

MATERIALS AND METHODS

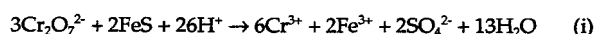
Materials

The iron sulphide, catalogue number of which is Merck-3908, was used as reductant in this study. This synthetic iron sulphide sample (SIS) in gross pellets was crushed, ground and then sieved to obtain various fractions. The fractionated material was dried at 60°C for 6 hours, then it was stored in a tightly closed jar throughout the study. The SIS sample of $< 53\text{ }\mu$ fraction was used in the study except for experiments where the effect of particle size was investigated.

A stock solution of Cr(VI) (1000 mg litre⁻¹) was prepared by dissolving K₂Cr₂O₇ in distilled water. Other 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 the study were in analytical grade.

Experimental Procedure

The experiments were carried out by using a flask shaker (Stuart Scientific, SF1 model) equipped with a temperature controlled water bath. 100 ml Cr(VI) solutions of desired concentration were combined with varying amounts of iron sulphide in a flask of 150 ml. The reaction mixtures were shaken at 500 cycle min⁻¹ at different temperatures 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 1.0, 1.5 and 2.0 stoichiometric amounts of Cr(VI) present in the solutions, by considering Equation (i). In addition, to determine the reduction capacity of SIS, a 0.25 g iron sulphide sample was successively treated with 100 ml Cr(VI) solutions (100 mg Cr(VI) litre⁻¹) the H₂SO₄ content of which is 2 stoichiometric amounts at 25°C for 45 min, until no reduction occurred.



At the end of the predetermined contact period, reaction mixture was filtered and then the pH_f of filtrates were measured by using pH meter (Shot CG 840). The filtrates were acidified with 1 ml of 15 % HNO₃ solution to prevent the precipitation of metal ions and they were analysed for Cr(VI), total chromium and iron.

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

Methods of Analysis

Mineralogical composition of SIS used in the study was determined by X-Ray diffractometer (Siemens, D-5000 model). A SIS sample was dissolved by utilising the lithium metaborate fusion-nitric acid dissolution method [12] and then iron was analysed by atomic absorption spectrophotometer (Perkin Elmer, 370 model). The analysis of sulphur was carried out gravimetrically by precipitating as BaSO₄ [13].

In the reduction study, the concentration of Cr(VI) in the solutions was determined colorimetrically with 1,5-diphenyl carbazide method [14] by spectrophotometer (Bausch and Lomb, Spectronic 20) while that of total chromium and iron were determined [15] by atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Mineralogical and chemical compositions of synthetic iron sulphide (SIS) are presented in Table 1. The SIS contains 61.03 % Fe and 32.82 % S, which means that it contains 90.25 % FeS in weight. The excessive amount of iron with respect to stoichiometric sulphur can be considered as metallic iron since XRD analysis shows that the troilite and metallic iron are main constituents of SIS used.

The reaction of Cr(VI) reduction by iron sulphide can be described by Equation (i). Since the reduction of Cr(VI) occurs in a strong acidic medium, it can be stated that the acid concentration plays a very important role on the reduction reaction. The results from the experiments performed with the solution (100 mg Cr(VI) litre⁻¹) of different acid concentrations (1.0, 1.5, 2.0 theoretical amount of H₂SO₄) at 5 g litre⁻¹ iron sulphide dosage for contact times varying from 5 to 120 min are given in Figure 1. The reduction extent of Cr(VI) increased gradually with increasing acid concentration and contact time. However, when twice the theoretical amount of H₂SO₄ was used, at the end of the contact period of 30 min, the reduction percentage of Cr(VI) reached 100 %. It was observed that the total chromium concentrations in treated solutions were lower than the initial concentrations for all experiments. However, the difference is more remarkable in strong acidic conditions and increased during the contact period of the first 45 min and thereafter became almost constant. As the reduction process went forward, the final pH_f of solutions ranged from 1.93 to 4.21. At this pH interval, the dichromate ions with negative charge may be adsorbed onto the positively charged surface of FeS present in excessive amount in proportion to the stoichiometric amount of Cr(VI), which causes a decrease in total chromium concentration in treated solution.

As seen from Figure 1, the total iron concentrations in treated solutions and the final pH values of solutions increased with the acid concentration and contact time. The iron concentrations determined in treated solutions were very high compared to those of reduced chromium. For example, in the experiments carried out with 1.0, 1.5 and 2.0 stoichiometric acid content, the total iron concentrations were found to be 26.7, 53.1 and 211.8 mg litre⁻¹, respectively, at the end of the contact period of 30 min. At the same conditions, it was found that the concentrations of reduced chromium were 26.9, 41.4 and 100 mg litre⁻¹. Where the Cr(VI) can not be

Table 1. Mineralogical and chemical compositions of synthetic iron sulphide.

Constituent	%	Mineral	Formula
Fe	61.03	Troilite	FeS
S	32.82	Iron	Fe
		Wuestite	FeO (minor amount)

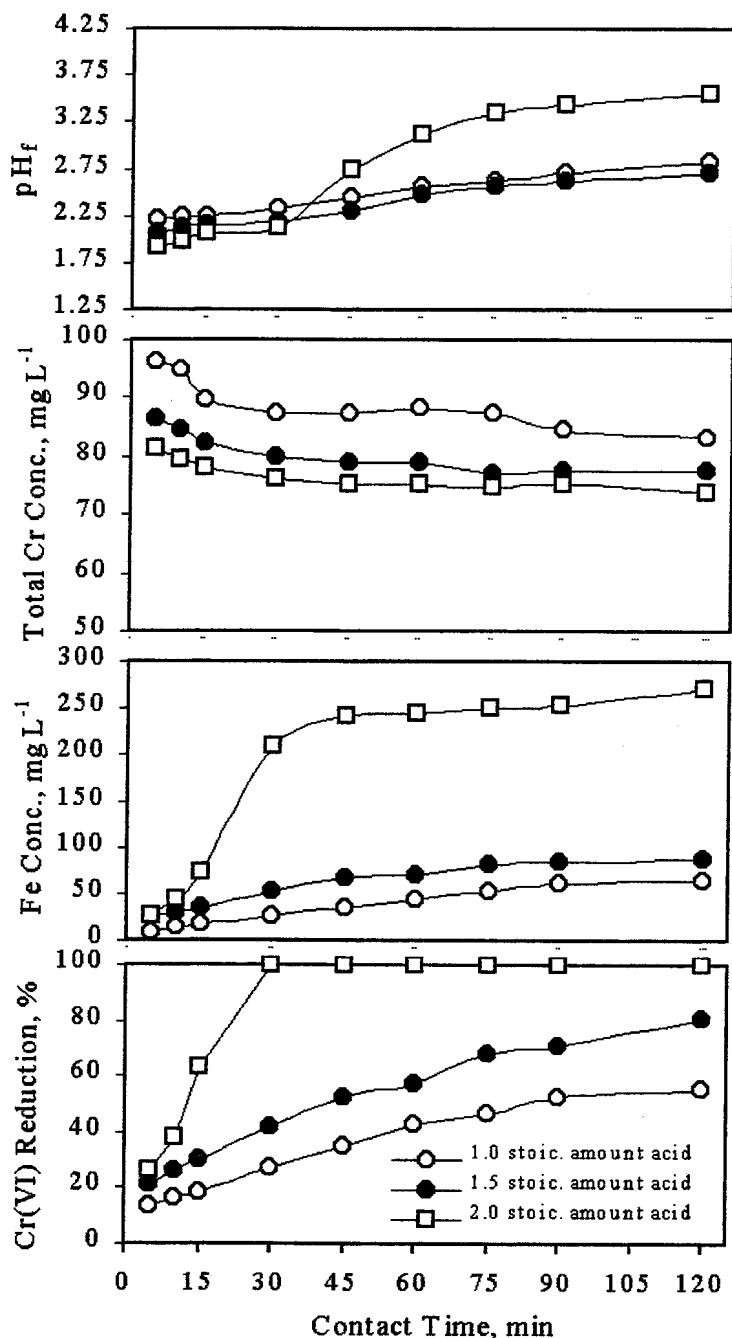
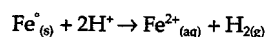


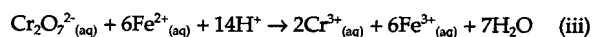
Figure 1. Effects of acid concentration and contact time on the Cr(VI) reduction (iron sulphide dosage, 5 g litre⁻¹ ; initial Cr(VI) conc., 100 mg litre⁻¹; temperature, 25°C)

detected in treated solution, it was assumed that all the Cr(VI) was reduced because the composition of the adsorbed phase could not be determined. When the above figures were considered, the molar ratios of reduced chromium to dissolved total iron were calculated as 1.07, 0.83 and 0.51, respectively, for the conditions mentioned above. Whereas, 3 moles reduced chromium are theoretically produced for each mole dissolved iron according to Equation (i). It can be clearly

seen that the reduction of Cr(VI) occurs nonstoichiometrically when dissolved iron concentration in treated solutions was considered. The nonstoichiometric reduction can be attributed to the amount of excessive acid and the metallic iron content of SIS. Metallic iron is readily dissolved by reacting with acid to form ferrous ions and it is possible that the formed ferrous ions may also contribute to the reduction of Cr(VI) ions (Equations ii and iii).



(ii) after all the Cr(VI) was reduced, however, may be explained by Equation (ii). The consumption of acid during this reaction leads to an increase in the pH values and precipitation of the ferric ions as hydroxide above pH 3.0.



That the total iron concentration continues to increase

is shown in Figure 2.

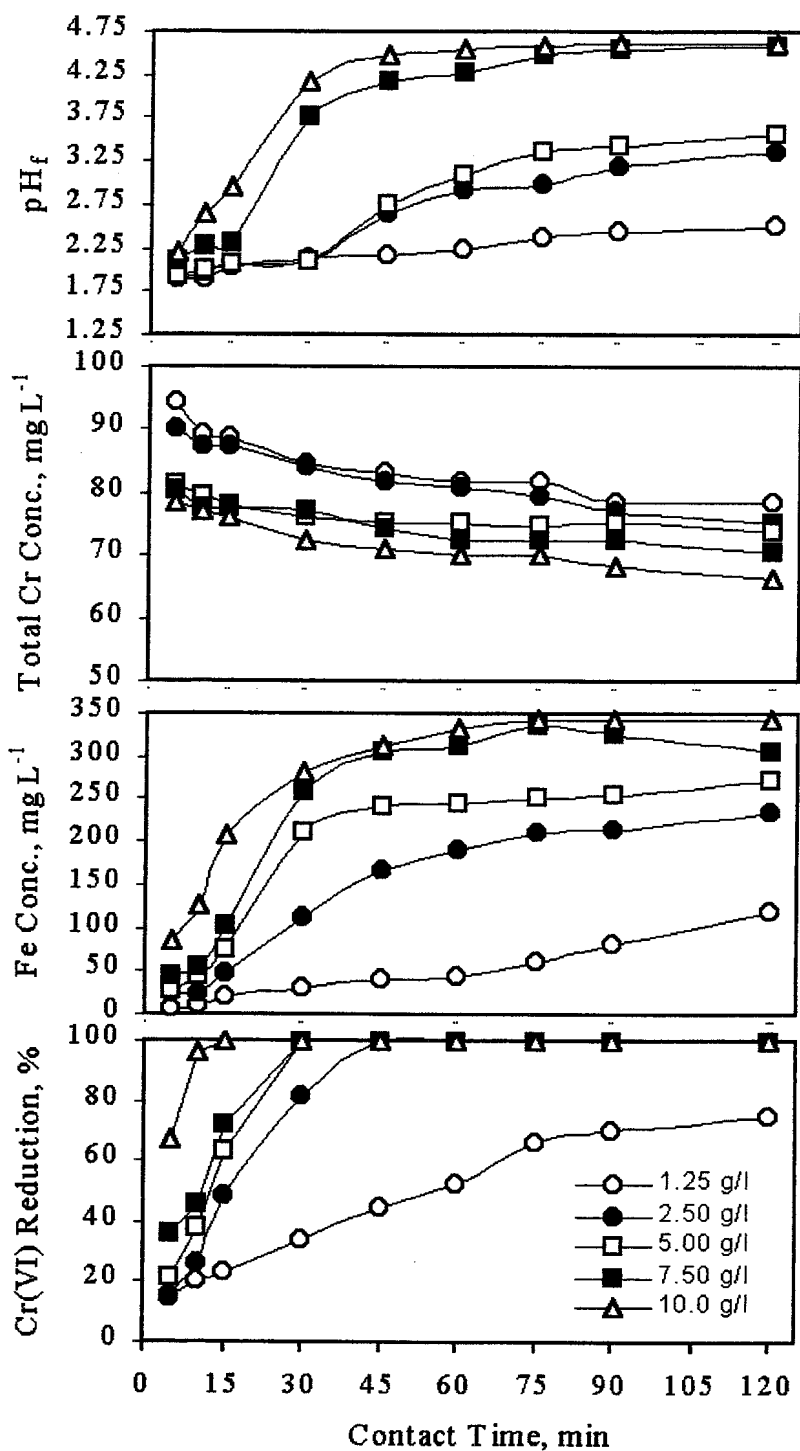


Figure 2. Effect of iron sulphide dosage with contact time on the Cr(VI) reduction. (2 stoichiometric H_2SO_4 ; initial Cr(VI) conc., 100 mg litre⁻¹; temperature, 25°C).

In the series of these experiments, the SIS dosages were taken in the range of 2.5 - 10 g litre⁻¹ whereas the amount of acid was 2.0 times of stoichiometry. With increasing SIS dosage from 2.5 to 10 g litre⁻¹, the contact time required for the reduction of the entire Cr(VI) declined from 45 to 15 min. The dosage of 1.25 g litre⁻¹ was not sufficient to complete the reduction of Cr(VI) even within 120 min. It is expected that the amount of solubilized iron increases depending upon an increase in the dosage of SIS. When the reductant dosages of 2.5, 5.0 and 10.0 g litre⁻¹ were used, the total iron concentrations in treated solutions were determined as 166.4, 241.8 and 327.0 mg litre⁻¹, respectively, at the end of contact time of 45 min. The dissolved iron in treated solution can be considered as another pollutant. Therefore, to reduce the amount of iron ions to pass into the solution, the subsequent experiments were carried out with a dosage of 2.5 g litre⁻¹. It may also be noted that after the Cr(VI) completely reduced, the concentration of iron did not show a significant increase with a rise in the dosage of SIS. The concentration of total chromium in treated solutions shows a decreasing trend with an increase in the dosage. However, in the experiment where the higher dosages were used, the difference between the initial concentration of Cr(VI) and total chromium concentration was higher than that of the experiments carried out with lower dosage. It can be clearly seen that the final pHs of the solutions increased with the dosage of reductant and contact time. Increasing solution pH up to approximately 3.0 causes the ferric ions, the concentrations of which are fairly high, to precipitate as hydroxide. Both the Cr(VI) and Cr(III) may also be adsorbed by the formed ferric hydroxide, which leads to a difference between the initial Cr(VI) concentration and that of total chromium.

The effect of initial concentration of Cr(VI) on the reduction process was investigated by treating the solutions of various concentrations (25-250 mg litre⁻¹) with SIS in the dosage of 2.5 g litre⁻¹. The obtained results are given in Figure 3. The maximum reduction yield of Cr(VI) was observed at initial concentration values between 100 and 150 mg litre⁻¹ by decreasing on either side of these concentrations. That the reduction of Cr(VI) was not completed at low concentration may be attributed to acid content since the amount of acid added to the solution is proportional to the Cr(VI) concentration. On the other hand, while the dosage of SIS used was kept constant, Cr(VI) concentration was varied during the experiments. Hence, the reduction percentage of Cr(VI) decreased at higher concentrations. The concentration of solubilized iron in treated solution increased with increasing that of Cr(VI). The reactivity of iron sulphide is, to a large extent, dependent on the amount of acid. Since the amount of acid added to the solution was determined with respect to the concentration of Cr(VI), increasing the concentration will cause an increase in acidity of the solution. For that reason, it is expected that the higher acid concentration, the more iron is dissolved in treated solution.

Figure 4 shows the results of the experiments carried out at different temperature of solution. It is clearly seen that

raising the temperature leads both the whole of the Cr(VI) present in the solution to be reduced in a shorter period of contact time and the total chromium concentration in treated solution to decrease. As a little fraction of Cr(VI) was reduced in the first ten minutes at 25 °C, at the same contact period the entire Cr(VI) was reduced at 65°C, showing the reduction process is endothermic. Since the adsorption phenomenon is responsible for the decrease of total chromium concentration, it can be stated that the adsorption process is also endothermic. Since the reduction extent of Cr(VI) is dependent on the consumption of acid and the reaction of SIS particles, the reduction process gives a rise in the final pH of solutions and the solubilized iron concentration. But it must be noted again that the reduction reaction occurs nonstoichiometrically.

In addition, the data obtained at different temperatures were analysed according to the shrinking particle model. The first order rate expression for this model given by [16] is:

$$1-(1-x)^{1/3} = kt \quad (iv)$$

Where, x is the fraction of reduced Cr(VI), t is the time and k is first order rate constant. The plot of $1-(1-x)^{1/3}$ against t gives a straight line at 25, 35 and 50°C (Figure 5) showing the applicability of this model. The values of k determined from the slopes of these lines were 0.025, 0.037 and 0.075 min⁻¹ for 25, 35 and 50°C, respectively. That the values of k increased with temperature and the applicability of the shrinking particle model to this process explains that the rate of the reduction reaction was controlled by dissolution of FeS from the surface of SIS particles. Activation energy of the reduction process was calculated as 38.4 kJ mol⁻¹ using Arrhenius equation [16] given as:

$$k = k_0 e^{-E/RT} \quad (v)$$

To investigate the effect of the particle size of SIS on the reduction process, portions of a 100 ml Cr(VI) solution were treated with 0.25 g SIS of various particle size for 45 min. The results are shown in Figure 6. All of the Cr(VI) was reduced for all fractions of SIS. This situation may stem from the excess amount of SIS in proportion to the stoichiometric amount of Cr(VI) and porous structure of the material produced by grinding the pellets with fine particles. But the data indicates an increase in the concentration of dissolved iron as the particle size decreases. This observation is in agreement with the fact that the reaction of small SIS particles is faster than the big ones since the small particles have a higher surface area per unit mass.

The results from the successive experiments done to determine the reduction capacity of SIS are given in Table 2. At the end of the 9th stage, the amount of Cr(VI) reduced by 0.25 g SIS was calculated as 59.5 mg. Under the same

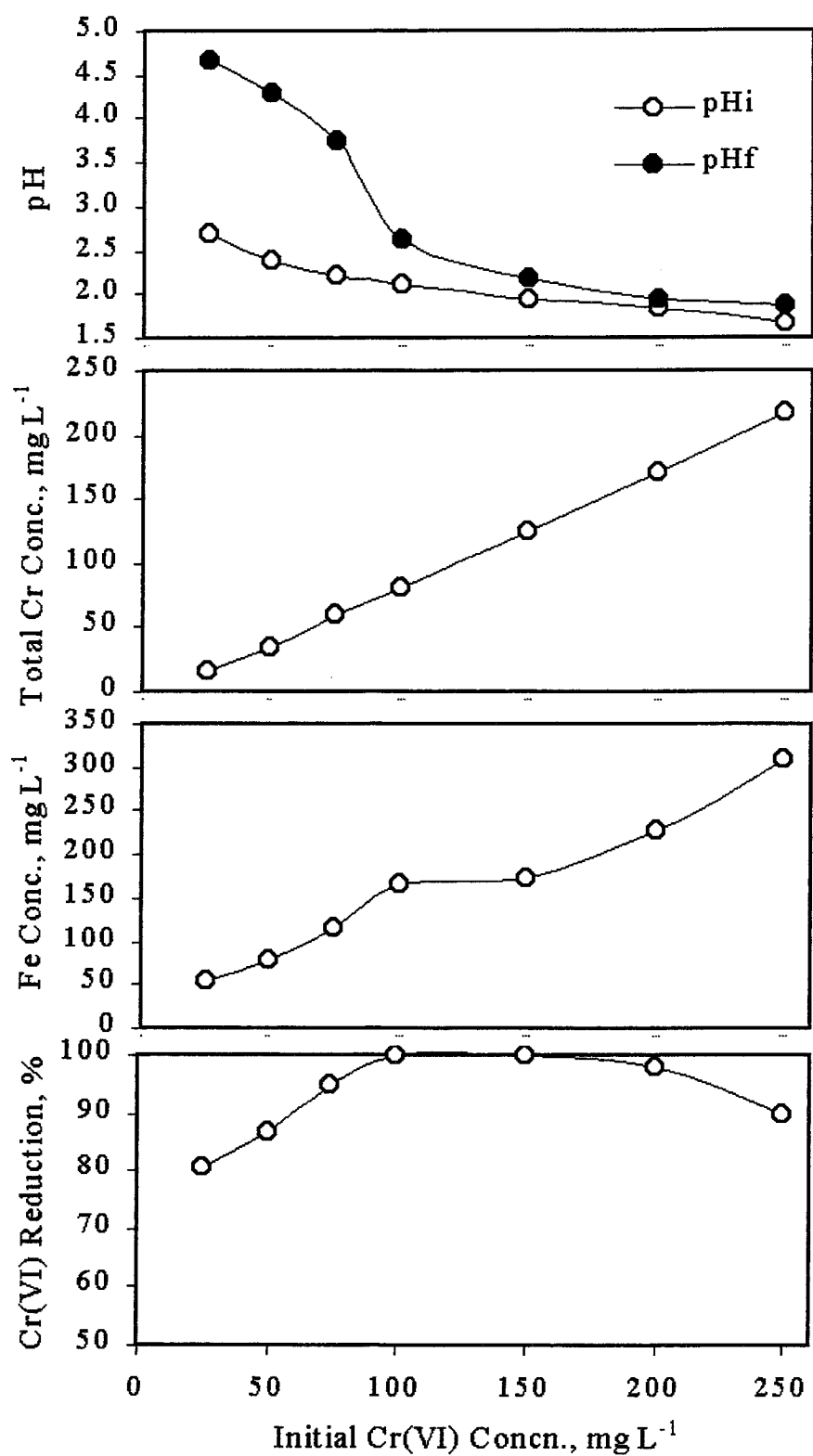


Figure 3. Effect of initial Cr(VI) concentration on the Cr(VI) reduction. (2 stoichiometric H₂SO₄; iron sulphide dosage, 2.5 g litre⁻¹; contact time, 45 min.; temperature, 25°C)

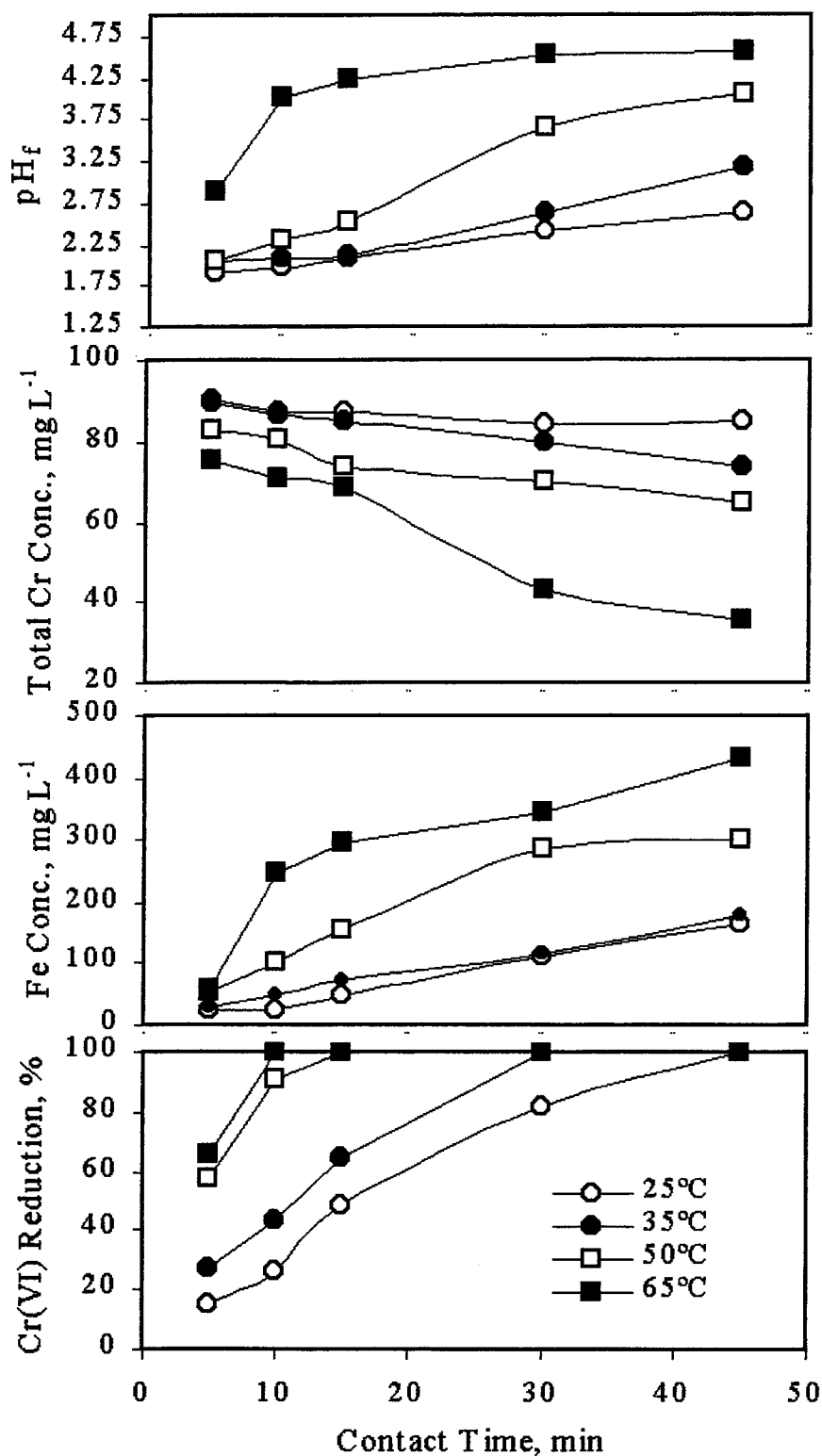


Figure 4. Effect of temperature with contact time on the Cr(VI) reduction. (2 stoichiometric H_2SO_4 ; initial Cr(VI) conc., 100 mg litre⁻¹; iron sulphide dosage, 2.5 g litre⁻¹).

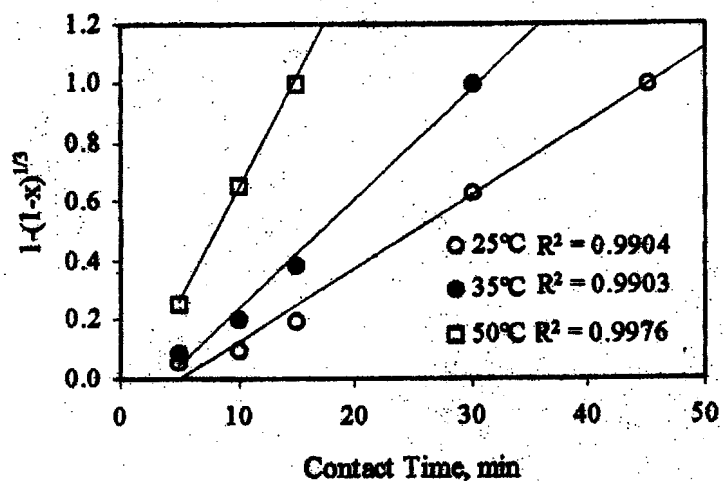


Figure 5. The variation of $1-(1-x)^{1/3}$ with contact time at various temperatures.

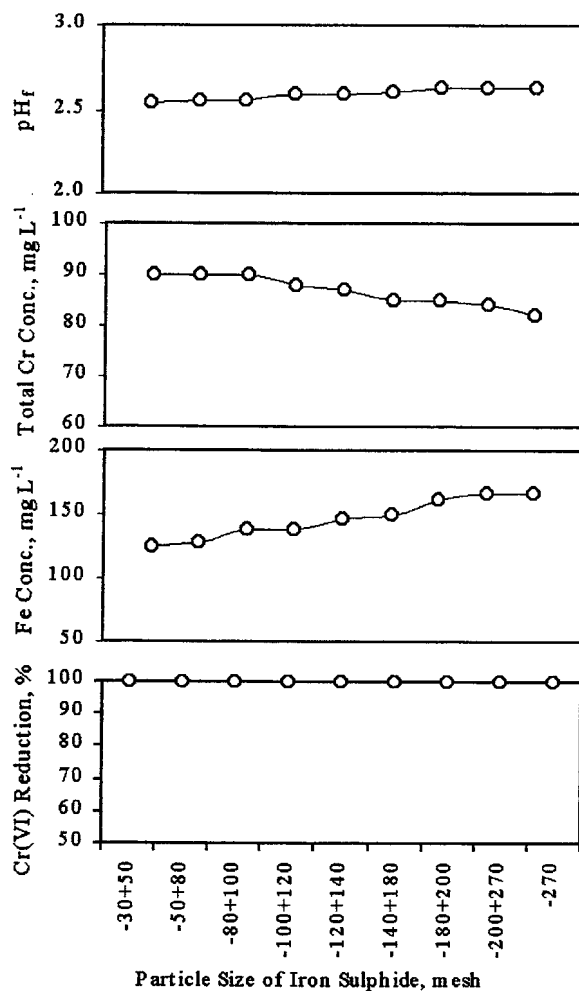


Figure 6. Effect of particle size of SIS on the Cr(VI) reduction. (2 stoichiometric H_2SO_4 ; initial Cr(VI) conc., $100 \text{ mg litre}^{-1}$; iron sulphide dosage, 2.5 g litre^{-1} ; contact time, 45 min; temperature, 25°C).

Table 2. The results of the successive experiments to determine the reduction capacity of SIS. (100 ml Cr(VI) solutions (100 mg Cr(VI) litre⁻¹, 2 stoichiometric acid) was successively treated with 0.25 g SIS for 45 min at 25° C).

Number of the Successive Experiments	pH _f	Cr(VI) Reduction, %	Fe Cons., mg l ⁻¹
1	2.63	100	166.43
2	2.61	100	57.73
3	2.40	100	32.00
4	2.28	100	19.20
5	2.19	79.83	15.67
6	2.16	56.05	13.90
7	2.14	39.11	14.25
8	2.10	14.30	9.58
9	2.06	5.65	5.65

conditions, the cumulative amount of iron solubilized from reductant was 33.4 mg. From these values the reduction capacity of SIS can be calculated as 238 mg Cr(VI) g⁻¹. In our previous studies Cr(VI) reduction by pyrite [8] and copper smelter slag [11] were investigated, the reduction capacity of these materials were reported to be 42.5 and 76.5 mg Cr(VI) g⁻¹ at similar conditions, respectively. The reduction capacity of SIS is very high compared to those of these materials, hence, the iron sulphide is a more suitable reductant for the Cr(VI) in aqueous solution.

CONCLUSIONS

The following conclusions may be drawn from this study where synthetic iron sulphide (SIS) was used to reduce the Cr(VI) in the aqueous solution.

1. The SIS can effectively reduce the Cr(VI) in the aqueous solution. The reduction efficiency is dependent on acid content of solution. The reduction process can be

completed in a short period of contact time when 2.0 stoichiometric acid is used with respect to Cr(VI).

2. The maximum reduction yield of Cr(VI) was observed by using a dosage of 2.5 g litre⁻¹ at initial Cr(VI) concentration values between 100 and 150 mg litre⁻¹.
3. By increasing the temperature of the solution, the reduction extent of Cr(VI) increased and the time required to reduce the entire Cr(VI) shortened.
4. The data of reduction reaction was fitted to first order shrinking particle model rate expression. The activation energy of reduction process was found to be 38.4 kJ mol⁻¹.
5. Cr(VI) in a 100 ml solution (100 mg litre⁻¹) can be completely reduced within 45 min at 25 °C by all fractions of SIS used in the study.
6. The total reduction capacity of SIS was calculated as 238 mg Cr(VI) g⁻¹ and this value is very high compared to those of pyrite and copper smelter slag used in our previous studies.

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