

## Remediation of sulfidic wastewater by catalytic oxidation with hydrogen peroxide

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### Abstract

Oxidation of sulfide in aqueous solution by hydrogen peroxide was investigated in the presence of hydrated ferric oxide catalyst. The ferric oxide catalyst was synthesized by sol gel technique from ferric chloride and ammonia. The synthesized catalyst was characterized by Fourier transform infrared spectroscopy, X-Ray diffraction analysis, scanning electron microscope and energy dispersive X-ray analysis. The catalyst was quite effective in oxidizing the sulfide by hydrogen peroxide. The effects of sulfide concentration, catalyst loading, H<sub>2</sub>O<sub>2</sub> dosing and temperature on the kinetics of sulfide oxidation were investigated. Kinetic equations and activation energies for the catalytic oxidation reaction were calculated based on the experimental results.

**Key words:** catalytic oxidation; wastewater; kinetic equation; hydrogen peroxide; sodium sulfide remediation

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### Introduction

Sulfides are toxic to living beings beyond a permissible limit of 0.2 mg/L (National Health and Welfare Canada, 1978). They are found to exist in water bodies in the form of dissolved sodium sulfide or hydrogen sulfide. Many industries like oil refineries, petrochemicals, tanneries, kraft paper mills, dyes and pigments etc. discharge sulfide containing effluents. The caustic scrubbing solution from a gas cracker contains sodium sulfide. Sulfides sometimes are found to be present in sewer networks also. It primarily originates from anaerobic sulfate respiration in bio-films on sewer pipe walls (Nieleesen *et al.*, 1998).

For the removal of sulfide from wastewater the most common process involves its oxidation to a more benign form sulfate (Malik and Chaudhuri, 1999; Ueno *et al.*, 1979; Hoffmann, 1977; Munter, 2001; Bain and Blowes, 2000; Spiller *et al.*, 1996; Iliev and Mihaylova, 2002; Linkous *et al.*, 2004; van der Zee *et al.*, 2007; Trapido *et al.*, 1998). The reported work on oxidation process can be divided broadly into four categories: (i) oxidation of H<sub>2</sub>S and Na<sub>2</sub>S in aqueous solution by dissolved oxygen; (ii) catalytic oxidation with oxygen and H<sub>2</sub>O<sub>2</sub>; (iii) biological oxidation of sulfide; (iv) precipitation, using a mixture of ferrous and ferric salts. Among these wet oxidation and precipitation, using a mixture of ferrous and ferric salts is competitive process (Kuhn *et al.*, 1983; Ellis, 1998; Padiaval *et al.*, 1995). Wet air oxidation at elevated temperature and pressure (433 K, 500 kPa) is a relatively

clean process as no solid residue can be formed. On the other hand, precipitation method produces sludge of iron sulfide which may possess disposal problem.

Biological oxidation of sulfides has also been used successfully in a limited number of applications (Nieleesen *et al.*, 2003). Catalytic oxidation of sulfide has also been reported by some researchers (Ueno *et al.*, 1979; Hoffmann, 1977; Bain and Blowes, 2000; Iliev and Mihaylova, 2002; Linkous *et al.*, 2004). Sakai *et al.* (1980) investigated sulfide oxidation by atmospheric oxygen in the presence of “Sulfur Black B” dye as a catalyst. The reaction was reported to be first order in sulfide concentration. Ueno *et al.*, (1979) made an exhaustive survey on the oxidation of sulfide. They carried out catalytic oxidation with dissolved oxygen using a number of catalysts including carbon black, ferric salts and few organic compounds. Nieleesen *et al.* (2007) studied the effect of FeCl<sub>3</sub> catalyst on the oxidation of sodium sulfide with dissolved oxygen. They analyzed the conversion data using first order equation for the removal of sulfide. The rate constant was found to be a function of FeCl<sub>3</sub> concentration.

Takenak *et al.* (2003) studied the oxidation of sulfide using hydrogen peroxide at low temperatures. They found that the decomposition of sulfide was five times faster at 258 K than at room temperature.

In the present work, the process for the catalytic oxidation of sodium sulfide in aqueous solution by hydrogen peroxide was studied. The catalyst (ferric oxide) was synthesized in laboratory and was characterized by scanning electron microscope (SEM), energy dispersive X-ray

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analysis (EDX), Fourier transform infrared spectroscopy (FT-IR), and X-Ray diffraction (XRD) analysis.

## 1 Material and methodology

### 1.1 Preparation and characterization of catalyst

Analytical grade ferric chloride was taken as a starting material for the synthesis of ferric oxide catalyst. A 30% ammonia solution was added dropwise to a concentrated solution of ferric chloride with stirring till the pH became 8.5. The slurry was washed repeatedly with water to remove excess chloride ions and then dried in an air oven at  $(110 \pm 5)^\circ\text{C}$ , powdered and stored. The catalyst was characterized by FT-IR spectroscopy (spectrum one, Perkin-Elmer, US), XRD analysis (D8 Advance, Bruker, Germany), SEM and EDX analysis (1430 VP, LEO, UK). The leachability of catalyst was checked by estimating  $\text{Fe}^{3+}$  in the filtrate after oxidation using atomic absorption spectrophotometer (Z-5000, Hitachi, Japan).

### 1.2 Analysis of sulfide and sulfate

Sodium sulfide of 60% purity was used to prepare the test solution. The concentration of sulfide in the solution was estimated by iodometric titration and colorimetric method using DR 5000 Hach UV-visible spectrophotometer (DR 5000, Hach, Germany). For the determination of sulfate, concentrated  $\text{BaCl}_2$  (reagent grade) was used and the sulfate concentration was measured according to the turbidity of the solution.

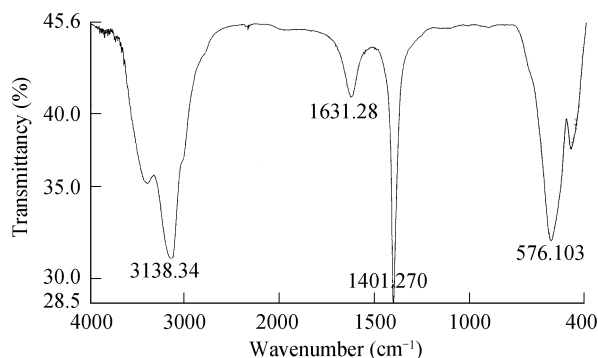
### 1.3 Methodology

Non catalytic oxidation of sodium sulfide by hydrogen peroxide at freezing point has been carried out in a propylene syringe (Takenaka *et al.*, 2003). This method is not easy and economical to apply on large and commercial scale. In the present work we have used an alternative but largely novel method of sulfide oxidation by hydrogen peroxide in the presence of catalyst. The catalytic oxidation of sulfide was carried out in a stirred beaker. Different dosages of catalyst were added to 500 mL sulfide solution followed by the addition of  $\text{H}_2\text{O}_2$  (30%) in different proportions. Samples were withdrawn with different intervals of time and analyzed for the unreacted sulfide and sulfate formed.

## 2 Results and discussions

### 2.1 Characterization of the catalyst

As shown in FT-IR spectra of the catalyst sample (Fig. 1), no stretching frequency of either free water (above  $3600\text{ cm}^{-1}$ ) as well as bonded water (above  $3400\text{ cm}^{-1}$ ) was observed. The spectral band at  $3139\text{ cm}^{-1}$  was assigned to the stretching vibration of traces of inner lying  $\text{OH}^-$  ions in the sample. Bending vibrations of the  $\text{OH}^-$  groups was observed at  $1632\text{ cm}^{-1}$  and  $1402\text{ cm}^{-1}$  (Jonas *et al.*, 2007). The band at  $1402\text{ cm}^{-1}$  was assigned to out of plane bending vibration whereas the band at  $1632\text{ cm}^{-1}$  was due to the in-plane bending vibration of  $\text{OH}^-$  group. The band



**Fig. 1** Fourier transform infrared (FT-IR) spectra of the ferric oxide catalyst.

at  $576\text{ cm}^{-1}$  was assigned to  $\text{Fe-O}$  stretching vibration. The material contains traces of isolated  $\text{Fe-OH}$  bonds and no free water. The cationic field of Fe was significant in the sample, which possibly due to the presence of more polarizing  $\text{Fe}^{3+}$  as the bending vibration of  $\text{OH}^-$  split in two planes. Thus, the material can be identified as hydrated ferric oxide or synthetic ferric oxide with 'defect'.

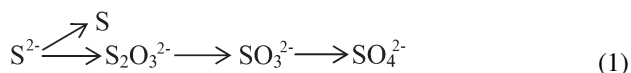
According to Duvenhage and Coville (1997), the peak at  $35.7^\circ$  is the most intense peak of  $\text{Fe}_2\text{O}_3$  in XRD analysis spectrum, and the result shows synthetic ferric oxide (Hematite) as the major crystalline phase (Fig. 2). The poor relative intensity of the phases indicated incomplete crystallization. The synthetic iron oxide catalyst was hydrated hexagonal non stoichiometric ferric oxide with stoichiometry,  $\text{Fe}_{1.833}(\text{OH})_{0.5}\text{O}_{2.5}$ . There was no phase change of iron oxide after oxidation, as evidenced from the XRD diagram (Fig. 2b) of the sample taken after oxidation.

In the SEM image of the sample (Fig. 3), spherical isolated particles of submicron size are observed. The particle size distribution was narrow and some local weak agglomerate formation was observed. Average particle size was less than 200 nm.

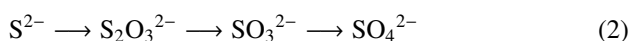
It was also confirmed from the EDX analysis study that the sample basically contained Fe, O and H as the major elements. Trace amount of Cl was also observed in the sample. It came from the unreacted ferric chloride which is the starting material for catalyst preparation.

### 2.2 Catalytic sulfide oxidation

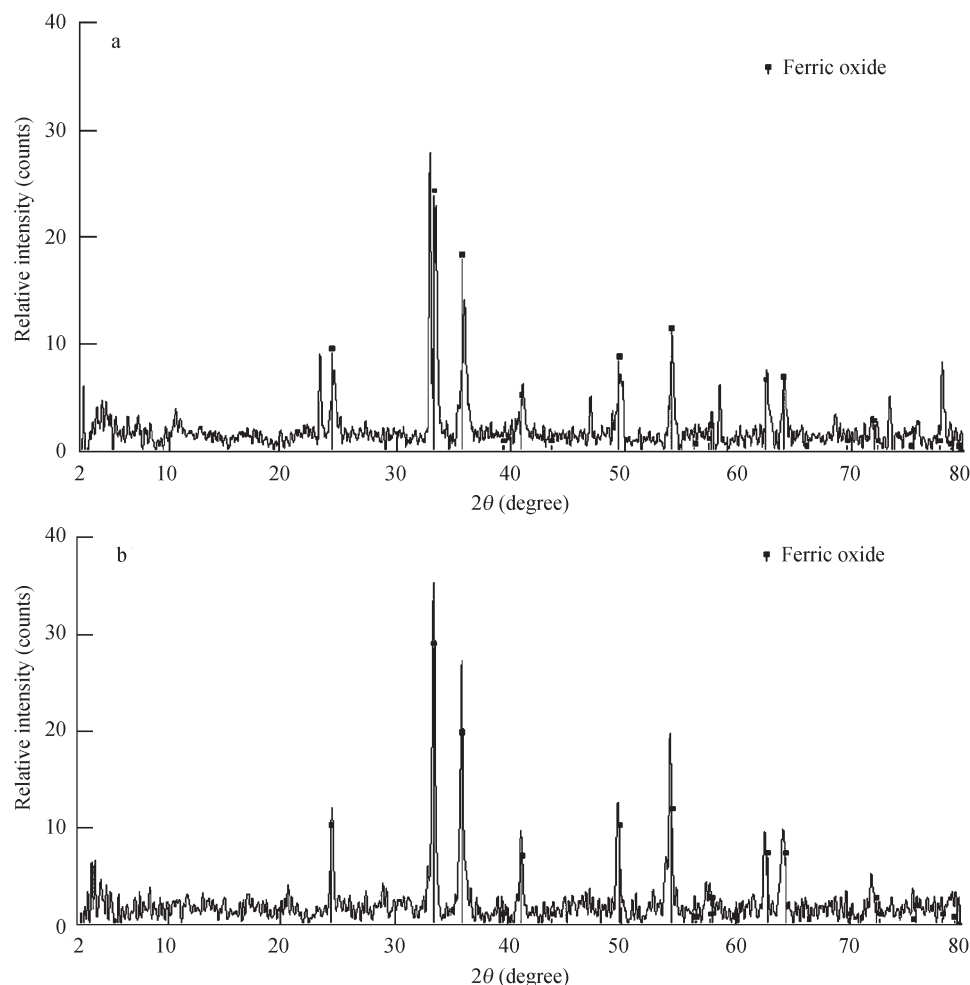
Oxidation of sulfide in an aqueous solution proceeds through the following reaction pathway (Ellisc, 1998):



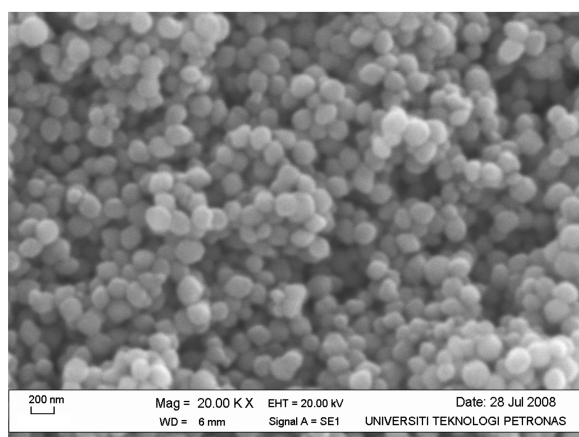
The rate as well as the final oxidation product depend upon the availability of oxygen and pH. The rate of sulfite oxidation to sulfate is very fast in an oxidizing environment. Therefore the formation of an intermediate  $\text{SO}_3^{2-}$  may be ignored and the scheme may be simplified as:



The important parameters that determine the rate of sulfide oxidation are the sulfide concentration,  $\text{H}_2\text{O}_2$  concentration and catalyst loading (Vakhitova *et al.*, 2005).



**Fig. 2** X-Ray diffraction analysis (XRD) diagram of the ferric oxide catalyst before (a) and after (b) oxidation.



**Fig. 3** Scanning electron microscope (SEM) image of the ferric oxide catalyst.

The pH of  $\text{Na}_2\text{S}$  solution is highly alkaline. The solution can be made nearly neutral by adding acid but  $\text{H}_2\text{S}$  could be generated in the solution. To avoid the formation of  $\text{H}_2\text{S}$  that might escape from the solution to some extent, all the experiments were conducted at the prevailing pH. However, the change of pH occurred in course of the oxidation process. As the oxidation proceeds, sulfide concentration decreases and the pH also decreases.

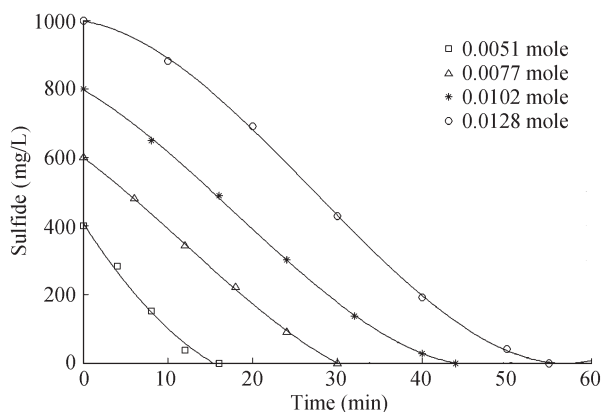
Figure 4 depicts the change in sulfide concentration with

time for four different initial values. All these data were collected with synthetic wastewater samples. The same amount of hydrogen peroxide 0.0702 mole (30% solution, W/W) was added to each batch of 500 mL sulfide solution. The initial rate of sulfide oxidation showed an appreciable dependence on the initial concentration. The rate appears higher at a lower initial concentration contrary to what was expected. Beginning with 0.0128 mole of sulfide solution, complete removal of the sulfide was achieved within about 55 min.

Figure 5b shows the effect of catalyst loading which was varied from 0.25 to 1.5 g in 500 mL feed solution. The time of complete sulfide removal varies from 17 to 90 min. The leachability of iron oxide was found to be 0.67% which indicates that the recovery of the catalyst is 99.33%. The pH of the solution decreased gradually from an initial value of 11.2 to nearly neutral value of 7 as shown in the Fig.5a.

The rate increases rapidly with temperature and the total time of sulfide oxidation changes significantly from 30 to 6 min as the temperature increases from 298.2 to 318 K (Fig. 6a).

Figure 6b shows the effect of hydrogen peroxide addition on sulfide oxidation. Rate of sulfide oxidation increased approximately five times by increasing hydrogen peroxide amount from 0.049 to 0.086 mole. In all cases of hydrogen peroxide addition, the concentration of sodium



**Fig. 4** Time evolution of sulfide concentration for different initial values.  $\text{H}_2\text{O}_2$  dose: 0.0702 mole; catalyst: 1 g.

sulfide has been kept constant (0.0077 mole) with 1 g of catalyst loading.

Sulfate concentration in solution was also measured. Since the oxidation of sulfite to sulfate in the presence of  $\text{H}_2\text{O}_2$  is fast, the solution virtually contains sulfide,

thiosulfate and sulfate. The concentration of thiosulfate can be calculated from the measured concentrations of sulfide and sulfate.

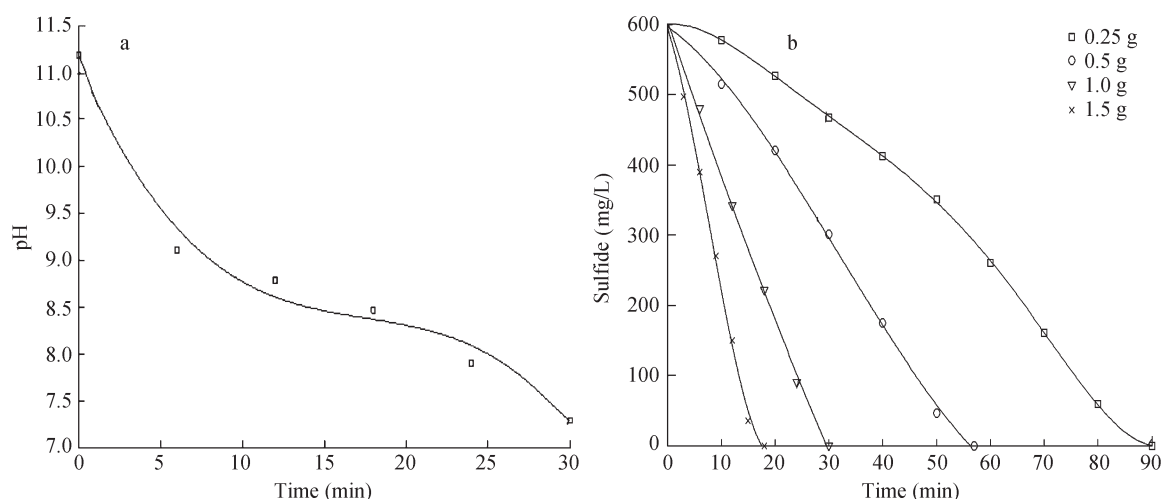
As shown in Fig. 7a, at different initial sulfide concentrations, sulfate formation rate was higher at high sulfide concentration initially, and later, the rate was higher at lower sulfide concentration. On the other hand, sulfate formation increased with increasing catalyst dosage (Fig. 7b) and increasing temperature (Fig. 7c).

### 2.3 Rate equation for sulfide oxidation

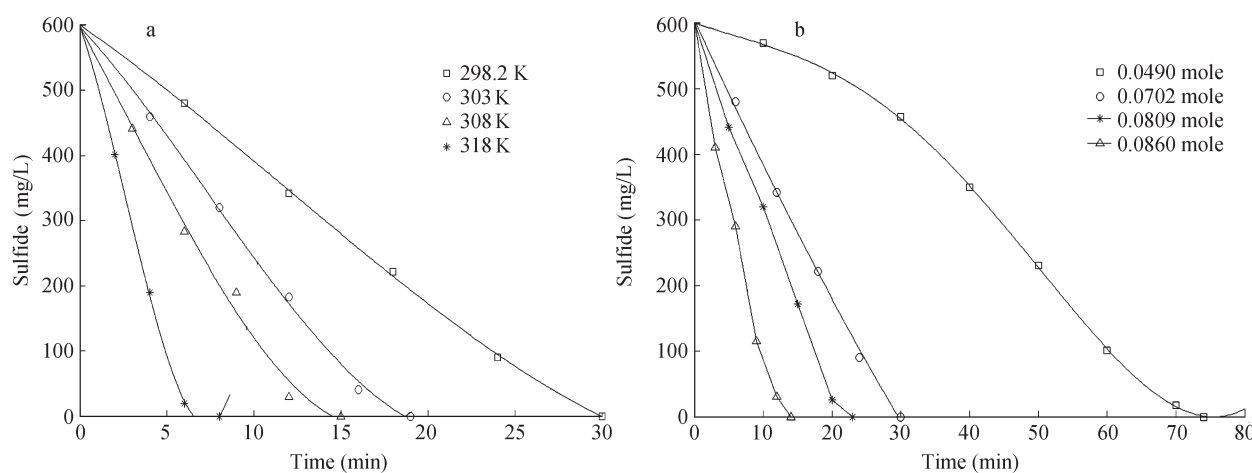
Rate of oxidation of sodium sulfide and hydrogen sulfide by dissolved oxygen has been quantified by power-law kinetics (O'Brien and Birkner, 1977). For catalytic oxidation with  $\text{H}_2\text{O}_2$ , we propose the following rate ( $r_{\text{S}^{2-}}$ ) equation (Eq. (3)).

$$r_{\text{S}^{2-}} = C_{\text{S}^{2-}}^{m_1} C_{\text{H}_2\text{O}_2}^{m_2} C_{\text{Fe}_2\text{O}_3}^{m_3} \quad (3)$$

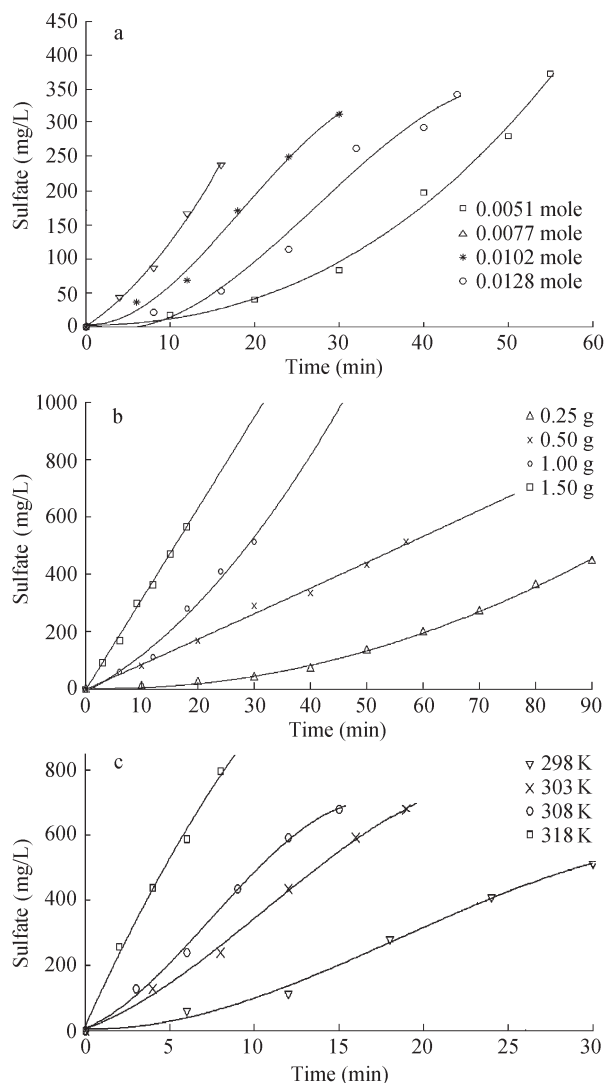
where,  $C_{\text{S}^{2-}}$  is the concentrations of sulfide,  $C_{\text{H}_2\text{O}_2}$  is the concentration of hydrogen peroxide and  $C_{\text{Fe}_2\text{O}_3}$  is catalyst concentration.



**Fig. 5** Relationship between time and pH during the catalytic oxidation of sulphide (a) and between time and sulfide concentration for different catalyst loadings (b).  $\text{H}_2\text{O}_2$  dose: 0.0702 mole; sulfide concentration: 0.0077 mole; catalyst: 1 g; initial pH: 11.2.



**Fig. 6** Time evolution of sulfide concentration at different temperatures (a) and  $\text{H}_2\text{O}_2$  additions (b). Catalyst: 1 g;  $\text{H}_2\text{O}_2$ : 0.0702 mole; sulfide concentration: 0.0077 mole; initial pH: 11.2.



**Fig. 7** Sulfate formation at different initial sulfide concentrations (a), catalyst dose (b), and temperatures (c). Catalyst 1 g;  $\text{H}_2\text{O}_2$ : 0.0702 mole; sulfide concentration: 0.0077 mole; initial pH: 11.2.

In this redox system where the oxidant ( $\text{H}_2\text{O}_2$ ) and the reductant ( $\text{S}^{2-}$ ) were present together in solution, it was not possible to estimate the concentration of hydrogen sulfide separately from time to time. We therefore, determined the kinetic constants from the initial rate and initial reactant concentrations, hydrogen peroxide and the catalyst loading.

A plot of the initial rate against sulfide concentration on

a logarithmic scale at a constant concentration of  $\text{H}_2\text{O}_2$  and catalyst loading showed a negative ( $m_1 = -0.88$ ) slope. Thus, the reaction order with respect to sulfide concentration is negative for this reaction although negative order reactions are less common. The reaction orders with respect to  $\text{H}_2\text{O}_2$  and the catalyst were similarly determined by plotting the initial rate against the respective concentrations on a logarithmic scale for constant values of all other parameters and variables. The plots of the initial rate of reaction against catalyst loading and against the  $\text{H}_2\text{O}_2$  concentration were linear. Thus, the reaction is first order with respect to both  $\text{H}_2\text{O}_2$  and catalyst concentrations ( $m_2 = 1$ ;  $m_3 = 1$ ). The reaction rate constant,  $k$ , was determined from the slope of the plot (Fig. 8a) of the initial reaction rate ( $Y$ -axis) against the product of three concentration terms ( $X$ -axis) in Eq. (3).

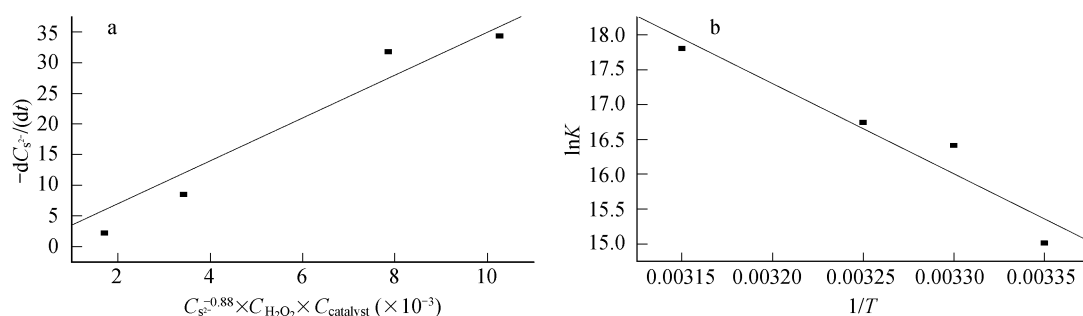
The exercise was carried out for the data collected at the four different temperatures. Figure 8b shows the Arrhenius plot (logarithmic values of rate constants on  $Y$ -axis against inverse of temperature on  $X$ -axis) of the rate constants. The activation energy determined from the slope of the line is  $E = 25.85$  kcal/mol.

## 2.4 Rate equation for sulfate formation

Power law rate equation for the sulfate formation is proposed as the following Eq.(4).

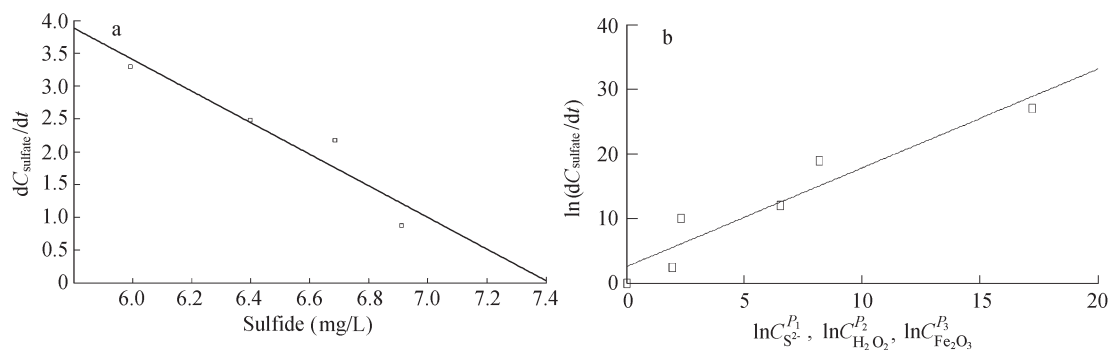
$$r_{\text{S}^{2-}} = C_{\text{S}^{2-}}^{p_1} C_{\text{H}_2\text{O}_2}^{p_2} C_{\text{Fe}_2\text{O}_3}^{p_3} \quad (4)$$

Order of reaction ( $p_1 = -2.4$ ) with respect to sulfide concentration was determined from the plot of the initial rate against sulfide concentration on a logarithmic scale at a constant concentration of  $\text{H}_2\text{O}_2$  and catalyst loading (Fig. 9a). The reaction orders with respect to  $\text{H}_2\text{O}_2$  and catalyst were similarly determined by plotting the initial rate against the respective concentrations. Plots of the initial rates of reaction against catalyst loading and against the  $\text{H}_2\text{O}_2$  concentration were linear. Thus, the reaction is almost first order with respect to both  $\text{H}_2\text{O}_2$  and catalyst concentrations ( $p_2 = 1.1$ ;  $p_3 = 1.5$ ). The reaction rate constant ( $K = 1.5$ ) was determined from the slope of the plot (Fig. 9b) of the initial reaction rate against the product of three concentration terms in Eq. (4).



**Fig. 8** Plot for determination of rate constant of sulfide removal (a) and Arrhenius plot of reaction rate for sulfide oxidation (b).





**Fig. 9** Plot for the determination of orders with respect to sulfide (a) and rate constant (b) for the sulfate formation.

### 3 Conclusions

Complete removal of sulfide in an aqueous solution was achieved by catalytic chemical oxidation process. From the present work following conclusions can be drawn: (1) rate of sulfide oxidation was found higher at lower initial sulfide concentration which shows an uncommon negative order of reaction with respect to sulfide; (2) rate of sulfide oxidation was found directly proportional to catalyst loading and hydrogen peroxide addition; (3) at higher temperature rate of sulfide oxidation by hydrogen peroxide in the presence of ferric oxide catalyst increases to a big extent; (4) the catalyst particles were relatively uniform in shape with < 200 nm average diameter, which is a nearly nano-range diameter; (5) the EDX analysis shows Fe, O and H as the major elements; (6) from the XRD picture it is clear that the main crystalline phase is ferric oxide.

The results of this study are expected to be useful for assessment of alternatives and actual remediation of sulfidic wastewater in chemical and allied industries.

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