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Removal of Ferrous Ion in Synthetic Waters by Catalytic Air Oxidation

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Catalytic air oxidation of ferrous ion in synthetic waters ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ solution) was studied at neutral medium in batch reactors. Sepiolite, ZnO, NiO, MgO, Co_3O_4, MoO_3., MnO_2 and $Al(OH)_3$ were separately used as catalyst. Iron(II) ion in water samples was analyzed by the bipyridine spectrophotometric method. Firstly, non-catalytic oxidation of Fe(II) in aqueous solution was investigated. However, low values of conversion percentage were obtained even if air was bubbled through the solution. An oxidation yield of 97 % was minimally obtained by resting only the solution at open air when an effective catalyst such as NiO was used. The activation energies were determined as 14.8 and 43.2 kJ/mol and the corresponding rate equations were obtained as $-r_A = 9.72\ e^{-1779/T}\ C_A$ and $-r_A = 1672\ e^{-5197/T}\ C_A$ for catalytic (NiO) and non-catalytic oxidation, respectively. The reaction order was found to be one with respect to Fe(II) concentration. Experiments were also conducted in a continuous system as a fixed bed reactor; however the obtained yields were very low.

Key Words: Water pollution, Ferrous ion, Air oxidation, Metal oxides, Sepiolite.

INTRODUCTION

Iron is a metallic element found in the earth's crust. Water percolating through soil and rock dissolves it. In addition to groundwater supplies, mine waters are also characterized by elevated concentrations of Fe(II) ions. When iron is dissolved in water, ferrous ion creates a clear solution. Iron usually does not present a health hazard in the household water supply; however, it can cause a variety of different nuisance problems such as staining, accumulation, taste and colour[1].

Ferrous ion is usually removed from water using chemical oxidants, which oxidize ferrous ion to the insoluble ferric state. The air oxidation can be carried out with lower cost by comparing to the use of chemical oxidants[2]. At the end of the oxidation, poor soluble compounds such as iron(III) oxides are formed and typically removed using a fitration system[3,4]:

$$2Fe^{2+} + \frac{1}{2}O_2 + 5H_2O \rightarrow 2Fe(OH)_3 + 4H^+$$

The oxidation of Fe(II) species in aqueous solution has been studied by many researchers[5-11]. Although the method studied is well known, more efficient catalysts are needed to be economically feasible. In this work, 8 different catalysts have been used for air oxidation of ferrous ions in water and the optimum catalyst has been tried to determine.

EXPERIMENTAL

It is known that the ferrous ion in water can be easily oxidized at basic medium by using air. However, very low yields have been obtained at non-basic solutions, especially at neutral ones[12]. Therefore, the present study was performed at neutral medium (Initial pH = 7) and room temperature (20 ºC) in a batch reactor. All reagents were of analytical grade. Distilled water was used after it was saturated to air. Fe(II) solutions were freshly prepared in four different concentrations (2, 5, 10 and 15 mg Fe^{2+}/mL) by dissolving the appropriate weights of $Fe(NH_4)_2(SO_4)_2.6H_2O$ in water. Ferrous ion was oxidated by blowing air (20.3 mL/s) through the solution or resting it at open air for residence times of 15 min. In order to catalyze the oxidation, 8 different compounds (2 g sepiolite, 1 g ZnO, 0.5 g NiO, 0.4 g MgO, 0.5 g Co_3O_4, 0.6 g MoO_3, 0.5 g MnO_2 and 1 g $Al(OH)_3$ per 100 mL solution) were used. Water samples were analyzed by the bipyridine spectrophotometric method[13]. All experiments were performed twice.

Experiments were performed in a continuous system too. For this purpose, the system in previous study was used[14] and the Fe(II) solution (50 mL/min) was passed downwards through a fixed bed reactor. The inner diameter and height of pyrex glass reactor used were 5.6 and 64 cm, respectively. Glass beads were placed as an inert packing at the column inlet and outlet. The height of catalyst in the middle part of the column was 3 cm. The catalyst was pellets prepared from NiO (5 %) and $Al(OH)_3$ (95 %) of which the lenght and diameter were 0.25 and 1.5 cm, respectively.

Experiments were also made to study the kinetics of oxidation with and without catalyst. For this purpose, Fe(II) concentrations *versus* time were measured. Rate constants and order of reaction were determined by these values. In order to calculate the activation energy of reaction, the studies were conducted at 3 different temperatures (16, 43 and 63 ºC). A thermostated bath was used to keep the solution temperatures constant[15].

RESULTS AND DISCUSSION

Oxidation yields obtained at various conditions: It is known that non-catalytic air oxidation of ferrous ion can not be performed with high conversion at neutral medium[12,16]. This result was supported in present studies and very low yields were obtained at the absence of catalyst. Therefore, the experiments were carried out catalytically. In the first part of experiments, the solution was rested at open air. Air was bubbled through the solution in the second one. At the end of the studies performed with a series of catalysts, the oxidation yields were calculated as conversion percents and they were plotted *vs.* the initial concentration (C_o) of ferrous ion in the solution. The results have been shown in Figs. 1-4.

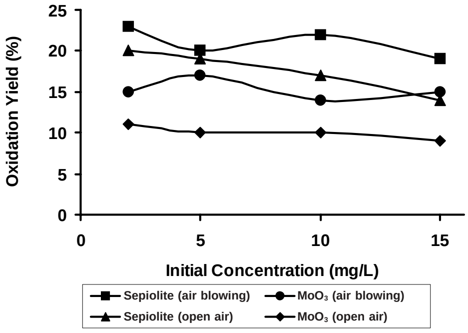

Fig. 1. Oxidation yields obtained with sepiolite and MoO_3

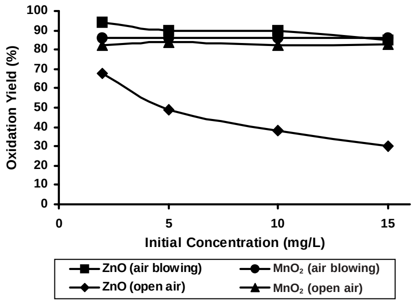

Fig. 2. Oxidation yields obtained with ZnO and MnO_2

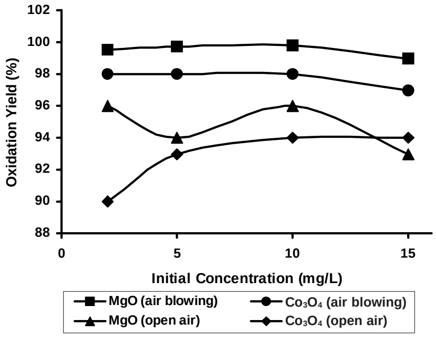

Fig. 3. Oxidation yields obtained with MgO and Co_3O_4

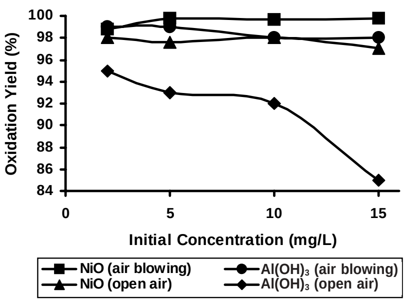

Fig. 4. Oxidation yields obtained with NiO and $Al(OH)_3$

Although the yields obtained with sepiolite are higher than those with MoO_3 catalyst, it is maximum 23 % even if air is blown to the solution (Fig. 1). As seen from Fig. 2, yields in the range of 30 to 94 % can be obtained by accelerating the reaction with ZnO or MnO_2. It is, however, possible to complete almost the oxidation by catalyzing with MgO or Co_3O_4 (Fig. 3) and also with NiO or $Al(OH)_3$ (Fig. 4). These results are agreed with the assumptions of Rönnholm *et al.*[6].

The yields achieved with the last four catalysts are 85 % minimum. When NiO was used, yields of 97 % or above have been obtained even if the solution was left at open air. Therefore, it can be stated that the nickel oxide is the most effective one among the eight catalysts used in this work.

As known, the properties of nickel oxide are related to its preparation method. Black nickel oxide has more oxygen and chemical reactivity while the green one is an inert and refractory material. However, both of them are used as a catalyst by admixing with a support material[17]. These catalysts produced by several techniques have been tested in various processes and the oxidation has been accelerated by them[18,19].

In light of these findings, it can also be said that higher yields can be achieved by blowing air to the solution instead of resting at open air. This result has also been observed by some researchers[16,20]. High yields can be cited to assisting of O_2 transfer by an increase in gas-liquid contacting efficiency[21].

Pellets were prepared in a proportion of NiO (5 %) and $Al(OH)_3$ (95 %) weightly from two catalysts used in this work. In this stage, nickel oxide was preferred as the most effective catalyst of this work. However, aluminium hydroxide was weightly used because of both its efficiency and economical feasibility. With these pellets, experiments were conducted in a continuous system in which the solution was passed downwards through a fixed bed reactor. It was aimed to simulate a trickling filter widely used in practice[22]. However, very low yields were observed in these conditions. This result was perhaps sourced from the shortened residence time of solution in the column and/or the decrease of porosity in pressured pellets.

Oxidation kinetics: It has been determined by many researchers[23,24] that the air oxidation of iron in water is first order with respect to Fe^{2+} concentration. In order to study the kinetics of oxidation, the values of Fe(II) concentration (C) *vs.* time (t) were measured at three different temperatures (16, 43 and 63 ºC) in the case of that without and with catalyst (NiO).

Assuming the reaction is first order and the measured Fe(II) concentrations *vs.* time was plotted and thus the semi-logarithmic plot is drawn linearly (Fig. 5). The plots drawn for other cases are also similar to this one. Hence, it can be said that the oxidation is first order as expected and the slope of semi-logarithmic plot represents the rate constant of reaction (k). In fact, this can also be inferred from the Figs. 1-4. As seen from there for the most cases, the conversion does not depends on the initial concentration.

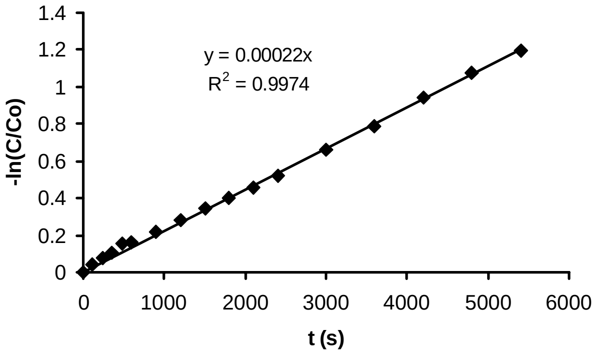

Fig. 5. Semi-logarithmic plot of Fe(II) concentrations *versus* time (Non-catalytic reaction, T = 63 ºC)

As shown in Table-1, rate constants are much higher in catalytic reactions by comparing to those without catalyst and they increase with an increase in temperature. In this case, the activation energy of reaction (E) can be determined by using the van't Hoff-Arrhenius equation[3]. The slopes of plots drawn as ln k *vs.* 1/T give the values of (-E/R) and the activation energy can be calculated (Fig. 6). As seen from Table-2 decrease of 28.4 kJ/mol in activation energy can be observed when an effective catalyst (NiO) was used in the oxidation.

TABLE-1
RATE CONSTANTS DETERMINED AT VARIOUS CONDITIONS

Reaction	Temperature (°C)	Rate constant (s^{-1})
Non-catalytic	16	0.000023
	43	0.000180
	63	0.000220
NiO-catalytic	16	0.021000
	43	0.035200
	63	0.046200

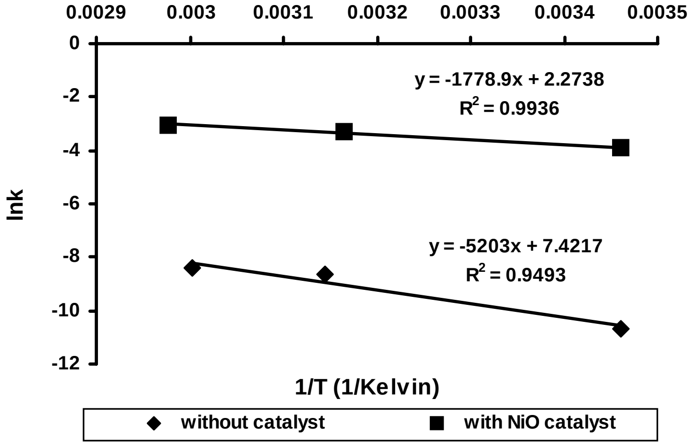

Fig. 6. Semi-logarithmic plots of k *vs.* 1/T

TABLE-2
VALUES OF ACTIVATION ENERGY FOR CATALYTIC AND NON-CATALYTIC OXIDATION

Reaction	Activation energy (kJ/mol)
Non-catalytic	43.2
NiO-catalytic	14.8

Van't Hoff-Arrhenius coefficients can also be found from the deviations in this graph and van't Hoff-Arrhenius equations are formed as shown below:

Non-catalytic oxidation : $k = 1672\ e^{-5203/T}$
Catalytic (NiO) oxidation : $k = 9.72\ e^{-1779/T}$

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