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Yu-Wen Lu[a]; Chun-Ping Huang[a]; Yao-Hui Huang[ab]; Chih-Ping Lin[a]; Hung-Ta Chen[b]
[a] Department of Chemical Engineering, National Chen-Kung University, Tainan, Taiwan [b] Sustainable Environment Research Center, National Cheng Kung University, Tainan, Taiwan

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Yu-Wen Lu,[1] Chun-Ping Huang,[1] Yao-Hui Huang,[1,2]
Chih-Ping Lin,[1] and Hung-Ta Chen[2]

[1]Department of Chemical Engineering, National Chen-Kung University,
Tainan, Taiwan
[2]Sustainable Environment Research Center, National Cheng Kung
University, Tainan, Taiwan

Abstract: New, efficient, and a cheap method for the removal of ferrous ion from aqueous in a fluidized bed reactor was developed. Different from the adsorption process in the treatment of iron species, the immobilization of iron oxide on support media in a fluidized bed never reaches saturation. Furthermore, the immobilized iron oxide is reusable in catalysis and adsorption. Silica sand (Si) and iron oxide (SiG) were employed as support media to remove Fe(II) from aqueous in a fluidized bed reactor. The oxidation rate of Fe(II) and the immobilization rate of iron oxide are strongly depend on pH value so the variation of solution pH is considered to be the major parameter. Furthermore, the aeration effect on iron removal efficiency is investigated. 97% of total iron was removed at pH 8 in the presence of SiG and 87% of total iron was removed at pH 6 in the presence of Si. When the initial pH was adjusted to 6 and was not adjusted during the reactions, the optimum total iron removal efficiency (97%) was found. The air aeration was provided to keep the dissolved oxygen in constant. Aeration air accelerates the oxidation of ferrous ion, but does not improve the total iron removal efficiency.

Keywords: Fluidized bed reactor, oxidation, iron removal, immobilization, iron oxide

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Address correspondence to Yao-Hui Huang, Department of Chemical Engineering, National Chen-Kung University, University Road, Tainan City 701, Tainan, Taiwan. Tel.: +886-2757575-62636; Fax: +886-6-2344496; E-mail: yhhuang@mail.ncku.edu.tw

INTRODUCTION

Iron, being the fourth most abundant element in the earth's crust, is a common constituent of groundwater (1). US EPA recommends the secondary drinking water regulation for dissolved iron as 0.3 mg/L (2). More than 80% of ground waters contain much higher than 0.3 mg/L of dissolved iron in Taiwan. Higher amount of dissolved iron in groundwater leads to discoloration, bad taste, and stains the laundry and plumbing fixtures. Deposited iron formed by oxidized iron(II) in the distribution system promote microorganisms growth, leading to high turbidity. The accumulations of deposited iron in the pipes reduce the carrying capacity, eventually blocking up the pipes. Hence, water supplies containing iron species result in pollution and operational problems (3). Recently, groundwater has been withdrawn to be the source of ultra pure water in some electronic industrials and semiconductor plants in Taiwan. Iron species are considered the major pollutants in wafer and electronic elements. Moreover, the applications of groundwater for electronic processes, lavation, and drinking water, iron species have to be removed. Ferrous ion is the major iron specie in groundwater due to the anoxic condition.

Conventionally, aeration, coagulation, and then filtration are the major processes for the removal of iron species from groundwater. The main drawbacks of these traditional processes are the production of large number of sludge, requiring large space for precipitating tank, and imperative disposal of iron precipitate. Sharma, S.K., et al. (2003) indicated that ferrous ion could adsorb on the surface of media by follow step (4):

$$\equiv S - OH + Fe^{2+} \longrightarrow \equiv S - OFe^{+}H^{+} \tag{1}$$

where $\equiv$S represents the surface of media.

The adsorbed iron is oxidized by the dissolved oxygen (DO) in aqueous and new adsorption sites are generated.

$$\equiv S - OFe^{+} \frac{1}{4} O_2 + \frac{3}{2} H_2O \rightarrow \equiv S - OFe\langle^{OH}_{OH} + H^{+} \tag{2}$$

$$\equiv S - OH + Fe^{2+} + \frac{1}{4} O_2 + \frac{3}{2} H_2O \rightarrow \equiv S - OFe\langle^{OH}_{OH} + 2H^{+} \tag{3}$$

Equation (3) represents the mechanism of the regenerated adsorption sites.

Sharma, S.K., et al. (2001) proposed a physicochemical mechanism, namely oxidation-floc formation (floc filtration) and adsorption-oxidation (adsorptive filtration), to describe this process (Fig. 1) (5). In floc filtration, Fe(II) in groundwater is oxidized to insoluble Fe(III) and the generated flocs are removed by filters. In adsorptive filtration, Fe(II) in anoxic groundwater is adsorbed on the surface of the filter media (6, 7), and then the adsorbed Fe(II) is oxidized to immobilized iron oxide on the filter media by O_2.

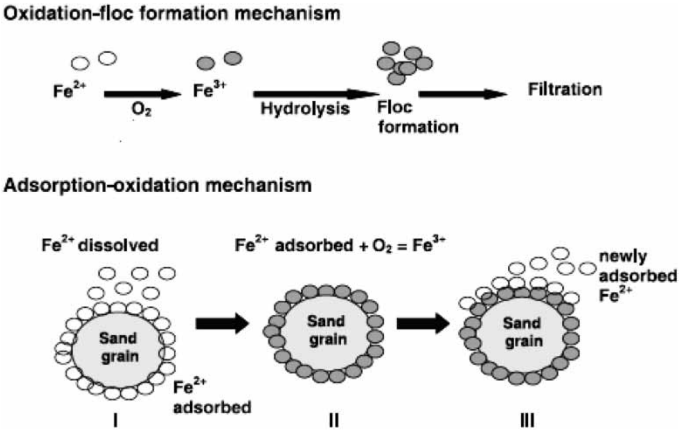


Figure 1. Physicochemical iron removal mechanism (5).

Diz H.R. and Novak J.T. 1998combined bioreactor and fluidized bed reactor (FBR) for the removal of iron from the acidic water (8). Firstly, the bacteria converted Fe(II) to Fe(III), using the energy available in this oxidation for growth in the bioreactor. Secondly, chemical precipitation of iron proceeded in a FBR. Recently, fluidized bed reactors have been extensive applied in the removal of cations from wastewater. In the previous study, Fe^{2+} was oxidized to immobilized iron oxide on supports by H_2O_2 at acidic condition in a fluidized bed reactor (9). The immobilized iron oxides are found to effectively adsorb heavy metal ions (10–12) and to activate H_2O_2 for the degradation of organic contaminants (13, 14). Hence, the immobilized iron oxides are applicable to be adsorbents and catalysts. Different from the adsorption process in the treatment of iron species, the immobilization of iron oxide on support media in a fluidized bed never reaches saturation. Hence, the advantages of iron removal in a fluidized bed reactor require smaller space, an unnecessary regeneration process and produced reusable byproduct (iron oxides).

However, the H_2O_2 is a relatively expensive oxidant in terms of the oxidation of Fe(II) and the acidic condition is unfriendly for environment. Recently, a new method for the removal of ferrous ion from aqueous was developed (15). Based on this method, the oxidant of Fe(II) was replaced by air or O_2 in a fluidized bed reactor at neutral condition. Iron oxide, SiG, is successfully prepared by this method. In this work, silica sand (Si) and SiG were employed as support media to remove Fe(II) from aqueous in a fluidized bed reactor. The oxidation rate of Fe(II) and immobilization rate of iron oxide are strongly depend on pH value so the variation of solution pH is considered to be the major parameter. Optimum pH for total iron removal efficiency should be found. Furthermore, the aeration effect on iron removal efficiency is also investigated.

MATERIALS AND METHODS

Fluidized Media

Virgin silica sands (Si) were washed by deionized water for several times, and then treated by HCl ($pH < 2$) to clean the surface of silica sands for 24 hours. Finally, the silica sands were rinsed by deionized water and dried at room temperature. The ferrous ion in ground water was oxidized by aerated air, and the iron oxide was simultaneously immobilized on non-porous silica sand at neutral pH in a fluidized bed reactor. The iron oxide, SiG, was withdrawn from the fluidized bed reactor after 6 months. SiG was washed by deionized water to avoid deposits and dried at room temperature before using.

Experimental Set Up

The experimental set-up, 10 L fluidized bed reactor (FBR), was shown in Fig. 2. There were 3000 g of the fluidized media (Si or SiG) filled into the reactor. The modelling groundwater solution contained 20 mg/L ferrous ion was prepared with tape water ($28 \pm 1^{\circ}C$, $[CO_3^{2-}] \sim 250 \pm 100$ ppb) and poured into the FBR. The sampling and measurements of dissolved oxygen (DO), temperature (T), oxidation reduction potential (ORP) and pH were positioned in the top of FBR. The solution pH was adjusted using NaOH. The chemicals employed in this study are listed in Table 1.

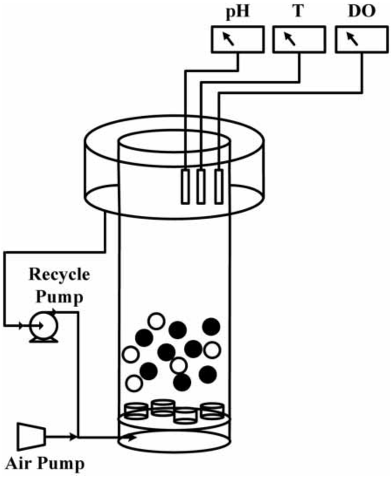


Figure 2. Fluidized bed reactor.

Table 1. Chemical and materials

Chemical	Purpose
$FeSO_4 \cdot 7H_2O$	Iron(II) source
NaOH	Alkalinity, pH control
H_2SO_4	Acidity, pH control
HCl	Washing
1,10-phenanthroline	Measurement of iron(II)
$CH_3COONa \cdot 3H_2O$	Measurement of iron(II)
CH_3COOH	Measurement of iron(II)

Measurements

Half of each sample was filtrated immediately on site with 0.2 μm membrane for measurement of iron (II). Ferrous iron contents of the samples were measured with 1, 10-phenanthroline method (16). Total iron content ([Fe]) of the samples without filtration was dissolved by concentrated H_2SO_4, and then was measured with atomic absorption spectrophotometer. Total iron removal efficiency (Fe rev.) is defined as $([Fe]_0 - [Fe])/[Fe]_0$. The definition of total iron removal is the iron species immobilized on support media rather than the formation of precipitate. If all the formation of iron species is precipitate in solution, the total iron removal efficiency is 0%. Furthermore, if all the formation of iron species is immobilized iron oxide on media, the total iron removal efficiency is 100%.

The SiG was identified from the nitrogen adsorption data obtained at the temperature of liquid nitrogen using an automated adsorption instrument (MicromeriticsASAP2010, USA). The Brunauer–Emmett–Teller (BET) surface area of the catalyst was obtained from the data of the isotherms. Morphology of the SiG was determined using a JEOL JSM-6700F HR-FESEM. The amount of amorphous iron oxide was estimated by the quantity of iron dissolved in an oxalate buffer according to the method of (17).

RESULTS AND DISCUSSION

Characteristics of Support Media

The characteristics of Si and SiG were listed in Table 2. The total immobilization iron of the SiG is 44.0 mg Fe/g-solid. 41.85 mg Fe/g-solid of amorphous iron oxide was dissolved by oxalate so it implies that 95.1% of iron oxide immobilized on the Si is amorphous type. Only rare amounts of iron oxide were immobilized on Si media, hence the grain size is similar due to very thin thickness of immobilized iron oxide. The specific surface area of SiG is higher than of Si media.

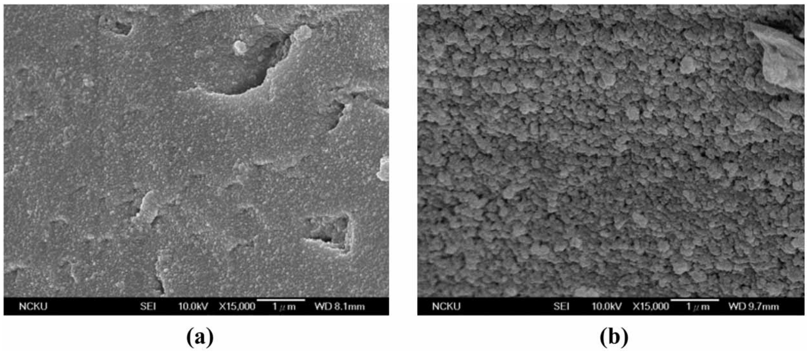
Table 2. Characteristics of the silica sand (Si) and iron oxide coated sand

Properties	Si	SiG
Color	White	Brown
Support	SiO_2	SiO_2
Total iron content (mg/g-solid)	0	44.0
Oxalate-soluble iron (mg/g-solid)	0	41.85
Surface amorphous iron (%)	0	95.1
Bulk density (g/cm^3)	2.43	2.63
Specific surface area (BET) (m^2/g)	0.76	3.48
Grain size (mm)	0.89	0.89

Figure 3 shows SEM micrographs of the Si and SiG. Si exhibits irregularly shaped (Fig. 3a) and the immobilized iron oxide, SiG, shows that iron species deposit on the surface of silica sand after being treated in the FBR for 6 months (Fig. 3b).

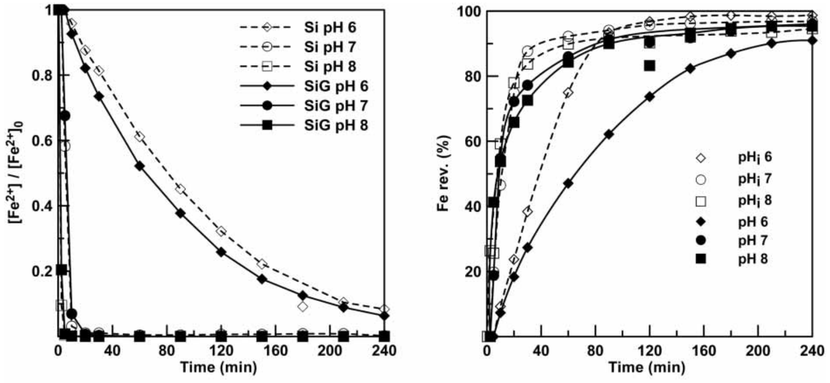
Effect of pH

Generally, the higher solution pH, the faster oxidation rate of ferrous ion does. Moreover, the precipitation rate of iron is also proportional to pH value. The oxidation rate of ferrous ion increases with increasing pH (Fig. 4a). Apparently, the oxidation of ferrous ion under pH 7 and 8 is quit fast so all the ferrous ion was oxidized within 30 minutes. Figure 4b indicates the effect of pH on the removal of total iron. For SiG, the total iron removal efficiency increases 10% to 30% when pH rises from 6 to 8. However, pH 6 is the optimum condition of total iron removal efficiency for Si. After the



(a) (b)

Figure 3. SEM micrograph of Si (a), 15000x and SiG (b), 15000x.



(a) (b)

Figure 4. (a) pH effect on the oxidation of ferrous iron. (b) pH effect on the total iron removal efficiency ($[Fe^{2+}] = 20\ mg/L$, $Si = 3000\ g$, $SiG = 3000\ g$, total solution volume $= 10\ L$).

oxidation of ferrous ion, the precipitation and the immobilization of iron species are competition reactions in the FBR. When the immobilization rate of iron on support media is slower than the oxidation rate of ferrous ion, the total iron removal is inefficiency due to the formation of iron precipitate. Obviously, the immobilization rate of iron species on SiG is faster than that on Si. On the other hand, virgin silica sand (Si) is relatively inefficient for the immobilization of iron species comparing to the iron oxide, SiG. 97% of total iron was removed at pH 8 in the presence of SiG and 87% of total iron was removed at pH 6 in the presence of Si. Based on the experiment, SiG was suitable to be the support of iron oxide.

The comparison of the pH effect with and without controlling was shown in Fig. 5. Figure 5a shows that the oxidation rate of ferrous ion under pH_i 6 (without controlling) is faster than that under pH 6 (with controlling). Furthermore, the total iron removal efficiency is about 97% and 90% at pH_i 6 and pH 6, respectively. The removal rate of total iron at pH_i 6 is much faster than that at pH 6. However, the system pH without controlling is slight increase with reaction time (data not shown) and the increasing pH lead to the oxidation rate of ferrous ion increase. The increasing pH is probably ascribed to the iron species which react with carboxylic ion. The mechanism of the increasing is not clear and is worthy of being investigated in the future. The dissolved oxygen (DO) is consumed by the oxidation of ferrous ion (Fig. 5c).

Effect of Aeration

The oxidation of Fe^{2+} by oxygen produces ferric (hydr)oxide (18). Accordingly, the oxidation of 20 mg/L ferrous ion consumes 3 mg/L oxygen.

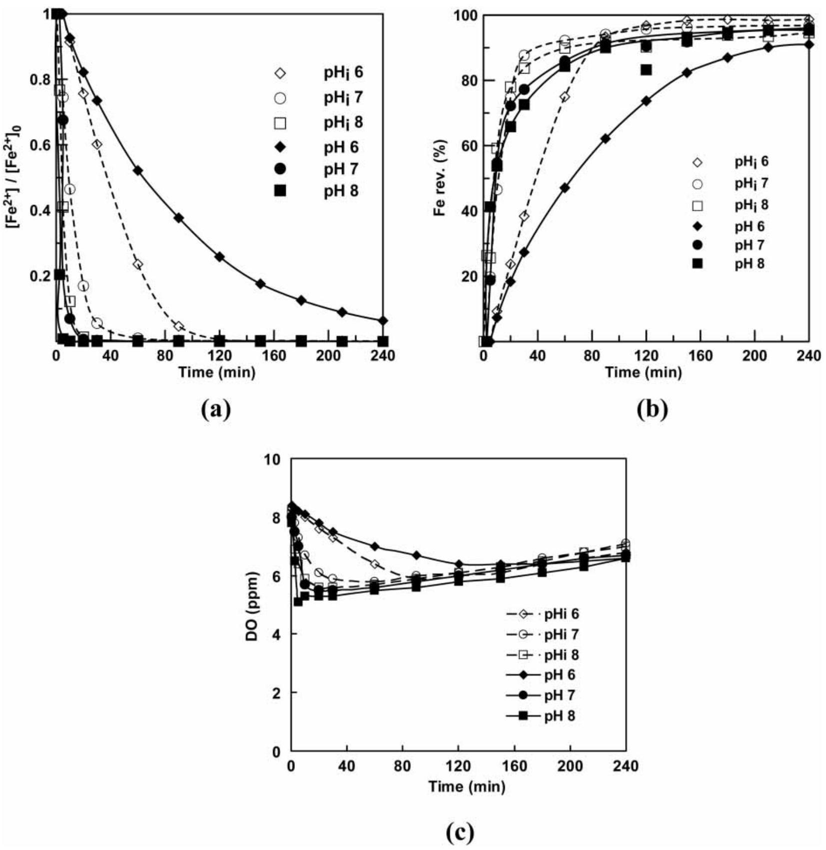


Figure 5. (a) Controlled pH effect on oxidation of ferrous iron. (b) Controlled pH effect on removal of total iron. (c) Variation of DO ($[\mathrm{Fe}^{2+}] = 20\ \mathrm{mg/L}$, SiG = 3000 g, total solution volume = 10 L).

Based on the result shown in Fig. 5c, the dissolved oxygen was enough to oxidize 20 mg/L ferrous ion.

$$\mathrm{Fe}^{2+} + \frac{1}{4}\mathrm{O}_2 + 2\mathrm{OH}^- + \frac{1}{2}\mathrm{H}_2\mathrm{O} \longrightarrow \mathrm{Fe(OH)}_{3(s)} \tag{4}$$

However, the drop concentration of DO may result in slower oxidation of ferrous ion. The air aeration was provided to keep the DO in constant. Figure 6 shows that the oxidation of ferrous ion and total iron removal efficiency at $\mathrm{pH_i}$ 6 were improved with aeration air; this result also consisted with the literature report (18). On the contrary, the aeration air exhibited negative effect on total iron removal efficiency at $\mathrm{pH_i}$ 7 and 8. Aeration air accelerates the oxidation of ferrous ion and precipitation of iron hydr(oxide) at $\mathrm{pH_i}$ 7 and 8 so it is an unfavorable situation of iron species immobilization.

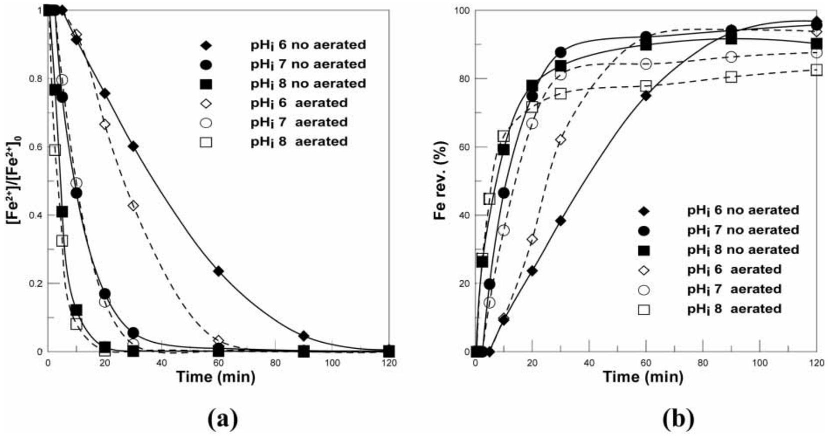


Figure 6. (a) Aeration effect on oxidation of ferrous iron. (b) Aeration effect on removal of total iron. ($[Fe^{2+}] = 20$ mg/L, SiG = 3000 g, total solution volume = 10 L).

On the other hand, the aeration led to rough mixing of bubbling in FBR and probably made mass transfer resistant for the immobilization of iron species. Based on these results, the aeration air is redundant because the mixture of liquid, solid and air is good enough for FBR.

CONCLUSIONS

- 97% of the total iron was removed at pH 8 in the presence of SiG and 87% of total iron was removed at pH 6 in the presence of Si. SiG is a better support for iron removal than silica sand.
- For SiG, the total iron removal efficiency increases 10% to 30% when pH rises from 6 to 8. However, pH 6 is the optimum condition of total iron removal efficiency for Si.
- The oxidation of ferrous ion and total iron removal efficiency at pH_i 6 were improved with aeration air, but the aeration air is redundant because the mixture of liquid, solid, and air is good enough for FBR.
- Practical application of this technology for the pretreatment of groundwater, which is the source of ultra pure water in an electronic plant, has been successful established.

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