Oxidation and immobilization of iron and manganese by a fluidized bed reactor
Yao-Hui Huang, Chun-Ping Huang, Yu-Wen Lu and Chun-Yu Lo

ABSTRACT
An iron and manganese species immobilization technology was developed in a fluidized bed reactor (FBR) with a new fluidized media, immobilized iron oxide (namely FeOx-30). The FeOx-30 catalyst exhibited excellent performance as a catalyst for the oxidation of Mn$^{2+}$. About 95% and 30% of the manganese species were immobilized on FeOx-30 and silica sand in FBR, respectively. The oxidation rates of Fe$^{2+}$ and Mn$^{2+}$ and the immobilization efficiencies of iron and manganese oxides strongly depend on pH value. Usually during oxidization the pH values of the solution containing Fe$^{2+}$ must be above 7, and Mn$^{2+}$ must be above 9. During this study, large amounts of iron species leached from the surface of FeOx-30 only when manganese was in the system. The surface of the FeOx-30 became fragile in a single system. However, the removal of iron and manganese species simultaneously was better than only the removal of manganese in an FBR. In the binary system, the optimum pH condition for immobilization of both iron and manganese species was pH 9. The higher catalyst loading in the binary system led to a higher removal efficiency of iron and manganese.

Key words | fluidized bed reactor, immobilization, iron, manganese, oxidation

INTRODUCTION
Water resources are extremely important for Taiwan, an island. Groundwater is an important water resource for drinking and cleaning in Taiwan. However, iron and manganese are commonly found in natural groundwater. They are used principally in the manufacture of iron and steel alloys, as an oxidant for cleaning, bleaching and disinfection in the form of potassium permanganate, and also as an ingredient in many other products (WHO 2007). Iron and manganese are usually present in groundwater as divalent ions (Fe$^{2+}$ and Mn$^{2+}$) (Ellis et al. 2000). The US EPA recommends that the secondary drinking water regulations for dissolved iron and manganese to 0.3 and 0.05 mg/L respectively (USEPA 2007). Recently, groundwater has been withdrawn as the source of ultra pure water in some electronic industries and semiconductor plants in Taiwan. Metal ions species are considered major pollutants in wafer and electronic elements. Moreover, in applications using groundwater for electronic processes, cleaning and drinking water, metal species have to be removed. Conventionally, the removal of iron and manganese from groundwater is carried out by means of oxidation and depth filtration processes. Oxygen and other oxidants, such as chlorine and potassium permanganate (KMnO$_4$), are generally used for the oxidation of Fe$^{2+}$ and Mn$^{2+}$ (Ellis et al. 2000). The solid products of oxidation (FeOOH·H$_2$O and MnO$_2$) are then precipitated or filtered through a granular bed, commonly green sand (WHO 2006). The main drawbacks of these traditional processes are the production of a large amount of sludge, the large size of precipitating tanks, the need for filters, and the need for the precipitates disposal. However, the first step in the treatment of Fe$^{2+}$ and Mn$^{2+}$ is the oxidation process. Aeration air is considered the cheapest oxidant for the oxidation process. The oxidation of Fe$^{2+}$ and Mn$^{2+}$ is strongly dependent on pH...
the pH value (Faust & Aly 1999). It is known that Mn$^{2+}$ oxidation in the laboratory is slow (requiring days) when the pH $< 9$, and that the oxygenation kinetics are autocatalytic (Sung & Morgan 1981). Goldberg (1961) first suggested the catalytic oxidation of manganese by oxygen on an iron oxide surface as a possible mechanism of ferromanganese nodule formation.

Fluidized bed reactors (FBR) have been extensively applied in the removal of cations from wastewater. In a previous study, ferrous ions were oxidized using H$_2$O$_2$ and iron oxides were immobilized on supports in acidic conditions in an FBR (Huang et al. 2000). It was found that the immobilized iron oxides effectively adsorbed heavy metal ions (Edwards & Benjamin 1989; Bailey et al. 1992; Lai et al. 1994; Lai et al. 2000; Smith & Chatterjee 2000; Huang et al. 2007a,b). Hence, the immobilized iron oxides were applicable for use as adsorbents and catalysts. The major limitation of adsorption process for the treatment of iron species is adsorption saturation. However, the immobilization of iron oxide on support media in an FBR can overcome the limitation of adsorption process. Furthermore, the advantages of iron removal in an FBR are that a smaller space is required, there is no need for a regeneration process and reusable byproducts (iron oxides) are produced.

A new method for the removal of ferrous ions from aqueous solution has been developed (Huang et al. 2006). Based on this method, the oxidant of Fe$^{2+}$ was replaced by air in an FBR under neutral conditions. Immobilized iron oxide (SiG) was successfully produced using this method. In previous work, silica sand (Si) and SiG were employed as support media to remove Fe$^{2+}$ from aqueous solution in a FBR. Furthermore, the new oxidized iron species continuously immobilized on SiG and new immobilized iron oxides (FeO$_x$-30) produced in the reactor (Lu et al. 2008). In this study, the new immobilized iron oxide, FeO$_x$-30, was employed as the fluidized media in the FBR for the treatment of the binary species, Fe$^{2+}$ and Mn$^{2+}$. The oxidation rates of Fe$^{2+}$ and Mn$^{2+}$, and the immobilization efficiencies of iron and manganese oxides, all strongly depend on pH value, so the variations in the pH of the solution is considered to be a major parameter. An optimum pH for total iron and manganese removal efficiencies should be found, and the system loading effect on iron removal efficiency is also a matter that requires investigation. The simultaneous oxidation and immobilization of iron and manganese species in an FBR is the main purpose of this study.

**MATERIALS AND METHODS**

**Fluidized media**

Virgin silica sands (Si) were washed with deionized water several times and then treated with HCl (pH $< 2$) for 24 hours to ensure it was clean. Then, the silica sands were rinsed with deionized water and dried at room temperature. A new immobilized iron oxide, FeO$_x$-30, was developed using a 10 L FBR in which ferrous ions were treated for 3 months (Lu et al. 2008).

**Experimental set-up and chemicals**

The experimental set-up included a 1.6 L FBR and is shown in Figure 1. 160 g (or 600 g) of the fluidized media (FeO$_x$-30) were placed into the reactor. The iron ions and manganese ions in the aqueous solution were prepared from FeSO$_4$$\cdot$7H$_2$O (Merck) and MnSO$_4$$\cdot$H$_2$O (Merck). The solution pH was adjusted using NaOH. The modelling groundwater...
solution, which contained Mn$^{2+}$ (2 mg/L) and Fe$^{2+}$ (20 mg/L), was prepared by using deionized water and poured into the FBR. The measurements of dissolved oxygen (DO), temperature (T) and pH were monitored in the top of the FBR. Also, the samples were withdrawn from the top of the FBR periodically.

**Measurements**

Half of each sample was filtrated immediately on site with a 0.2 μm membrane to measure the ferrous ions and dissolved manganese ions. The ferrous ion content of the samples was measured with a 1,10-phenanthroline (Riedel-de Haen) method (Stookey 1970). The dissolved manganese ions were measured using an atomic absorption spectrophotometer. The total iron ([Fe]) and manganese ([Mn]) content of the samples without filtration were dissolved in concentrated H$_2$SO$_4$ and then were measured with an atomic absorption spectrophotometer. The immobilizations of iron and manganese were defined as ([Fe]$_0$ − [Fe])/[Fe]$_0$ and ([Mn]$_0$ − [Mn])/[Mn]$_0$. The immobilizations of iron and manganese indicated that the iron and manganese species were immobilized by support media rather than through the formation of a precipitate. If all of the iron or manganese species formed were precipitates in solution, the immobilization of iron or manganese was 0%. Furthermore, if all iron or manganese species formed were immobilized into fluidized media, the immobilization of iron or manganese was 100%.

The FeO$_x$-30 was identified from the nitrogen adsorption data obtained at the temperature of liquid nitrogen using an automated adsorption instrument (Micromeritics ASAP2010, USA). The Brunauer–Emmett–Teller (BET) surface area of the catalyst was obtained from the isotherm data. Morphology of the FeO$_x$-30 was determined using a JEOL JSM-6700F HR-FESEM. An XRD powder diffraction measurement of FeO$_x$-30 was performed on a powder diffractometer (Rigaku RX III) using Cu Kα radiation. The accelerating voltage and current were 40 kV and 30 mA. The amount of amorphous iron oxide was estimated by the quantity of iron dissolved in an oxalate buffer according to the method referenced in (Schwertmann & Cornell 2000).

**RESULTS AND DISCUSSION**

**Characteristics of FeO$_x$-30**

The characteristics of Si and FeO$_x$-30 are listed in Table 1. The total immobilized iron of the FeO$_x$-30 is 65.83 mg Fe/g-solid. 65.56 mg Fe/g-solid of amorphous iron oxide was dissolved by oxalate, implying that 99.9% of the immobilized iron oxide was of an amorphous type. Only small amounts of iron oxide were immobilized in the Si media, hence the grain size was similar because of the thinness of the immobilized iron oxide. The specific surface area of FeO$_x$-30 was higher than that of Si media.

**Table 1** | Properties of support and FeO$_x$-30

<table>
<thead>
<tr>
<th>Properties</th>
<th>Support</th>
<th>FeO$_x$-30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>White</td>
<td>Black</td>
</tr>
<tr>
<td>Material</td>
<td>SiO$_2$</td>
<td>Iron oxide</td>
</tr>
<tr>
<td>Total iron content (mg/g-solid)</td>
<td>– 65.83</td>
<td></td>
</tr>
<tr>
<td>Oxalate-soluble iron (mg/g-solid)</td>
<td>– 65.56</td>
<td></td>
</tr>
<tr>
<td>Surface amorphous iron (%)</td>
<td>– 99.9</td>
<td></td>
</tr>
<tr>
<td>Bulk density (g/cm$^3$)</td>
<td>2.43</td>
<td>2.67</td>
</tr>
<tr>
<td>Specific surface area (BET) (m$^2$/g-solid)</td>
<td>0.759</td>
<td>12.8</td>
</tr>
<tr>
<td>Average grain size (mm)</td>
<td>0.89</td>
<td>0.90</td>
</tr>
</tbody>
</table>

**Figure 2** shows SEM micrographs of the Si and FeO$_x$-30. Si exhibits an irregular shape (Figure 2a), and FeO$_x$-30 shows a flat surface iron species (Figure 2b). **Figure 3** shows the XRD patterns of Support (silica), FeO$_x$-30, and the standards of SiO$_2$ and iron oxides. The main diffraction peaks of the FeO$_x$-30 were compared with α-FeOOH, β-FeOOH, γ-FeOOH, α-Fe$_2$O$_3$ and SiO$_2$. Accordingly, FeO$_x$-30 was identified as an amorphous iron oxide.
The effect of fluidized media for the removal of Mn$^{2+}$

In previous work, ferrous ions were successfully oxidized and immobilized on different fluidized media (Lu et al. 2008). A new immobilized iron oxide, FeO$_x$-30, was applied for the removal of manganese in a FBR. Figure 4a shows that the FeO$_x$-30 is much better than silica sand for the removal of manganese. If there were no fluidized media in the reactor, the Mn$^{2+}$ could not be oxidized within 6 h (data not shown). About 95% and 30% of manganese species were immobilized on FeO$_x$-30 and silica sand in the FBR, respectively. Hence, the iron oxide, FeO$_x$-30, proved to be a good catalyst for the oxidation and immobilization of manganese species. Obviously, large amounts of iron species (without filtration) leached from the surface of FeO$_x$-30 in the presence of manganese (Figure 4b). The leached iron species caused the solution become turbid. The oxidative removal of Mn$^{2+}$ from the solution was catalyzed by FeO$_x$-30 surface, and iron was leached from the surface of FeO$_x$-30 during the catalysis, while manganese from solution was immobilized.

The effect of solution initial pH for single and binary systems

Generally, the higher the solution pH, the faster the oxidation rates of Fe$^{2+}$ and Mn$^{2+}$. However, the pH conditions required for the oxidation of Fe$^{2+}$ and Mn$^{2+}$ with oxygen are different. Usually, the pH values for the oxidation of Fe$^{2+}$ and Mn$^{2+}$ are above 7 and 9 respectively. The catalyst, FeO$_x$-50, was used for the oxidation and immobilization of iron and manganese species at different initial solution pH levels ($pH_i$) in the FBR. The oxidation and immobilization efficiency of ferrous ions in the presence of manganese (binary system) at $pH_i$ is shown in Figure 5a. The ferrous ions were easily oxidized from $pH_i$ 7 to 9. However, almost 100% of the iron species were immobilized on FeO$_x$-30 at a $pH_i$ of 9 in the presence of...
manganese. On the other hand, about 20% and 50% of iron hydroxides (i.e. precipitate) were not removed by immobilization and generated in the system at pH of 8 and 7, respectively. Figure 5b shows that the dissolved oxygen (DO) decreased due to the oxidation of Fe$^{2+}$ and Mn$^{2+}$.

The removal of dissolved manganese may include oxidation and adsorption in single and binary systems (Sung & Morgan 1981). The oxidation efficiency of Mn$^{2+}$ is shown in Figure 6a. The oxidation rates of Mn$^{2+}$ for single and binary systems in the FBR increased with increasing pH$_7$. Furthermore, the maximum oxidation levels of Mn$^{2+}$ were proportional to pH$_7$ for single and binary systems. On the other hand, the immobilization of manganese species on FeO$_{30}$ at different pH$_7$ is shown in Figure 6b.

In fact, the oxidation of Fe(II) completed quickly in less than 60 minutes while the removal efficiencies of Fe(II) at pH 7 and 8 became constant after about 120 minutes compared to the slow increase in the manganese removal efficiencies. This may mean that some Mn(II) species at pH 7 and 8 might be adsorbed on the surface of FeO$_{30}$ in a way of replacing the surface iron species and covering some sites to preventing the prorogation of adsorption-oxidation chains for Fe(II) species. The behaviors of iron and manganese at pH 9 were quite different from those at pH 7 and 8, which might suggest a different mechanism. At pH 9, the initial formation of Mn(II) and Fe(II) hydroxides might be very significant. For a binary system, the immobilization of manganese increases with increasing
pH. However, the immobilization of manganese first increased and then dropped for a single system at each pH. When only manganese existed in the system, a lot of iron species leached from the surface of FeO<x>30. The surface of FeO<x>30 became fragile in a single system. The results generally showed that a single system with only manganese was not favorable for immobilization of Fe(II) due to the leaching of iron species from the surface of FeO<x>30, and a binary system in the presence of iron species was not favorable for removal and immobilization of manganese species at pH 7 and 8.

In the binary system, the interactions between Fe<sup>2+</sup> and Mn<sup>2+</sup> protected the FeO<x>30 from leaching iron species or the extra presence of Fe species caused more adsorption of Mn(II) species. On the other hand, the treatment of Fe<sup>2+</sup> and Mn<sup>2+</sup> in the FBR simultaneously was demonstrated to be a good technique at a pH of 9. In the binary system, the optimum pH condition in the range of tested conditions for immobilization of both iron and manganese species was pH 9.

**Effect of catalyst loading**

The catalyst loading in the reactor is an important parameter that can greatly affect the catalysis process. Generally, a higher catalyst loading leads to higher removal efficiency of iron and manganese. Figure 7 plots the immobilization of manganese and iron against reaction time for various loadings of FeO<x>30. Increasing the catalyst loading from 100 to 375 g FeO<x>30 per litre promoted the immobilization substantially, from 10 to 20% at pH of 7 and 8. The immobilization of both iron and manganese decreased slightly at a pH of 9. However, the additional alkalinity increased the cost of the treatment process. Thus, the immobilization process at a pH of 8 proved more economical than that at a pH of 9. About 99% and 97.6% of iron and manganese were immobilized onto 375 g FeO<x>30 per litre at the pH of 8.0, respectively.

**CONCLUSIONS**

The new immobilized iron oxide, FeO<x>30, is a useful catalyst for the oxidation and immobilization of manganese species. About 95% and 30% of manganese species were immobilized on FeO<x>30 and silica sand in the FBR, respectively, at a pH of 8. In the binary system, the optimum pH condition for the immobilization of both iron and manganese species was 9. Increasing the catalyst loading from 100 to 375 g FeO<x>30 per litre substantially promoted the immobilization from 10 to 20% at pH of 7 and 8. The FeO<x>30 was a by-product of the treatment of ferrous ions in groundwater. Hence, the catalyst, FeO<x>30, was cheap and feasible for applications involving oxidation, adsorption and immobilization processes.
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