Desalination and Water Treatment
www.deswater.com

28 (2011) 265–269
April

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doi: 10/5004/dwt.2011.1160

Combined electro-photochemical oxidation for iron removal from ground water

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Received 18 March 2009; Accepted 1 December 2010

ABSTRACT

Iron in water presents health hazard, its presence in water may cause taste and staining problems. Currently applied water treatment techniques consist of a combination of different methods to achieve the elimination of harmful pollutants. The aim of this study is to investigate the efficiency of the photo-assisted electrochemical oxidation process for the removal of dissolved iron as a cheaper technology. This process could be used at room temperature and low pressure without the need for special equipment and complex operation. The photo-electrochemical cell used in this study was composed of carbon cathode, aluminum anode and high pressure mercury lamp. The effect of the irradiation time, initial concentration of iron, amount of electrolyte and current intensity on the removal efficiency of iron was investigated through series of batch runs in a photo-electrochemical reactor. Results indicated that higher iron removal was obtained at neutral pH of the solution, 20 min irradiation time, 125 ppm of NaCl as electrolyte and (0.25 A) current intensity. By this technique, the ferrous ion was oxidized and is precipitated easily as ferric ions.

Keywords: Iron removal; Electrochemical; Photochemical; oxidation; Heavy metal; Drinking water

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1. Introduction

The quality of drinking water is of great public interest nowadays, the presence of iron compounds in groundwater and eventually in drinking water is a serious environmental problem. When iron is present in both surface and groundwater, even at low concentrations, it can be linked to various water quality problems and its removal is essential. Well water from the faucet or tap is usually clear and colorless. However, when water containing colorless, dissolved iron is allowed to stand in a cooking container or comes in contact with a sink or bath tube, the iron combines with oxygen from the air to form reddish-brown particles (commonly called rust) [1,2].

The rusty or brown stains on plumbing fixtures, fabrics, dishes, and utensils cannot be removed by soaps, detergents, bleaches or alkaline builders. Over time, iron deposits can build up in pressure tanks, water heaters, and pipelines, reducing the quantity and pressure and creating problems in water supply systems.

When it is present beyond recommended level, special attention should be paid to the problem. It causes aesthetic and operational problems, such as bad taste and color, staining and deposition in the water distribution system leading to high turbidity. The highest permitted limit of iron concentration for drinking water is 0.2 mg/l [3,4].

Chlorination is widely used for oxidation of divalent iron. However, the formation of trihalomethanes (THMs) in highly colored water may be a problem. Ozone may not be effective for oxidation in the presence of humic or

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fulvic materials. In many cases these oxidants represent the major cost item of the water treatment process [5,6].

In recent years, various treatment technologies have been employed to enhance water quality by removing inorganic contaminants. Both photo and electrochemical oxidation technologies recently have become more popular in water treatment. The use of these processes are considered as attractive options in solving the issues concerning iron removal of water especially if another compounds such as ammonia, total dissolved solids or natural organic matter (NOM) are found [7]. Nowadays, there has been great interest in the development of practical electrochemical methods, such as anodic oxidation and indirect electro-oxidation, for the destruction of toxic and bio-refractory organic pollutants [8]. However, anodic oxidation usually requires either high voltage or special electrode material, such as Pt/Ti [9], PbO_2 [10], doped SnO_2 [11], boron-doped diamond, etc. [12]. Alternative methods based on indirect electro-oxidation always involve the electro-generation of other strong oxidants, such as ClO^- obtained from anodic oxidation of Cl^- in alkaline medium [13] or H_2O_2 formed from the two electron reduction of O_2 at a graphite cathode [14]. The latter method is more attractive because the residual oxidant can decompose by itself, leaving no secondary pollution. However, its direct application in pollutants treatment was also greatly limited for the insufficient oxidative ability. To solve this problem, Fe(II) or Fe(III)was introduced into the system, constructing an electro-Fenton's reagent [15] as one of a special class of oxidation techniques defined as advanced oxidation processes (AOPs). These processes are characterized by the capability of exploiting the high reactivity of hydroxyl radicals.

Free hydroxyl radical ($OH^\bullet$) is a non selective and very powerful oxidant agent able to oxidize organic and inorganic pollutants in water and is generated from chemical, electro and photochemical (by using light irradiation) processes [16].

In this work, a combined photo-electrochemical oxidation technique was investigated with regard to the removal of iron from water since little information is available on this approach. The removal of iron from synthetic solution using bench-scale photo- electrochemical oxidation system was evaluated using different concentrations levels of iron at different current intensity.

2. Experimental

2.1. Materials

Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was used as a source of iron in form of Fe (II), supplied by S.D. Fine Chem. Ltd. Distilled water was used throughout. Pure sodium chloride was used as electrolyte, purchased from Merck.

2.2. Experimental set-up

A laboratory UV-assisted electrochemical unit was used for the batch experiments. The schematic diagram of the experimental set-up used is shown in Fig. 1. It consists of a cylindrical photo reactor (1.2 l), made from quartz, with a coaxial and immersed medium pressure UV mercury lamp used as the UV emitter and light source (Heraeus TQ150, input energy of 150 W) emitting a polychromatic radiation in the range from 100 to 280 nm wavelength. The lamp emitted a power of 6.2 W in the UV-C ($100 < \lambda < 280$ nm) range (indication Heraeus), corresponding to 1.32×10^{-5} Einstein s^{-1}. The UV lamp is equipped with a cooling water jacket to maintain the temperature of the reaction of wastewater at room temperature. There is one cooling circle for cooling UV lamp. The UV system made from quartz glass is placed coaxial inside the reactor vessel, which is available for the transfer of UV irradiation. The reaction chamber is filled with water containing iron, which is between the reactor walls and UV lamp system. The electrochemical system was constructed in the photochemical reactor equipped with the working electrodes of aluminum plate as anode and carbon cathode. The process was performed at room temperature and the mixing was accomplished by using continuous magnetic stirrer.

2.3. Procedures and analysis

Solutions of different iron concentrations were prepared as model for groundwater containing iron by dissolving definite concentrations of $FeSO_4 \cdot 7H_2O$ in distilled water. Definite amounts of NaCl were added as supporting electrolyte. Iron was removed from water by using different oxidation techniques such as UV oxidation, electrochemical oxidation and

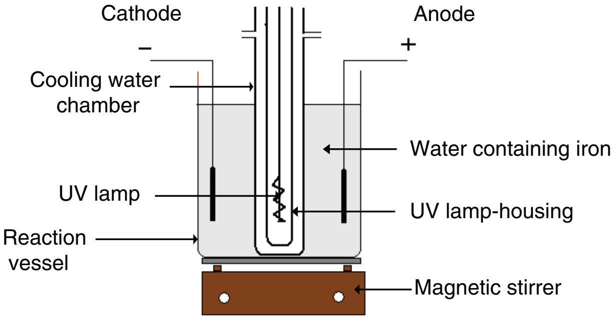

Fig. 1. The schematic diagram of the experimental set-up.

combined UV-electrochemical oxidation. The efficiency of the process was evaluated by measuring iron removal of the samples and at the end of each experiment. Samples are filtered first and then iron was measured by using atomic adsorption (Percken Elmar 1100B), from Germany [17].

3. Results and discussion

3.1. Comparative removal behavior

Before iron can be filtered, they need to be oxidized to a state in which they can form insoluble complexes. Oxidation involves the transfer of electrons from the iron or other chemicals being treated to the oxidizing agent. Iron exists in ferrous ions (Fe^{2+}) form, depending upon the pH value and dissolved oxygen concentration. At neutral pH and in the presence of oxygen, ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}), which readily forms the insoluble iron hydroxide $Fe(OH)_3$ [18,19,20].

A first series of experiments were performed by using different oxidation techniques such as UV radiation, electrochemical and combined UV-electrochemical oxidation to know the corresponding oxidizing power of these processes. As an example, Fig. 2 shows the comparative % iron removal versus reaction time for the different oxidation processes. A quite slow removal of iron by using UV light only was occurred to attain only about 50% within 25 min of reaction time. This evidences the generation of a very small concentration of the main oxidant $OH^•$ from the decomposition of water due to the combination of UV light and the presence of iron as photo-catalyst. Better results were obtained by using electrochemical oxidation to attain about 87% iron removal within 20 min of reaction time. Thus is attributed to the following:

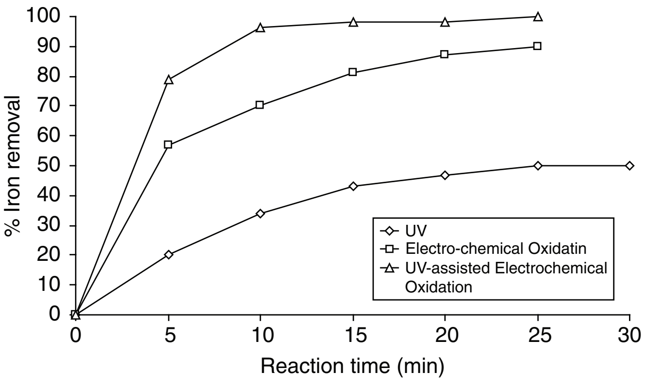

Fig. 2. Removal of iron by using different oxidation processes. [Initial iron concentration 3 ppm, 150 W, 0.25 A, pH 6.8]

a) In electrochemical oxidation (electro-Fenton process), hydroxyl radicals could be produced at the surface of a high-oxygen over voltage anode from water oxidation [21–25]
b) Electro generation of hydrogen peroxide (H_2O_2) formed from the two-electron reduction of O_2 at a graphite cathode [26,27].

The oxidizing H_2O_2 can be enhanced in the presence of catalytic Fe^{2+}, due to the formation of hydroxyl radicals from the classical Fenton's reaction between both species [28,29] (Eq. (1)).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^• \qquad (1)$$

The produced ferric ion from Eq. (1) would be reduced to ferrous ion at the cathode [30] (Eq. (2)). This would induce Fenton chain reaction efficiently.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (2)$$

To avoid (Eq. (2)), the electro-Fenton process was enhanced by UV light. As can be seen from Fig. 2, the quicker iron removal found by combined UV-electrochemical oxidation where 98.5% iron removal was attained within 15 min reaction time due to the generation of more hydroxyl radicals with the enhancement of electrochemical oxidation with the presence of UV light (electro-photo-Fenton process).

Moreover, in both electrochemical and combined UV-electrochemical oxidation processes, by using aluminum as anode in the electro-cell, aluminum ions (Al^{3+}) are formed which reacts with hydroxyl ions (OH^-) and forms aluminum hydroxide as flocks which adsorb ferrous ions and co-precipitate together.

3.2. Effect of initial iron concentration

Fig. 3 represents the relationship between change in iron concentration and reaction time at different initial iron concentration. The relationship is represented with linear relation, which is described with first order reaction as shown in Eq. (3).

$$\ln (C_A/C_{A0}) = -k_0 t \qquad (3)$$

where C_{A0} and C_A are the initial iron concentration and the iron concentration at t reaction time and k_0 is the first order reaction rate constant.

As observed from Fig. 3, the reaction rate of removal of iron by combined UV-electrochemical oxidation is increased with the increase of initial iron concentration which is attributed that at high initial iron concentration are needed to carry out the

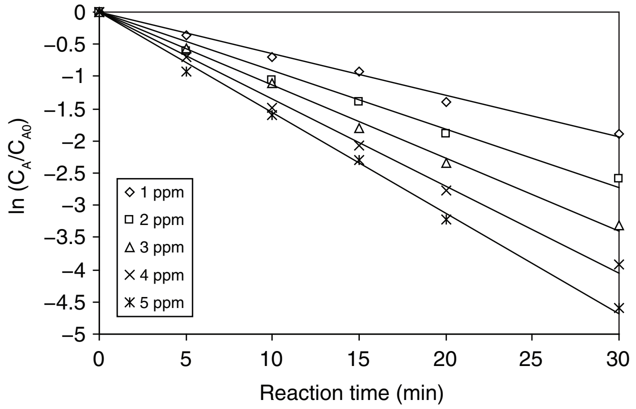

Fig. 3. Effect of initial iron concentration on removal of iron by UV-assisted electrochemical oxidation process. [I150 W, 0.25 A, pH 6.8]

electro-Fenton reaction for more generation of free hydroxyl radicals the responsible oxidizing agent for removal of iron.

3.3. Effect of NaCl as electrolyte on the current intensity

The supporting electrolytes of this combined UV-electrochemical oxidation system, such as H_2SO_4, $NaClO_4$, Na_2SO_4 and NaOH, in an aqueous solution have been reported in literature [31–33]. However, the combined UV-electrochemical oxidation reactions of organic and inorganic species in 1–3% NaCl solution have rarely been mentioned [34]. In this work, the relationship of amount of NaCl aqueous solution added as electrolyte and the current intensity on combined UV-electrochemical oxidation of iron ion was systematically studied. As can be seen from Fig. 4, a linear proportional relationship was found between amount of the electrolyte added and the corresponding applied current, where the current intensity increases with the increase of the amount of electrolyte added. On addition of 125 ppm of NaCl, the current intensity was recorded as 0.27 A.

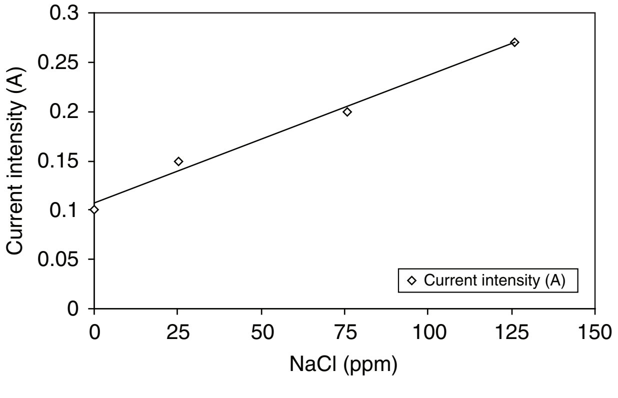

Fig. 4. Relationship between the amount of electrolyte added and the current intensity on the UV-assisted electrochemical oxidation process. [Initial iron concentration 3 ppm, 150 W, pH 6.8]

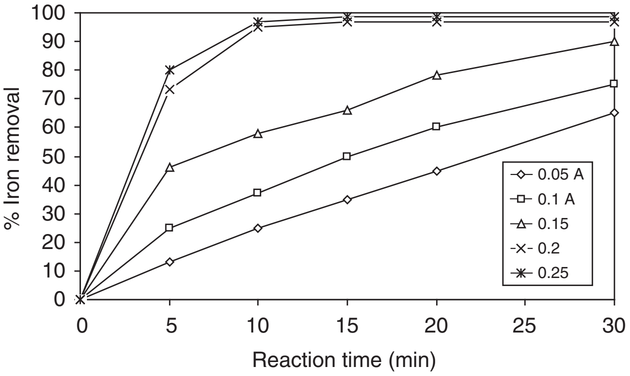

Fig. 5. Effect of current intensity on the removal of iron by using UV-assisted electrochemical oxidation process. [Initial iron concentration 3 ppm, 150W, pH 6.8]

3.4. Effect of applying current intensity

As the increase of the applying current intensity from 0 to 0.2 A, the removal of iron increased up to 97% within 15 min only of reaction time. This trend can be mainly associated with the electro-generation of higher H_2O_2 concentration causing more $OH^{\bullet}$ by Eq. (3) and hence, a faster abatement of iron in the medium. Further increasing the current intensity from 0.2 A to 0.25 A, the iron removal increased slowly from 97% to 98.7% as shown in Fig. 5, indicating that within this range the iron removal is not limited by mass transfer at the anode. The applying current intensity significantly promotes the iron removal, but it has a limitation of promotion when the applying current intensity is higher than 0.25 A.

4. Conclusions

It has been demonstrated that combined UV-electrochemical oxidation process is a very effective and promising method for removal of iron from groundwater. Within very short reaction time not exceeded 20 min, the removal of iron reached 99 % with less consumption of current intensity (0.25 A) without the use of external oxidizing agent. Both free hydroxyl radicals and hydrogen peroxide oxidizing agent are generated through this process, which they are responsible to remove the iron from water. All these characteristics make this approach to be an appropriate solution for removal of iron, and other heavy metals from groundwater.

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