

Dyes wastewater treatment by reduction-oxidation process in an electrochemical reactor packed with natural manganese mineral

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Abstract: A novel technology which combined electrochemical process catalyzed by manganese mineral with electro-assisted coagulation process was proposed in this study. The mineralization of organic pollutant from simulated dye wastewater containing an azo dye Acid Red B (ARB) was experimentally investigated using this method. It was found that the manganese mineral could catalyze the electrochemical process dramatically. The TOC removal percentage of electrochemical treatment catalyzed by manganese mineral was 43.6% while the TOC removal percentage of the process using the manganese mineral alone and using the electrolysis alone were 9.3% and 20.8%, respectively. Moreover, it was found that combined electrooxidation with electro-assisted coagulation process could more effectively eliminate ARB. After a period of 180 min electrooxidation and 300 min electroreduction, almost 66.9% of TOC was removed, and the dissolved Mn^{2+} could be effectively removed. The effects of the order of oxidation and reduction, the proper ratio electrooxidation/reduction time, and current density on the removal efficiency were investigated in detail. In addition, a proposed mechanism of manganese-mineral-catalyzed electrooxidation-reduction process was discussed in this paper.

Keywords: manganese mineral; electroreduction; electrooxidation; catalyze; Acid Red B

Introduction

In recent years, widespread contamination of groundwater by persistent organic pollutants has been recognised as an issue of growing importance that has focused the attention of the industrial and academic world (Polcaro *et al.*, 2000). The growing pollution of our hydrosphere has stimulated the need for developing new technologies for water and wastewater treatment. The electrochemical technology, which is well known as “a clean method of wastewater treatment”, has lots of advantages, such as its unique ability to oxidize and reduce compounds at a well-controlled electrode potential, offers many interesting possibilities in environmental engineering (Simonsson, 1997). Recently, electrochemical methods for the treatment of wastewater have attracted a great deal of attention (Simonsson, 1997; Rajeshwar *et al.*, 1994; Grimm *et al.*, 1998).

While electrochemical techniques are more environmentally friendly than the chemical methods in polluted water treatment, a significant drawback is that parasitic reactions, such as electrolysis of water, often compete with electrolysis of the contaminant and lower energy efficiency (Rodger and Bunce, 2001). There is a need for improvement of the electrochemical techniques efficiency. Recently some methods that have been tried to overcome these problems have been reported. In particular, three-dimensional electrode systems, such as packed and

fluidized bed electrodes, are gaining increased technical importance. This is because they have a more extensive interfacial electrode surface and allow the application of considerably higher current density than two-dimensional electrodes (Bockris and Kim, 1997). It has been recognized widely that the rate of conversion within an electrochemical reactor can be increased substantially by the use of the three dimensional electrode with its extensive specific surface area in comparison to conventional two-dimensional electrodes (Simonsson, 1997; Bockris and Kim, 1997; Xiong and Karlsson, 2002).

In addition to electrooxidation, there are several other electrochemical technologies available for wastewater although our understanding of these processes is less advanced. One of these technologies is assisted electrochemical coagulation (Canizares *et al.*, 2002).

The natural manganese mineral was used as catalyst for its potential oxidizing agent for organic pollutants (Stone and Morgan, 1984a, 1984b; Ulrich and Stone, 1989; Liu and Tang, 2000). In this paper, pellets of manganese mineral were arranged in a fixed bed mode to two electrochemical compartments. In anode compartment, manganese mineral may catalyze electrooxidation of organic pollutants, while in the cathode compartment the metal ions which dissolved from mineral may form hydrate in basic solution, which can coagulate organic pollutant. Both electrooxidation and coagulation can remove pollutants in

the water.

1 Materials and methods

1.1 Characteristics of electrochemical reactor

Fig.1 shows a schematic view of the apparatus experimental set-up. A stainless steel sheet was used as cathode (0.8 dm × 0.9 dm). The anode was a half-tone of titanium coated with ruthenium (0.8 dm × 0.9 dm), which was known as Dimensional stable anode (DSA[®]) and widely used in alkaly-chlorine plants. The distance between the anode and the cathode was 3.0 cm. Pellets (4—14 mesh, from which the fraction with of 0.25 cm diameter was selected) of manganese mineral were arranged in a fixed bed between anode and cathode plate. The electrolyte was re-circulated throughout the system by peristaltic pumps. The anodic compartment was separated from the cathodic one by an anionic exchange membrane. The experiment worked with a flow-by configuration (current flow perpendicular to the electrolyte flow).

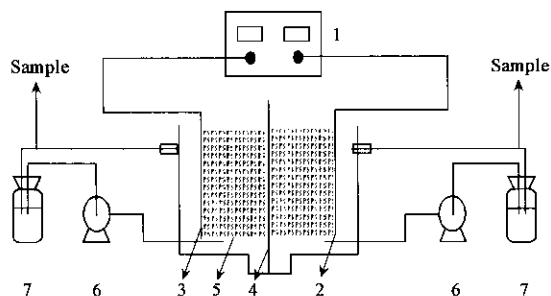


Fig.1 Experimental set-up

1: D.C. power supply; 2: Ni cathode plate; 3: RuO₂/Ti anode plate; 4: anionic exchange membrane; 5: manganese mineral; 6: pump; 7: reservoir

1.2 Materials

The natural manganese mineral samples were collected from Henan Province, China. Its granularity was between 0.1—0.2 mm. The organic substrates in the mineral were removed by burning in muffle furnace at 800 °C for 2 h under an oxygen flow. The natural manganese mineral was characterized by X-ray powder diffraction (Rigaku Model D/Max-2500; Japan). The BET surface areas (5.86 m²/g) of the manganese mineral were determined using the N₂/BET method (ASAP Model 2000). An azo dye ARB was selected as the model compound, which was commercial dyes and used without further purification. Its chemical structure was given in Fig.2. All other chemicals were of analytical grade. Deionized and double distilled water was used throughout this study.

1.3 Experimental procedures

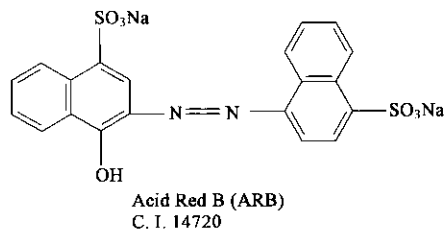


Fig.2 Chemical structure of ARB

The electrolytic treatment runs were performed batch-wise. A 1000 ml volume of dye solution was added to the electrochemical reactor packed with manganese mineral samples. The electrolysis was then carried out at constant current density. The combining electrooxidation/reduction experiments were carried out as follows: firstly the ARB was electrooxidized (in anode compartment) and electroreduced (in cathode compartment) for certain time then electroreduced and electrooxidized by exchanging the electrodes. After the reaction started, the samples were withdrawn at regular intervals, that is 0, 30, 60, 120, 180, 270, 360 and 480 min, then filtered through a 0.45- μ m syringe-end filter. Total organic carbon (TOC) in water was measured by Phoenix 8000 TOC analyzer (Tekmar-Dohrmann Co. USA). The concentration of Mn (II) in filtrate was analyzed by atomic absorption spectrophotometer (AAS, Model Z-6100).

2 Results and discussion

2.1 Manganese mineral

Characterization of natural manganese mineral X-ray diffraction spectrum of the natural manganese mineral is shown in Fig.3. It could be seen that even if the mineral contained a lower silicon component, the stronger peaks of SiO₂ were produced at d-spacing of 3.350, 4.271 and 2.460 × 10⁻¹⁰ m due to its perfect crystalline properties. In addition, the three major peaks of manganese oxide were found, a strongest peak at a spacing of 2.716 × 10⁻¹⁰ m, a broad weak peak at 3.845 × 10⁻¹⁰ m followed by a weak peak at

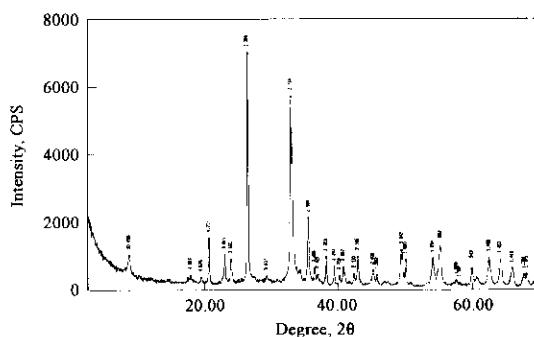


Fig.3 X-ray diffraction spectrum of natural manganese mineral

2.353×10^{-10} m. These d-spacings of peaks were consistent with those reported for α - Mn_2O_3 ($MnO \cdot MnO_2$) (Liu and Tang, 2000). Furthermore, the appearance of peaks at $1.842, 2.520$ and 3.690×10^{-10} m is mainly contributed to by the presence of hematite in the mineral. Therefore, these results showed that silicon, manganese and ferric were major components of the mineral.

2.2 Effect of manganese mineral and electrochemical process on the removal of ARB

The degradation of ARB was carried out at four approaches as follows: (1) using manganese mineral alone; (2) using electrochemical process alone; (3) using electrochemical process catalyzed by manganese mineral and (4) firstly electrooxidation catalyzed by manganese mineral for 180 min then reduction for 300 min. The results were shown in Fig.4.

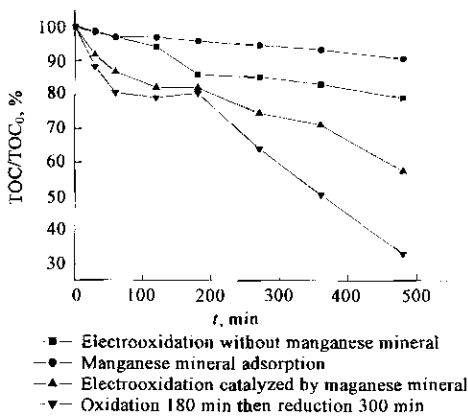


Fig.4 Removal effect at various processes

It could be found that the elimination rate of ARB remarkably increased when the electrolysis process catalyzed by manganese mineral. After 480 min treatment, the TOC removal percentage was 43.6% while the TOC removal percentage of the process using the manganese mineral alone and using the electrolysis alone were 9.3% and 20.8%, respectively. This result suggests that the manganese mineral can catalyze the electrochemical process for degradation of ARB in water. At the same time, when ARB firstly was electrooxidized for 180 min then reduced 300 min, the TOC elimination rate dramatically reached to 66.9%. And it could be found that much coagulant formed in the solution of electrolysis cell.

2.3 Removal of TOC in different ratios of oxidation time and reduction time

To clarify the influence of different ratios of oxidation time and reduction time on TOC removal, several tests in 500 mg/L ARB aqueous solution were

carried out with the ratios of 480 min/0 min, 60 min/420 min, 180 min/300 min and 360 min/120 min, respectively. As shown in Fig.5, the TOC removal rate of the ratios of oxidation/reduction at 180 min/300 min was much better than the others. The difference might be related with the dissolution concentration of Mn^{2+} shown in Fig.6.

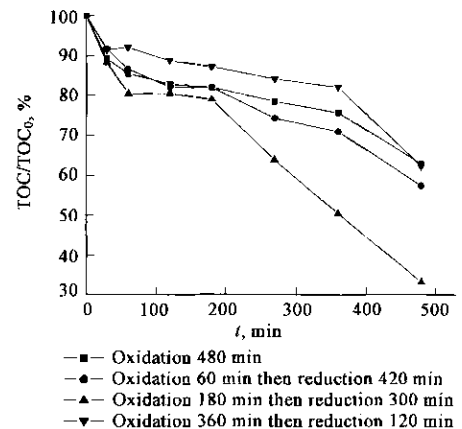


Fig.5 Effect of different ratios of oxidation and reduction time on the elimination efficiency as a function of electrolysis time

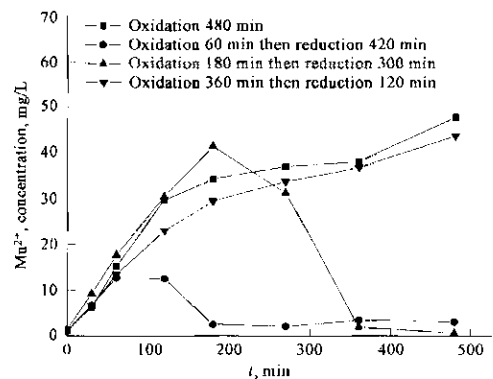
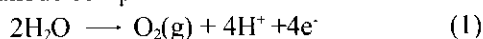


Fig.6 Solubility of manganese oxide in natural manganese mineral as a function of time at different oxidation and reduction time

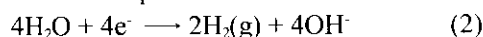
It had been confirmed that at pH 7.2 Mn(III/IV) oxides was almost insoluble and in blank experiments with out organic reductant, and the dissolved manganese was only less than 3% of the total manganese added (Stone and Morgan, 1984b). In addition, no Mn dissolution was observed at pH higher than 8. The amount of dissolved Mn^{2+} might increase with a decrease of pH value and an increase of particle concentration. This phenomenon could be explained from two aspects: one was that Mn (II) in the crystal structure of α - Mn_2O_3 , as a result of high mobility, released from solid surface to solution in acidic aqueous solution; the other was that Mn (IV) in the

crystal structure can be reduced thermodynamically to Mn(II) at low pH (Liu and Tang, 2002). In the "anode" compartment the pH of solution may decrease gradually because of the electrolysis of water (Equation (1)). Fig.6 suggested that the concentration of Mn^{2+} was increasing with prolonging electro-oxidation time. It could also be observed that when the time of electrooxidation was 60 min or 180 min, the Mn^{2+} concentration decreased obviously when reduction began. This also resulted from the electrolysis of water (Equation (2)) that might provide OH^- to neutralize the H^+ , and then the solution might transform into alkaline. The Mn^{2+} might integrate OH^- and form $Mn(OH)_2$.

In the anode compartment:



In the cathode compartment:



Moreover, as shown in Fig.6, when electro-oxidation time was too long, such as oxidation 360 min and reduction 120 min, the following electroreduction reaction could not neutralize the H^+ in a relatively short period. The Mn^{2+} might not form floc in acid solution and the flocculation could be in effect. When current density was 0.36 A/dm^2 , 180 min oxidation and 300 min reduction might be a better ratio.

2.4 Removal of TOC in different ratios of reduction time and oxidation time

Simultaneously the removal of ARB by combining electroreduction/oxidation was carried out in the "cathode" compartment. The influence of different ratios of reduction time and oxidation time on the elimination of ARB is given in Fig.7.

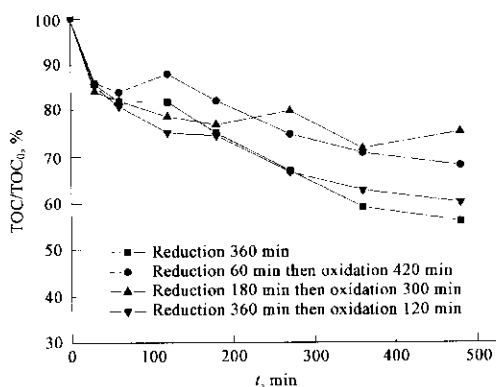


Fig.7 Effect of different reduction and oxidation time on the elimination efficiency as a function of electrolysis time

The best TOC removal was obtained when there was no electrooxidation reaction happening. With lessening of reduction, the TOC removal might

decrease. The flocculation of $Mn(OH)_2$ was the main cause of TOC removal in the "cathode" compartment, and the electrooxidation of anode was minimum effect. The reduction of $Mn(IV)$ to $Mn(II)$ by the electroreduction reaction might enhance the dissolution of manganese oxide. The pH of solution increased in the electroreduction reaction, the dissolved Mn^{2+} might form coagulant in basic solution. The coagulant could flocculate and adsorb the organic pollutant in the solution. Electrooxidation reaction may decrease pH value, and the coagulant might be dissolved over again and the organic matter might release. This could be confirmed by the Mn^{2+} concentration shown in Fig.8. As given in Fig.8, firstly oxidation 60 min then reduction 420 min the Mn^{2+} concentration might increase as soon as the electrooxidation happened. And the concentration was increasing with prolonging the oxidation time. The concentration of 420 min electrooxidation might reach to about 37 mg/L. So high concentration of Mn^{2+} ion in the discharged water might lead to polluting the environment. Combination with previous discussion, the electrooxidation/reduction process might be better than electroreduction/oxidation process.

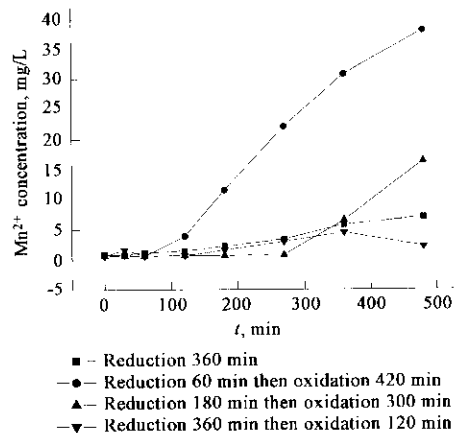


Fig.8 Mn^{2+} solubility of manganese oxide in natural manganese mineral as a function of time at different oxidation and reduction time

2.5 Effect of current density on combining electro-oxidation/reduction process

In the electrochemical treatment, current density was a main factor which might effect the efficiency. The effect of applied current density on the efficiency in the electrooxidation/reduction process catalyzed by manganese mineral is given in Fig.9.

From Fig.9, it was observed obviously that the TOC removal efficiency improved effectively with the increase of current density from 0.12 A/dm^2 to 0.50 A/dm^2 . The TOC removal rate was 70% when the

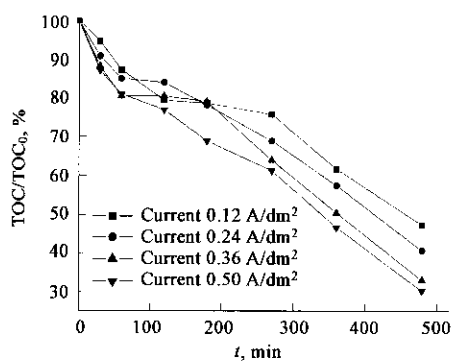


Fig. 9 Effect of current density on the elimination of ARB as function of electrolysis time (firstly oxidation 180 min then reduction 300 min)

current density was 0.50 A/dm^2 , while the removal rate was 53% when current density was 0.12 A/dm^2 . Increasing current density could enhance both the electrooxidation of ARB and the dissolution of Mn^{2+} . When the reduction reaction began, more coagulant might form when the current density was higher because of the higher dissolved Mn^{2+} and OH^- concentrations. From Fig.10 it could be found that the higher the current density was, the higher the Mn^{2+} concentration in the period of 180 min electrooxidation was. And after 300 min reduction, the Mn^{2+} concentration decreased to a very low concentration (only about 1 mg/L). That suggested that when the ratio of electrooxidation/reduction was 180 min/300 min, the manganese mineral could effectively catalyze the degradation of ARB and the dissolved Mn^{2+} might fully be utilized to flocculate organic pollutant.

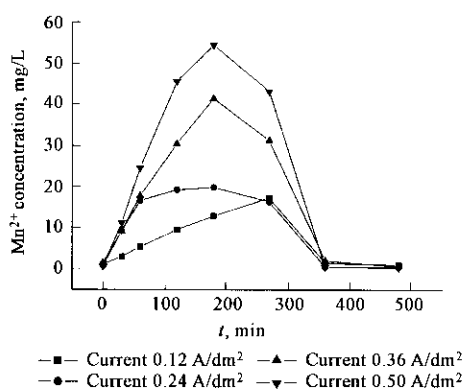
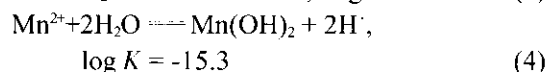
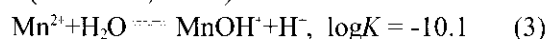


Fig.10 Mn^{2+} concentration in the solution at different current density as a function of electrolysis time (firstly oxidation 180 min then reduction 300 min)

2.6 Proposed mechanism of AR14 removal by combination catalyzed electrooxidation with electroassisted coagulation

The catalyzed electrooxidation mechanism had been discussed in our previous paper (Liu and Qu,

2002). Proposed mechanism for manganese mineral catalyzed electrooxidation and electro-assisted coagulation process was illustrated as follows: Firstly in the oxidation process: (1) diffusion of ARB dye into the boundary; (2) formation of a surface complex between the adsorbate and oxide; (3) desorption of oxidized organic substrate and movement of reduced Mn(II) from the crystal lattice to the adsorbed layer; (4) desorption of Mn^{2+} and diffusion of products away from the surface. Secondly in the reduction process: (1) Mn^{2+} reacted with OH^- formed coagulants ($\text{Mn}(\text{OH})_2$)(Eqs.(3) and (4)) in the aqueous phase(Dean, 1985); (2) adsorption of soluble or colloidal pollutants on coagulants and removal by sedimentation or flotation(Can *et al.*, 2003).



3 Conclusions

Combined electrochemical process catalyzed by manganese mineral with electro-assisted coagulation process was employed to remove the ARB dye from wastewater. The investigation on removal efficiency of the dye showed that the manganese mineral could catalyze the electrochemical process dramatically. The TOC removal percentage of electrochemical treatment catalyzed by manganese mineral was 43.6% while it was 9.3% and 20.8% using the manganese mineral alone and using the electrolysis alone were, respectively. TOC removal would be improved by combined electrooxidation with electro-assisted coagulation process. After a period of 180 min electrooxidation and 300 min electroreduction, the TOC removal reached almost 66.9% and the dissolved Mn^{2+} concentration was only 1 mg/L in discharged water. This was attributed to the adsorption and flocculation of $\text{Mn}(\text{OH})_2$ in the reduction process. The operating variables, such as the order of oxidation and reduction, the proper ratio of electrooxidation/reduction time, and current density were investigated to determine their effects on the removal efficiency. It had been observed that firstly oxidation then reduction might benefit to ARB removal. In a period of 480 min electrolysis, 60 min electrooxidation and 420 min electroreduction was efficient to remove TOC at current density 0.36 A/dm^2 . Higher current density benefited to both electrooxidation and coagulation.

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