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Double catholyte electrochemical approach for preparing ferrate-aluminum: a compound oxidant-coagulant for water purification

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Abstract: Ferrate is an excellent water treatment agent for its multi-functions in oxidation, disinfection, coagulation and adsorption, but its coagulation ability depends on its dosage and is after its oxidation. This paper focuses on preparing a new kind of ferrate combined with alum to enhance its coagulation function for water purification. An effective electrolysis reactor was designed and employed in the test. Some key parameters in the process of electrolysis concerning the preparation efficiency, such as the current density, temperature and alkalinity were also investigated. The proper conditions for ferrate-alum preparation were determined. Under the condition of 5V given voltage, 6h electrolyzing interval, below 2% alum concentration (in weight), a combined liquid ferrate-alum products was successfully prepared, which contained 0.0294 mol/L $\text{Fe}(\text{O}_4)^{2-}$ and 0.0302 mol/L total soluble ferron with 2% Al_2O_3 . There was no insoluble ferron produced by controlling an optimum electrochemical condition.

Keywords: combined ferrate-alum; electrochemical preparation; oxidation; coagulation

Introduction

Ferrate is a kind of iron compound existing in its +6 states with a very strong oxidizing power in aqueous solution. High quality of purified water can be obtained by using this multi-functional agent according to its particular chemical properties (Farooq, 1986): (1) Excellent disinfecting function. Recent work has shown that halogens and other strong oxidants commonly used for disinfection may generate toxic residuals, such as trihalomethanes. While other investigations showed that ferrate has the same biocidal capacity compared with monochloramine and can not yield any after-pollution at all. (2) Good effect of removing pollutants (Waite, 1978). Iron (VI) ferrate can give a more efficient removal than potassium permanganate, chloride and other oxidant to the poisonous and harmful inorganic and organic constituents in waste. This characteristic is provided by its powerful oxidation and effective absorption caused by newly formed ferric hydroxide colloid in its reaction. (3) Well coagulation effectiveness (Luca, 1978). The newly generated Fe (III) during Fe (VI) oxidation-reduction process is a kind of good coagulants. In addition, as an oxidant-absorbent, it is also a useful reagent for coagulation aids in water treatment. Hence, Fe (VI) ferrate can be taken as a multi-functional chemical agent in water treatment with above special characteristic (Murmamann, 1974; Martinez, 1986). Accordingly Fe (VI) ferrate should have a great potential for investigation and application.

In all of the characteristics of ferrate, the oxidation and coagulation are the most important properties for taking it as a kind of new and useful water purification agent. For the ordinary surface water, the cooperated effect of oxidation and coagulation can promote effectively the water treatment efficiency. However, the coagulation effect is after its oxidation process, as well the dosage of ferrate is often low, so its coagulating effect may not be very good. Therefore, it will be very meaningful to enhance its coagulation ability by combining some coagulants in the preparing process. This paper studied the electrochemical process to prepare combined ferrate-alum using alkaline solution containing NaAlO_2 as the anolyte. The results was a ferrate combined with AlO_2^- with an excellent oxidation capacity and a coagulation function better than that of an ordinary ferrate.

1 Experiments

1.1 Materials and instrument

30% – 40% sodium hydroxide was used for catholyte. The anolyte used was 40% sodium hydroxide containing 1% – 3% Al_2O_3 that was prepared with aluminum bits dissolving in 45% NaOH solution and was regulated to 40% of NaOH in using. The stabilizer was prepared with 50% NaCl and 50% Na_3PO_4 .

Chromium trichloride, sulfuric acid, phosphoric acid, nitric acid, ammonium ferrous sulfate, ammonia, diphenylamine-4-sulfonic acid sodium salt and 5-sulfosalicylic acid were used to analyze the concentration of ferrate and total ferron.

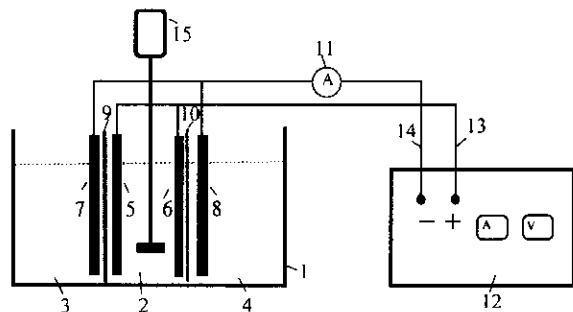


Fig. 1 The installation of ferrate preparation

1. electrolysis cell; 2. anolyte chamber; 3, 4. catholyte chamber; 5, 6. iron sheet; 7, 8. nickel sheet; 9, 10. ion exchanged membrane; 11. current meter; 12. electrolytic rectifier; 13, 14. copper lead; 15. stirrer

The electrolysis reactor for preparation of ferrate-alum is illustrated as Fig. 1. It consisted of an electrolytic rectifier (WY-10A-1), an electrolysis cell including double anolyte chambers and one catholyte chamber. The anode and cathode were made of 2 iron sheets (100×70 mm) and 2 nickel sheets (100×70 mm) respectively. The gap between electrode and membrane was 0.55 cm, so the interval between the anode and cathode was 1.1 cm. The surface of each electrode should be parallel to the plane of the membrane and the anode must be polished before electrolyzing.

1.2 Preparation process of ferrate

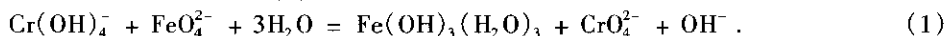
600 ml 40% sodium hydroxide containing 1% – 3% NaAlO_2 and 0.3% stabilizer was put into the two anode chambers and 300 ml 40% NaOH solution were put into the cathode chamber. A certain content of stabilizing reagent composed of 0.1% NaCl and 0.1% KI was added in the anolyte. It was preferable for the membrane to submerge in the liquid. When electrolysis started, the stirrer was kept in 50 r/min.

In electrolyzing, the given voltage should be a little higher than the needed by both iron-solving and ferrate-generating. The used voltage was about 3 – 5V, and in this condition, the current was 1 – 4A. The products prepared using this method was a kind of combined reagent composed of ferrate and NaAlO_2 in solution.

1.3 Analytical methods

1.3.1 Analytical method of FeO_4^{2-}

The concentration of ferrate in the anolyte electrolyte was analyzed by using the method of chromite oxidation, which is based on the Reaction (1).



Diphenylamine-4-sulfonic acid sodium salt was employed as indicator and the ferrate was measured by using ferrous sulfate solution, the concentration of ferrate can be calculated according to Equation (2).

$$C_{\text{FeO}_4^{2-}} = \frac{V_{\text{Fe}^{2+}} M_{\text{Fe}^{2+}}}{3V_s} \quad (2)$$

$V_{\text{Fe}^{2+}}$ is the volume of ferrous sulfate; $M_{\text{Fe}^{2+}}$ is the concentration of ferrous sulfate; V_s is the volume of sample.

The concentration of total ferron was measured by using EDTA with 5-sulfosalicylic employed as indicator. In this method, all the compounds in the solution must be degraded into Fe (II) by advanced disposal of acidating and pH remains at 2. The concentration of the other ferric compounds in this solution would finally be obtained by eliminating the known concentration of ferrate from that of total ferron.

1.3.2 Analytical method of Al

Al was measured using a titrimetric analysis based on the reaction of Al with EDTA. Details of the analytical procedure are given elsewhere (Li, 1981).

2 Results and discussion

2.1 The relationship between ferrate concentration, electrolysis time and current density across the anode

Current density was an essential parameter in electrolyzing and played an important role in controlling anode-solting rate and species of ferrate products. The results of experiments suggested that there exist in some relationship between current density, efficiency of ferrate generation and the electrolysis time in the certain given voltage.

The results are illustrated as Fig. 2. The concentration of Al_2O_3 in anolyte was 2%. If dividing the relevant curve into 4 parts, it could be found that the optimum electrolysis condition for ferrate generation was not in part B contended the peak of current density, but in part C that the current density was almost stable. At the same time preferred operational time was also required.

In the beginning of electrolysis, the current density increased gradually which is shown in the first district of Fig. 2. Because of the influence of alum in the anolyte, the current density was higher than no alum in this period, and reached to the peak current density early. In this period purple ferrate could be seen clearly in the electrolyte around the anode. However at this time the concentration of ferrate

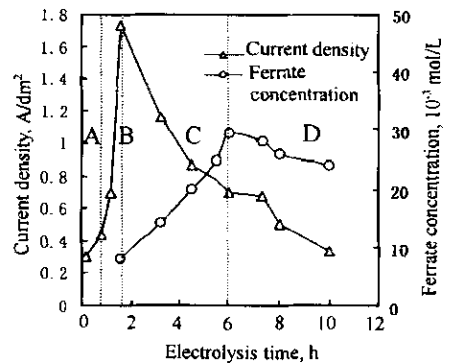


Fig.2 Relationship between ferrate concentration, current density and electrolysis time

was too low to be detected. This was the starting period of ferrate preparation. The operational time in part B was in a range from 0.8 to 1.7 hours. In this period the concentration of ferrate began to increase obviously accompanied with a sharp rise of current density. In part C, the electrolyzing time was for 1.7 to 6 hours. This was the most effective period for ferrate production. During this period, the current density was turned to decreasing gradually while the concentration of ferrate was still increasing effectively. The maximum concentration was acquired after 6 hours of electrolysis, and this was also the mature period of the entire electrolysis process. In the following fourth district, the current density across the anode begins to decline quickly. The ferrate concentration was no longer raising with the electrolysis time but presented some declining trend. The presentation of alum did not influence the pH of electrolyte and the concentration of ferrate after finishing electrolysis, but the current density was promoted in the electrolyzing periods, so the electrolysis time was shorted. Therefore, the optimum electrolysis condition of ferrate preparation could be described as the current density around $0.46\text{A}/\text{dm}^2$ by controlled the voltage and electrolysis for 6 hours.

2.2 The relationship among ferrate concentration, electrolysis time and temperature of the electrolyte

The preparation experiment in this part was carried out in the following conditions: the anolyte was 40% NaOH solution containing 2% Al_2O_3 , the working voltage was 5V. In electrolyzing, the change of ferrate concentration and temperature of anolyte with the electrolysis time is shown in Fig. 3. If dividing the Fig. 3 into 4 parts like in Fig. 2, some relationships between these three factors can be observed in different electrolysis periods. The first part was the beginning period for electrolysis and ferrate producing. In this period both temperature and ferrate were going up slowly, and ferrate could be observed but could not be detected. When entering the second district, the temperature of anolyte was going up quickly and the ferrate concentration began to increase. In the third part, the temperature of anolyte remained stable while the concentration of ferrate rising rapidly and reached the maximum value. In the fourth part of Fig. 3, ferrate in the anolyte tended to decompose and the concentration of it decreased continuously with a significant drop of both temperature and current density. At this time, the $\text{Al}(\text{OH})_3$ precipitation could be

observed in the anolyte, which would also accelerated the decomposition of ferrate. The results indicated that the electrolysis preparation of ferrate should be carried out in the period 3 and 4 where the temperature was going up and then kept stable. Therefore, in order to get the maximum ferrate content of products and prevent its decomposition, the electrolyzing must be over before the temperature of anolyte began to drop.

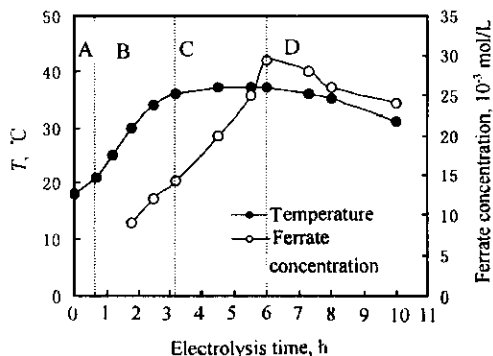


Fig.3 Relationship between ferrate concentration, temperature and electrolysis time

2.3 The change of alkalinity in electrolyzing

At the same experimental conditions as 2.2, the results about the change of alkalinity in electrolysis are shown in Table 1. The alkalinity of both anolyte and catholyte were almost no change in the electrolyzing process. After 7 hours of electrolysis, the alkalinity of electrolyte in the three chambers maintained as same as in the beginning of the electrolysis. This suggested that alkalinity has no effect on electrolyzing process, and therefore the alkalinity did not need to be adjusted in all electrolyzing period. However, the alkalinity should be more higher than in the condition no alum, otherwise, $\text{Al}(\text{OH})_3$ precipitation would produced.

Table 1 Alkalinity change in electrolyte during electrolyzing process

Electrolysis time, h	0	1	2	3	4	5	6	7	8	9	10
Concentration of OH^- in anolyte, mol/L	1.0	1.0	1.0	1.09	1.09	1.09	1.08	1.08	1.08	1.08	1.08
Concentration of OH^- in catholyte, mol/L	1.0	1.0	1.0	1.0	1.0	1.0	1.09	1.09	1.09	1.09	1.08

2.4 The composition of combined ferrate produced in anolyte

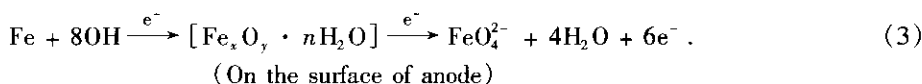
The experiments were performed using the alkalinity electrolytes containing 1%, 2% and 3% Al_2O_3 respectively. The working voltage was 5V and the electrolysis time was 6h. The results are shown in Table 2. The electrolyzing process could go on smoothly when the electrolyte contained 1% and 2% Al_2O_3 , and there were no $\text{Al}(\text{OH})_3$ precipitation was observed. In this condition, the concentration of ferrate in the combined liquid products was 0.0294 mol/L that equated to 1.63% Na_2FeO_4 in weight percent. The content of Al_2O_3 in the liquid product was still 1% as in the beginning. However, the experiments found that $\text{Al}(\text{OH})_3$ precipitation produced only after 2 hours later in the electrolyzing process by using the electrolyte contained 3% Al_2O_3 . In this case, ferrate was decomposed on line and the preparation could not be carried out. Therefore, when using the alkalinity solution containing alum, the content of Al_2O_3 should be lower than 2% in solution.

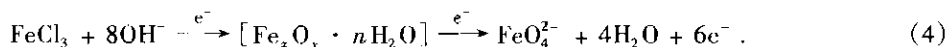
2.5 Mechanism of generation and decomposition of ferrate in preparation process

Ferrate may derive from either anode directly or ferric ion oxidized in anolyte during the electrolysis process.

Table 2 The species of ferrate in anode solution

Al_2O_3 % in 40% NaOH solution	Total Fe, mol/L	Ferrate concentration, mol/L	Percentage of total Na_2FeO_4 , %	Percentage of ferrate in total ferron, %	Percentage of other species of Fe, %
1	0.0306	0.0298	1.65	97.39	2.61
2	0.0302	0.0294	1.42	97.35	2.65





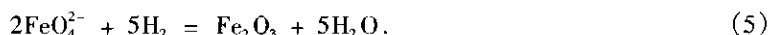
(Transport from solution to the anode surface)

$n \geq 1$ in Equation (3) and (4). It is thought that ferric oxy-hydroxide complexes (e.g. $\text{Fe}_x\text{O}_y \cdot n\text{H}_2\text{O}$) must be generated at first in the presence of OH^- . These complexes are then converted electrochemically to ferrate ions no matter which methods be taken.

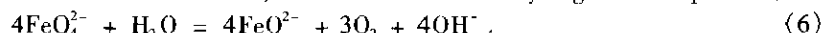
According to this mechanism, using a membrane-type electrolysis reactor had some advantages in improving current efficiency and lowering power consumption. These came from the two effects are as follows.

(1) Effectively preventing ferrate from electrochemical reduction in anolyte.

(2) Successfully preventing the ferrate ion from chemical reduction by hydrogen produced on cathode surface, as Reaction (5).



When newly formed ions diffuse into the solution, some of them will slowly degrade as Equation (6).



Therefore, stabilizing ferrate ion against decomposition and improving preparation efficiency are the key technology in ferrate preparation. However, at the presence of alum, when alum excesses a certain concentration in anolyte, the Reaction (7) will take place:



The precipitation of $\text{Al}(\text{OH})_3$ can absorb FeO_4^{2-} and result in its decomposition and then be settled.

The further relevant investigations are carrying out.

3 Conclusions

Using alkalinity solution containing a certain content of alum, a kind of combined ferrate-alum as a new water purification agent was prepared. A designed electrochemical reactor for the process is double anodes and single cathode separated by a kind of membrane. The determined conditions for ferrate-alum preparation are: given voltage is 5V; electrolyzing time is 6h; alum concentration is below 2% in weight. In above condition, the liquid product with 0.0294 mol/L FeO_4^{2-} and 2% Al_2O_3 (in weight percent) was prepared. The efficiency of production can be improved by controlled above parameters to optimum and chose effectual membrane. In addition, adding some stabilizer to anolyte can reduce decomposition of ferrate effectively. This method will be suitable for ferrate-alum to be prepared and dosed on line.

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