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Short Communication

Recovery of Dissolved Metals from Beneficiation Wastewater by Electrochemical Oxidation

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Beneficiation wastewater, grew out of the mine industry, has made a very wide range of pollution owing to the large amount of metals such as Fe, Ni, and Mn contained in it. The materials for selectively recover the including metals in beneficiation wastewater was highly demanded. In our work, an electrochemical method was explored to produce the highly required materials (neutralizing agents). In the direct oxidation reaction, the graphite electrode demonstrated the best performance with highest rate compared with BDD electrode and titanium electrode. Salt bridge was used as a connecting medium owing to its lowest Fe ions loss resulted from the slower migration rate of Fe into the catholyte. The catholyte produced by electrochemical methods has been applied as a neutralizing agent due to the high pH value. The potential of the usage of catholyte in selective recovery of dissolved metals in beneficiation wastewater has verified the successful use of electrochemical methods.

Keywords: Beneficiation wastewater; Electro-oxidation; Recovery; Fe; Precipitation

1. INTRODUCTION

Beneficiation wastewater, grew out of the mine industry, has polluted the environment seriously owing to the direct discharge. Recently, a large amount of wastewater was produced during the mining and beneficiating process. The discharge of the produced wastewater in China is approximately 150 million tons per year, which occupied 30% of the total metal smelting wastewater. The produced wastewater features large volume and complex substances, which makes a very wide range of pollution. The soil, the downstream surface water and the ground water has been found to be contaminated by beneficiation wastewater. Unfortunately, various metals such as Fe, Hg, Cu, Ni, Al, Zn, Mn, Pb, Cd, and As has dissolved in beneficiation wastewater due to its low pH and motility [1]. Nearly all the heavy metals caused in the metallurgical operations can be found in beneficiation wastewater. The concentration of the dissolved metal ranged from 10^{-6} to 10^{2} g/L. Consequently, the removal of dissolved metals has been extensively studied by many research groups [2-7].

Varieties of methods have been explored for the treatment of beneficiation wastewater. An active treatment by adding a chemical-neutralising agent was the most widespread technique for mitigating acidic effluents [8]. The pH of beneficiation wastewater increases through the addition of the alkaline material. And the increased pH will enhance the chemical oxidation rates of ferrous iron. Besides, a large amount of the dissolved metals will precipitate as hydroxides and carbonates. Finally, an iron-rich sludge including various other metals was produced. Varieties of neutralising reagents (e.g., lime, slaked lime, sodium hydroxide and calcium carbonate) which differ in efficiency and cost have been developed. Thus, the select of suitable neutralising reagents is of great importance. For example, the efficiency of sodium hydroxide is about 1.5 times higher than that of lime, while the cost is nine times more expensive. When calcium-containing neutralising reagents are applied, the removal of sulfates can be achieved. Despite the effective treatment of beneficiation wastewater by the active chemical technique, some disadvantages still exist, such as the high cost and the formation of bulky sludge which needs disposal. Therefore, many refinements have been developed for raising efficiency and reducing cost. To selectively remove some components such as molybdenum and arsenic in beneficiation wastewater, the reagents was added in a multiple-stepped way for controlling pH continuously [9]. What's more, in order to promote the aggregation of precipitates in settling ponds, all kinds of flocculating reagents are tried to be used. Actually, after the addition of alkali, only 2-4% solids were in the produced sludge and the rest was water. However, a sludge that composed of ca. 20% solids could be obtained by recycling the firstly obtained sludge into lime-holding tanks. Furthermore, the concentration of solids in the sludge can be increased to ca. 50% upon dewatering [10].

Anoxic limestone drains has been explored as an alternative approach for increasing the pH of beneficiation wastewater. Although alkali was still added to beneficiation wastewater in this system, the ferrous iron was maintained in the reduced form without oxidation, and then formed ferric hydroxide precipitation on the limestone. Afterwards, the performance of neutralising agent was reduced severely owing to the formation of precipitation. Due to increasing pressure of CO_2 within drain, the dissolution rate of limestone was accelerated. Therefore, the content of alkalinity was increased up to 275 mg/L, much higher than that obtained in an equilibrium open system (50-60 mg/L) [11]. Anoxic limestone drains are not suitable for treating all beneficiation wastewater, despite the lower cost to produce alkalinity than constructed compost wetlands. When the concentration of ferric iron or aluminium in beneficiation wastewater was significantly high, performance of anoxic limestone drains could be fine in short term. However, the drain permeability gradually decreased as the formation of hydroxide precipitation, which caused the loss of efficiency of the drain within 6 months. Besides, in the case of the usage of anoxic limestone drains in treating aerated mine waters, beneficiation wastewater was highly required to pass through an anoxic pond before the addition of anoxic limestone drain, which could decrease the concentration of dissolved oxygen in order to prevent iron oxidation. Moreover, the formation of manganous carbonate and ferrous carbonate within anoxic limestone drains was another drawback, which possibly resulted to the incongruent dissolution of the limestone gravel [12-27].

Electrochemical methods have been investigated for the determination and removal of metals. As revealed by the Wang's work, arsenic was co-precipitated with iron hydroxide by pH adjustment using electrochemical method and then removed from beneficiation wastewater [28]. Aji et al. had explored electrocoagulation and monopolar iron as the electrode to remove heavy metals from wastewater [29]. Besides, Ni was also removed by electrochemical precipitation as shown by Subbaiah et al. [30]. However, the selectivity of metals in the recovery process was not considered in all the experiments mentioned above. The simultaneous occurrence of two reactions namely oxidation reaction of Fe(II) and precipitation of metals should also be carefully considered. For example, the pH range for Zn precipitation is similar to that for Fe(II) (3~4), which easily leads to the precipitation of Fe(II) and Zn at the same time. Thus, Fe(II) should be firstly oxidized to Fe(III) of which the precipitate pH range was about 7~8 [31].

In our work, the oxidation reaction of Fe(II) during the electrochemical reaction was studied. The dissolved metals were expected to be removed from beneficiation wastewater selectively by the produced anolyte and catholyte during the electrochemical reaction.

2. EXPERIMENTS

2.1. Materials and apparatus

All the chemicals are labeled with the analytical grade. The actual beneficiation wastewater used herein was obtained from Yuantong, Hebei, Chian. And the initial concentrations of Fe, Al, Cu, Zn, Ca, Mg and other parameters were shown in Table 1. In the electrochemical reaction, three different electrodes (titanium, boron doped diamond (BDD), and graphite electrode) were applied as the anode and the cathode adopted a titanium electrode. For the sake of migrating ions between the anolyte and catholyte, a cation exchange membrane, anion exchange membrane, and salt bridge were explored. The cation exchange membrane was firstly boiled in a mixture of H_2O_2 and deionized water (30% v/v), then soaked in 0.5 M H_2SO_4 and deionized water for each 1h, respectively [32].

Table 1. Initial composition and parameters of beneficiation wastewater

Fe (mg/L)	Al (mg/L)	Cu (mg/L)	Zn (mg/L)	Ca (mg/L)	Mg (mg/L)	pH	ORP (mV)	Sulfate (mg/L)
242	35.6	26.7	19.3	93.5	18.6	2.5	251	1.315

2.2. Electrochemical reaction recovery

A reactor including two 500 mL bottles connected by Pyrex glass tubing was used in the electrochemical method. During the whole experiment, 200 mg/L of Fe(II) was used as the anolyte while 0.3 M $NaHCO_3$ was used as catholyte, then the capacity of electrolytes for oxidizing and neutralizing was evaluated. The oxidation reaction of Fe(II) was occurred in the anolyte and afterwards the catholyte was added to the anolyte for precipitation. The effects of current intensity (0, 50, 100, and 150 mA/L) and anode material on the oxidizing capacity were studied. Besides, the loss of Fe ions was also investigated with varying connecting media. Fe(III) was analyzed as Fe(II) after precipitation using a solution including 10% hydroxylamine. The quantity of oxidized Fe was determined by spectrophotometer (UV-1800 UV-VIS Spectrophotometer, Shimadzu) using ferrozine method [33, 34]. Besides, inductively coupled plasma optical emission spectroscopy (iCAP 7200 ICP-OES, Thermo Fisher) was explored to measure the concentrations of other metals.

3. RESULTS AND DISCUSSION

The oxidation experiments of Fe(II) were investigated in the prepared oxidation reactor. Fig. 1 depicted the oxidation rate constants with varying Fe ions concentrations. The oxidation reaction of Fe(II) was assumed as a first-order reaction and the rate constant could be calculated based on the concentration of Fe(II) in the anolyte. As can be shown in Fig.1, the oxidation reaction rate of Fe(II) to Fe(III) in the anolyte was linearly related with the electrical current intensity. That is, faster oxidation rates can be obtained with higher current intensity. The oxidation rate constants were 0.0375, 0.3881, 0.5422, and 0.6370 $h^{-1}$with the current intensities of 0, 50, 100, and 150 mA/L, respectively. It can be seen that the amount of Fe oxidized reached to a plateau, after then was not changed with increase in the total electrical charge in the system.

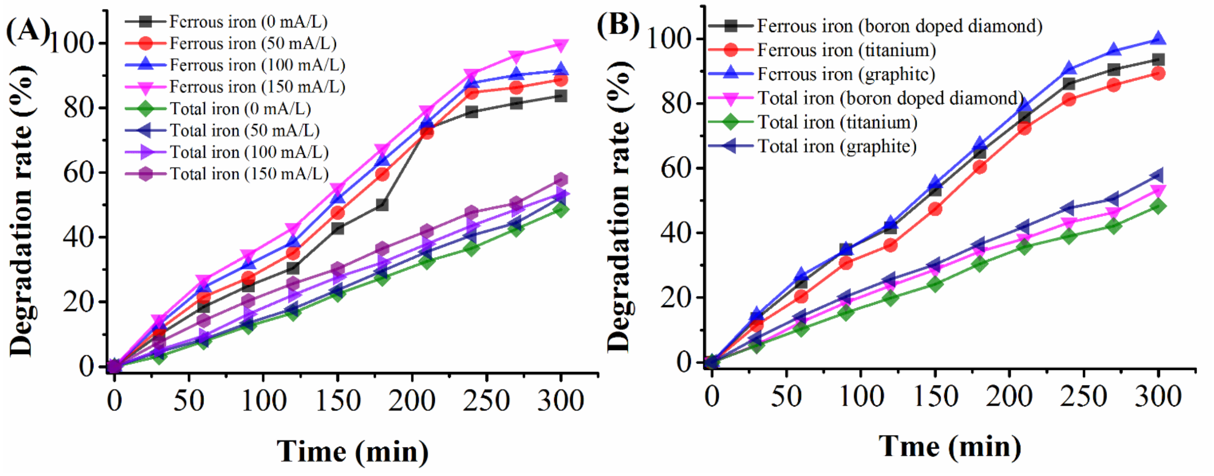

Figure 1. Electro-oxidation profiles of ferrous iron and total iron using (A) different current density (B) different electrode materials.

The relationship between the amounts of oxidized Fe with the applied amounts of electric charge was investigated and the results were shown in Fig. 1B. Firstly, the amount of oxidized Fe increased with increasing electrical charge, and then reached to a plateau. The total electrical charge used for the oxidation of Fe(II) was approximately 800 C in the system. The effect of electrode materials was investigated. And the concentrations and oxidation reaction rates of Fe ions in anolyte were show in Fig. 1C. Obviously, the graphite electrode demonstrated the best performance with highest rate. The reaction rate constants obtained on graphite, BDD, and titanium electrodes were 0.5455, 0.4421, and 0.2654 h^{-1}, respectively. Besides, the oxidation reaction occurred on the BDD electrode was more effective than that on titanium electrode, owing to the estimated reason of more hydroxyl radicals (OH•) generated on BDD electrode than titanium electrode [34, 35]. The oxidation rate of Fe(II) on the graphite electrode was very fast and possibly as a result of its hydroquinone groups that contained in most carbon materials. The hydroquinone groups can be oxidized to quinone groups that would react with Fe(II) [36]. Therefore, acidic Fe(II) solution can be successfully oxidized and neutralized by electrochemical method. However, the problem of Fe ions loss due to the transport of Fe to the catholyte across the membrane was existed and required to be solved.

The effects of connecting media on the concentrations and oxidation reaction rates of Fe(II) in anolyte was investigated and the results were shown in Fig. 2. The loss of Fe ions is defined as the changed compared with initial concentration. As can be seen in Fig. 2, the loss of Fe(II)/Fe(III) caused by cation exchange membrane, anion exchange membrane and salt bridge was nearly 65, 45, and 25%, respectively. Besides, the oxidation reaction rates of cation exchange membrane, anion exchange membrane and salt bridge were 0.5512, 0.4907, and 0.3775 h^{-1}, respectively. Compared with previous reported oxidation rate using boron doped electrode [37], our result showed a slightly enhancement. In contrast to the anion exchange membrane, the cation in anolyte will migrate to the catholyte when using cation exchange membrane as connecting media. The very fact of transport of ions across membrane caused the difference of reaction rates between cation exchange membrane and anion exchange membrane. Moreover, Fe ions would migrate to the catholyte and precipitated on the membrane, which accounted for most of the Fe ions loss. Fortunately, owing to the slower migration rate of Fe ions into the catholyte, less Fe ions loss was achieved with salt bridge as connecting media. Despite the slower reaction rate obtained by salt bridge than other connecting media, the reaction rate of salt bridge was slower than that of other connecting media, it had the lowest Fe(II)/Fe(III) loss rate. Therefore, salt bridge was used as a connecting medium.

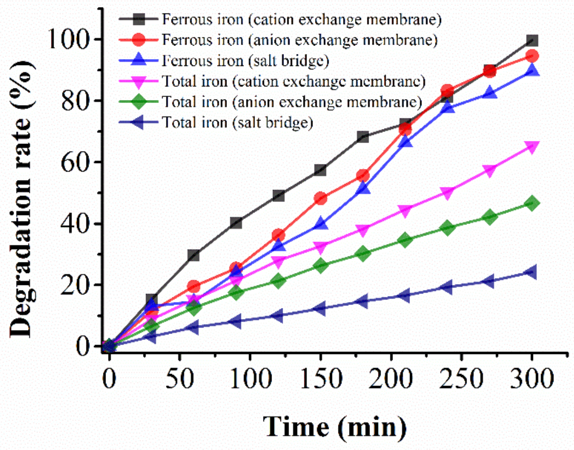

Figure 2. Electro-oxidation profiles of ferrous iron and total iron using different connecting media.

The neutralizing performance of the catholyte was evaluated. Regardless of current intensity and anode material, the final pH measured was approximately 8.6, which differed from the theoretically estimated value 12. The pH of the anolyte and catholyte slowly decreased and increased, respectively. The oxidation-reduction potential in the anolyte rapidly increased for 30 minutes and then increased slightly while the catholyte oxidation-reduction potential decreased rapidly for 30 minutes and then slowly decreased. The electrical conductivity using salt bridge in anolyte increased more than cation exchange membrane and anion exchange membrane, it may be because the various anion in salt bridge migrated to anolyte [38]. The difference between the actual and theoretical pH was resulted from the consummation of hydroxide ion (OH^-) in the formation of Fe(III) precipitation in the catholyte or on the membrane surface. Actually, the electrochemical preparation process of neutralizing agents and its usage for neutralizing acidic medium was separated in indirect oxidation experiments. During the electrochemical process for producing agents, the PH of final catholyte was high up to 11 after 24 h. Thus, the prepared catholyte could be used as a neutralizing agent with the expectation to be effective in the process for selective precipitation. Moreover, the Fe ions loss and membrane fouling due to the formation of Fe precipitation could be prevented in the indirect oxidation system.

Electrical power consumption during the experiment was calculated according to the voltage change with time, and the results were presented in Fig. 3 It can be seen that the energy consumption of the electrode sorted in the following order: titanium anode > graphite anode > BDD anode. However, the two factors (oxidizing potential and electrical energy consumption) synthesize together, decided that the graphite anode was the most effective electrode for the oxidizing reaction of Fe(II). As to the connecting media, salt bridge was the most effective one due to the slower migration rate of ions than other connecting media.

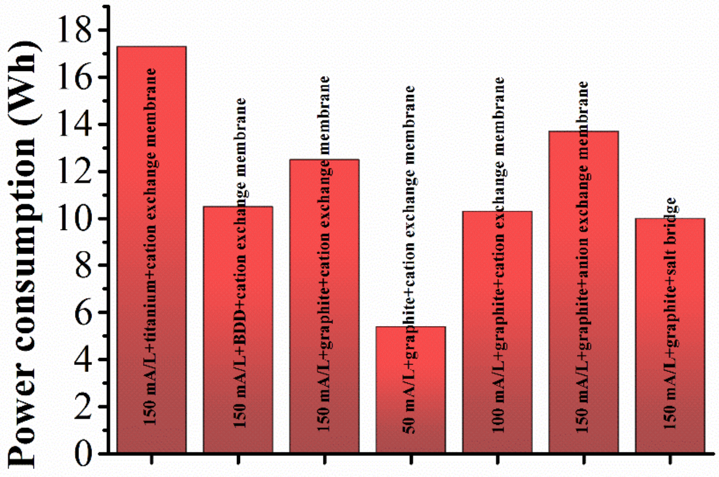

Figure 3. Electrical power consumptions profiles.

In the direct oxidation reaction, Catholyte was used as a neutralizing agent rather than chemicals (e.g., NaOH or $CaCO_3$) (Table 2). As can be seen from Table 3, in the case of catholyte used, the recovery yields of Fe, Al, Zn and Cu were 99.56, 90.23, 75.35 and 63.25%, respectively. Besides, the selectivities of Fe, Cu, Zn and Al were 0.98, 0.91, 0.95 and 0.87, respectively. The recovery yields of Fe and Al, and the selectivity of Fe obtained using Catholyte as the neutralizing agent were higher than that obtained using chemicals. However, when Catholyte used, bad news was that the recovery yields of Cu and Zn, and the selectivity of Cu and Al decreased. Although the recovery yield and selectivity obtained by using Catholyte were slightly different with that obtained by using a chemical neutralizing agent, metals could selectively precipitate by pH adjustments. Thus, exploring catholyte as a neutralizing agent for the selective removal of metals from beneficiation wastewater is completely feasible. Rather than normal DC power supply, solar cell was adopted to prepare the anolyte and catholyte. The basically same ORP could be achieved with the use of solar cell. The final PH of catholyte increased to 11 after 75 h. More time was required herein due to weather conditions. In general, solar cell was successfully applied to supply power for electrochemical reaction.

Table 2. Recovery yield from beneficiation wastewater using the neutralizing agent made by electric reaction (performed at 100 mA/L).

Recovery content	pH condition	Recovery yield (%)	Selectively
Zn	7.8	75.35	0.95
Al	5.4	90.23	0.87
Fe	4.1	99.56	0.98
Cu	6.2	63.25	0.91

4. CONCLUSIONS

The production of catholyte for the selective removal of dissolved metals in beneficiation wastewater via electrochemical methods was investigated in our study. In the direct oxidation reactor, 100mA/L was sufficient for the reaction. Owing to the quinone compounds contained in graphite, the fastest reaction rate for Fe(II) oxidation which generally occurred on the electrode surface was obtained on the graphite electrode. When the cation exchange membrane and anion exchange membrane used for connecting media, the loss of Fe also took place because of the precipitation in catholyte. Salt bridge was an excellent connecting media due to the less Fe loss. The catholyte produced by electrochemical methods could be used as a neutralizing agent due to the high pH value, which demonstrating as a catholyte promising material for selectively remove metals in beneficiation wastewater. The results have verified the successful use of electrochemical methods in the production of oxidizing and neutralizing agents, which further reduce the use of chemicals. Rather than normal DC power supply, solar cell was used for supplying electric power, which effectively reduce energy consumption.

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