Optimal Conditions for Treating Acid Mine Drainage by Bentonite-Steel Slag Composites

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Abstract: The Acid Mine Drainage has characteristics of low pH, high concentrations of heavy metal ions, such as Fe^{2+} , Mn^{2+} , Cu^{2+} and Zn^{2+} . In this paper, the composite particles that consisted of bentonite and steel slags were used to dispose the Acid Mine Drainage. Bentonite is the mineral materials and can adsorb heavy metal ions excellently. The steel slags are alkaline and industrial solid waste for the treatment of the Acid Mine Drainage. The main influencing factors, such as adsorbent dosages, shaking rates, concentrations of heavy metal ions, temperatures, adsorption time and pH value were studied by the static experiment. Increasing the adsorbent dosages and the concentrations of the heavy metal ions, speeding up the shaking rates, raising the temperatures, extending the adsorption time and improving pH would improve the removal efficiencies of heavy metal ions. Through considering the removal efficiencies and the treatment costs, the optimum reaction conditions for the four kinds of heavy metal ions were obtained. The adsorbent dosage 21 mg/L, the rotational speed 120 r / min, the temperature 25°C, adsorption time 100 min and the initial wastewater pH 7. The four kinds of heavy metal ions existed independently in the simulated mine wastewater. The highest initial concentrations of Fe^{2+} , Mn^{2+} , Cu^{2+} and Zn^{2+} were 150 mg/L, 100 mg/L, 170 mg/L and 140 mg/L respectively. The removal rates were 93.42%, 92.64%, 93.86% and 95.17% respectively. The determination of the particles' SEM-EDS Microscopic characterization showed the composite particles could play a part in neutralizing, absorbing and the chemical precipitation. The acidity decreased notably and the heavy metal ions of Fe^{2+} , Mn^{2+} , Cu^{2+} and Zn^{2+} were adsorbed and precipitated effectively. The research results can extend the practical engineering application of the composite particles.

Keywords: Acid Mine Drainage, heavy metal ions, bentonite-steel slag composite particles, adsorb, precipitate, influencing factors, technologic conditions

1. Introduction

The environmental pollution of acid mine wastewater includes two aspects: acid wastewater and heavy metal ions. So mine acid wastewater treatment is also aimed at the above two aspects. It is reported (Lei and Sun 2008) that separations of heavy metal precipitation were the use of metal hydroxide and sulfide precipitation of different solubility products. Under the control of different precipitation conditions, the specific ions were precipitated and separated. It is reported (Peng 2010) that treatment of Fe^{2+} , Fe^{3+} , Mn^{2+} and Zn^{2+} in acid mine wastewater by two stages, neutralization of lime and sodium hydroxide. It is reported (Xiao et al 2015) that by means of shaking-absorption tests, a comparative experiment studied the effects of bentonite, steel slags, bentonite-steel slag composite powder materials, bentonite-steel slag composite particles on the treatment of acid mine wastewater containing Zn^{2+} . It is reported (Xue et al 2013) that adsorption removal of Cu (II) from aqueous solution by basic oxygen furnace slag (BOFs) which was activated by the mechanochemistry process was investigated. It is reported (Rapacz-kmita et al 2016) that the influence of the organophilisation process on the properties of resulting organobentonite fillers and their capability to improve the

mechanical properties of clay/polymer nanocomposites were investigated. It is reported (Shabani et al 2014) that the adsorption activity of perlite nanoparticles for removal of Cu^{2+} , Fe^{2+} and Mn^{2+} ions at Iran Sarcheshmeh copper acid mine drainage was discussed. It is reported (Xiao and Wang 2011b) that bentonite has highly adsorptive capacities with large internal surface areas. It is reported (Yang et al 2010) that the special porous structures of steel slags not only have good adsorptive properties, but also have alkaline and mineral constituents of Ca_3SiO_5 and Ca_2SiO_4 etc. The hydrolyses of steel slags can release a large amount of alkalinity and neutralize the acid in the mine wastewater. It is reported (Wang et al 2010) that calcination could evaporate the molecular water and organic. They were removed from the bentonite's surface and structure layers, so that adsorption properties of the particles were enhanced.

Therefore, in this experiment, bentonite and steel slags were mixed according to the ratio of 5:5, the amount of binder of Na_2CO_3 was 5% of the total mass of the composite adsorbent, making of composite particles.

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2. Test Section

2.1 Material and equipment

Sodium bentonite was bought from the shop of Wan Peng Bentonite mine which located in Heishan county Liaoning Province. Slags were generated from the steel-making factory in Binzhou city of Shandong Province. The agglomerant was NaCO_3 . Heavy metal ions in form of Fe^{2+} , Mn^{2+} , Cu^{2+} and Zn^{2+} in simulated water. Z-2000 Atomic Absorption Spectrophotometer, HZ-9811K two speed of constant temperature oscillator, PHS-3C pH meter, MY3000-6 intelligent coagulation test stirrer, BSW-6-12 box-type muffle furnace, BS244S electronic balance, FEI Quanta200 scanning electron microscope (SEM).

2.2 Preparation of composite particles

Mixing the bentonite and steel slags with the ratio of 5:5 well, the amount of binder of Na_2CO_3 was 5% of the total mass of the composite adsorbent, combining all materials well. A certain proportion of distilled water was added for several times and stirred with a glass rod. Heavy hammer vibrated and crushed, then the composite materials were extruded to granulation. The diameter of the particles was 2mm, calcination temperature was 500 °C for 1.5 hours. Bentonite-steel slag composite particles were made well though the above processes.

2.3 Test methods

(1) Determination of optimum reaction conditions: The experiment was divided into 4 groups, each group of 10 conical flasks whose capacity is 250 ml. Simulation of mine wastewater containing Fe^{2+} , Mn^{2+} , Cu^{2+} and Zn^{2+} by adding 100 ml, their ions' concentration was 100 mg/L, 35 mg/L, 20 mg/L and 25 mg/L. The prepared bentonite-steel slag composite particles were put into each conical flask, finally to seal the conical flask strictly. To study the influencing factors, such as the dosage of the adsorbent, the shaking rate, the temperature, the adsorption time and pH, affected the removal of heavy metal ions. The residual concentrations of four heavy metal ions were measured under different reaction conditions. During the experiment, if the specified factor changed, other factors must unchanged.

(2) Determination of the highest initial concentration of heavy metal ions: Under the above optimum reaction conditions, the other steps were also divided into 4 groups, each group of 10 conical flasks whose capacity is 250 ml. Simulation of mine wastewater containing only one ion of Fe^{2+} , Mn^{2+} , Cu^{2+} and Zn^{2+} by adding 100ml, their concentration was different. The residual metal ions' concentrations were determined in each group, when simulation of mine wastewater contained only one ion of Fe^{2+} , Mn^{2+} , Cu^{2+} and Zn^{2+} . The removal rates were all above 90%, what the highest initial concentrations of the heavy metal ions were.

(3) SEM-EDS analysis of bentonite-steel slag composite particles could reveal morphological changes of the surface of composite particles before and after adsorption. The composite particles played a part in neutralizing, absorbing and the chemical precipitation.

3. Results and Discussion

3.1 Influencing factors on adsorption

(1) Effect of adsorbent dosage on adsorption

According to Test method (1), pH of water samples was 7 and temperature of constant temperature oscillator was 25 °C with the speed of 120 r/min continuing absorbing for 100 minutes. Under the different dosages of composite adsorbent, the results of residual concentration and removal effects of the four heavy metal ions were exposed. The results are shown in Figure 1.

Figure 1. Effect of adsorbent dosage on adsorption.

Figure 1 shows with the increasing of the dosages of the composite adsorbent of bentonite-steel slag, the removal rates of heavy metal ions increased gradually. When the adsorbent dosages were 3 g/L to 13 g/L, the adsorption rates of Fe^{2+} and Cu^{2+} increased rapidly. With the adsorbent dosages more than 13 g/L, the adsorption capacities of Fe^{2+} and Cu^{2+} remained constant. When the adsorbent dosages were 3 g/L to 19 g/L, the removal rates of Zn^{2+} maintained an obviously upward trend and the removal rates of Mn^{2+} increased incrementally. The removal rates of the four heavy metal ions were gentle until the adsorbent dosages reached 21 g/L.

It is reported (Fu et al 2009) that because the concentrations of Fe^{2+} , Mn^{2+} , Cu^{2+} and Zn^{2+} were given in solution, with the increase of the dosages of complex adsorbent, the adsorption capacities of heavy metal ions increased gradually and the adsorption removal rates increased. Above all, the optimal dosage of the new composite adsorbent was 21 g/L.

(2) The shaking rate

When pH of water sample was 7, at different shock speeds, other test conditions followed the above. The results are shown in Figure 2.

From Figure 2, when the shaking rates were from 0 r/min to 80 r/min, the overall removal rates showed upward trends. The removal rates of Mn^{2+} and Zn^{2+} increased faster than those of Fe^{2+} and Cu^{2+} . As the shaking rates were 80 r/min to 120 r/min, the removal rates of four kinds of metal ions increased slowly. As time went on, removal rates tended to balance. If the shaking rates were too large, the strength of composite particles was too easily destroyed, furthermore, increasing the costs of removing metal ions. In conclusion, the best shaking rate was 120 r/min.

Figure 2. Effect of the shaking rate on adsorption.

(3) The temperature of the experiment

When the shaking rate was 120 r/min, at different temperatures, other test conditions followed the above. The results are shown in Figure 3.

Figure 3. Effect of temperature on adsorption.

As shown in Figure 3, the reaction temperatures of bentonite-steel slag composite particle adsorbent were from 10 °C to 20 °C, with removal rates of metal ions increasing significantly. While the growth rates slowed down from 20 °C to 25 °C, the removal rates kept constant after 25 °C. Considering the treatment of actual water temperatures, the reaction temperature was identified 25 °C.

(4) The reaction time

The reaction temperature was 25 °C, at different adsorption time, other test conditions followed the above.

The results are shown in Figure 4.

From Figure 4, when the reaction time from start to 50 min, the adsorption rates of Fe²⁺, Mn²⁺, Cu²⁺ and Zn²⁺ increased rapidly with the composite adsorbent. During the time 50 min to 100 min, the growth rates were slow slightly, after 100 min the adsorption quantities tended to balance. It is reported (Xiao and Li 2011a) that because the surface of composite particles contained material with adsorption effects, such as disconnect chemical bonds and hydroxyl radicals and so on, the metal ions could be adsorbed. The best reaction time was confirmed for 100 minutes by summarizing the experimental results.

Figure 4. Effect of reaction time on adsorption.

(5) The initial wastewater pH

Adsorption of 100 min under different pH, other test conditions followed the above, as shown in Figure 5.

Figure 5. Effect of pH on adsorption.

Effect of waste water pH on removal of metal ions of bentonite-steel slag are given in Figure 5. The adsorption rates of four kinds of heavy metal ions increased rapidly from 2 to 6 and then levelled off. The pH was more than 6, the removal rates reaching to more than 90%. It is reported (Lei et al 2013) that when pH was low, H⁺ would occupy the adsorption sites of the composite particles, competing with metal ions. On the contrary, pH was too high, metal ions would also occur hydrolysis and precipitation. So the optimum pH was tested 7.

3.2 Effects of ions concentration on adsorption

According to Test method (2), based on the above optimum reaction conditions, the composite particle adsorbent of bentonite-steel slag was added 21g/L, pH of wastewater sample was 7 and temperature of constant temperature oscillator was 25 °C with the speed of 120 r/min continuing absorbing for 100 minutes. When the metal ions of Fe²⁺, Mn²⁺, Cu²⁺ and Zn²⁺ existed alone and the removal rates attained more than 90%, the highest initial concentrations of the four heavy metal ions were investigated. The results are shown in Figures 6, 7, 8 and 9.

Figure 6. Removal rate of Fe²⁺ at different initial concentrations.

Figure 7. Removal rate of Mn²⁺ at different initial concentrations.

Figure 8. Removal rate of Cu²⁺ at different initial concentrations.

Figure 9. Removal rate of Zn²⁺ at different initial concentrations.

As shown in Figures 6, 7, 8 and 9, initially, the quantitative composite particle adsorbent can provide sufficient adsorption sites for metal ions. Therefore, the adsorption rates of metal ions were more than 90% by the composite adsorbent of bentonite-steel slag in a certain range. Beyond the adsorption capacity range, adsorption removal rates decreased rapidly. When usages of the composite particle adsorbent were 21 g/L, the highest initial concentrations of Fe²⁺, Mn²⁺, Cu²⁺ and Zn²⁺ were 150 mg/L, 100 mg/L, 170 mg/L and 140 mg/L respectively.

3.3 Structure and properties of composite particles

The configurations of particles were compared before and after adsorption. Through scanning electron microscope, SEM-EDS analyses of composite particles were obtained before reactions and after adsorbing Fe²⁺, Mn²⁺, Cu²⁺ and Zn²⁺. The results are shown in Figure 10.

From the comparisons of SEM diagrams before and after adsorption, the surface of the composite particles was uneven after the adsorption, parts of holes were blocked at the same time. Combining the EDS spectra, the contents of Fe and Mn in the surface of the composite particles were increased after adsorbing of Fe²⁺ and Mn²⁺. The elements of Cu and Zn were detected on the surface of Cu²⁺ and Zn²⁺ after adsorption. It is reported (Mende et al 2016) that thus it can be seen the surface of the composite particles can adsorb the ions of Fe²⁺, Mn²⁺, Cu²⁺ and Zn²⁺ through electrostatic attraction, surface adsorption, surface complexation and chemical precipitation. The specific surface areas of the composite adsorbent enlarged to continue absorbing and coagulating the ions.

Figure 10 (a) SEM-EDS spectra of composite particles before adsorption.

(b) SEM-EDS diagram of composite particles adsorbed Fe^{2+} . (d) SEM-EDS diagram of composite particles adsorbed Cu^{2+} . (c) SEM-EDS diagram of composite particles adsorbed Mn^{2+} . (e) SEM-EDS diagram of composite particles adsorbed Zn^{2+} .**Figure 10.** SEM-EDS spectra of composite particles before and after adsorption.

4. Conclusions

(1) The static experiment studied the main influencing factors. It provided the best reaction conditions in which the composite particles disposed heavy metal ions of the Acid Mine Drainage. The optimum conditions for adsorbing heavy metal ions by bentonite-steel slag composite adsorbent were the optimal dosage of the composite adsorbent of 21 g/L, the shaking rate of 120 r/min, temperature of 25 °C, adsorption time of 100 minutes

and the initial wastewater pH of 7.

(2) When the four kinds of heavy metal ions existed independently in the simulated mine wastewater and the highest concentrations of Fe^{2+} , Mn^{2+} , Cu^{2+} and Zn^{2+} were 150 mg/L, 100 mg/L, 170 mg/L and 140 mg/L, the removal adsorption rates were 93.42%, 92.64%, 93.86% and 95.17% respectively.

(3) SEM-EDS spectra showed that the contents of Fe^{2+} , Mn^{2+} , Cu^{2+} and Zn^{2+} increased on the surface of composite particles. The results showed that the composite adsorbent has a good effect on the removal of heavy metal ions from wastewater under the optimum reaction conditions. This method will be worthy of popularization and application.

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