Preparation of two nanometer magnetic flocculants and treatment of slime wastewater

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Abstract. Nano Fe3O4 was prepared by co-precipitation method and loaded into cellulose and biochar to prepare Fe3O4-chitosan-cellulose and Fe3O4-chitosan-biochar. XRD, FT-IR, SEM and energy spectrum showed that the target product was obtained. Fe3O4-chitosan-cellulose and Fe3O4-chitosan-biochar flocculant used in coal slime water treatment respectively. The results showed that water turbidity and COD removal rate of Fe3O4-chitosan-cellulose were 96.90% and 78.34% respectively and the water turbidity and COD removal rates of Fe3O4-chitosan-biochar on slurry water were 94.05% and 73.89% respectively. Fe3O4-chitosan-biochar treatment is better.

1. Introduction
With the development of economy, the pollution and shortage of water resources have become more and more serious[1]. The effective removal of micro-pollutants in water is a challenging frontier research subject. Flocculus method is one of the important methods for pollution prevention and control[2-5]. Nanometer magnetic flocculant has many excellent properties due to its size and surface effect, such as high coercivity, superfluidity, high specific surface area and low Curie temperature[6-8]. Majeed down[9] prepared Nano Fe3O4 NPs (ultra-small magnetic iron oxide) by co-precipitation method and optimize the polymer ligand concentration. Then further improved the performance of polymer of saturation magnetization Rh110 and successfully removal of fluorescent dyes. Xing et al[10] used acidity-containing wastewater to prepare Nano Fe3O4 for treatment of acidic red wastewater, and could also treat azo in wastewater in a short time. Wang, et al[11] prepared magnetic composite flocculant in solid-liquid separation by gravity and magnetic, compared with the traditional flocculants can remove turbidity, reduce the settlement of flocculation body at the same time, reduce the dosage of flocculant, reduce the water content of floc. It can dispose sewage efficiently and reach the purpose of recycling[12-14].
This experiment through co-precipitation prepared nano Fe3O4[15], which through sol-gel method using chitosan as adhesive[16]. Fe3O4 was loaded respectively to biochar and cellulose which nano magnetic composite flocculant was prepared. Slurry water was difficult to deal because of high concentration, fine granularity, high proportion of clay minerals. We can use nanometer effect and Fe3O4 applied to the sedimentation treatment of high concentration slime water. The effect of flocculus was evaluated.

2. The experiment

2.1. Materials and instruments
Materials: The straw were collected from the shenyang jianzhu university calamus stalk. Chemicals used during the study were FeCl₃•6H₂O, FeSO₄•7H₂O, polyethylene glycol, chitosan and ammonia are all analytical pure, etc. All chemicals used were of reagent grade and used without further purification.

Water sample: the slime water selected in this experiment was taken from Shanxi coal washing wastewater.

Instrument: Infrared spectra of the prepared magnetic flocculation samples were recorded with FTIR. Infrared spectrometer records magnetic flocculation samples. Infrared spectra of the prepared magnetic flocculation samples were recorded with X-ray diffractometer. Metallographic microscope records magnetic flocculation samples.

2.2. Test

2.2.1. Preparation of magnetic nanometer flocculant.
- Preparation of biological carbon: locally collected calamus straw were dried and grinded through 100 mesh sieve. Then the treated powder was through pyrolysis of 2 h in the muffle furnace at 500 °C. After natural cooling the biological carbon was washed by 3mol/L hydrochloric acid and distilled water to clean and remove ash and surface residue. Then store biological carbon in the dryer.
- Preparation of cellulose: locally collected calamus straw were cleaned and stored the dryer. The dried calamus grinded through 100 mesh sieve and soaked by 0.1mol/L KMnO₄ for 24 hours. The processed cellulose was washed with distilled water to clean by neutral. Then store cellulose in the dryer.
- 4.0g chitosan was added to 200mL deionized water, heated at 45 °C water and stirred at 3000 r/min until completely dissolved. Put 2.6g FeSO₄•7H₂O and 3.9g FeCl₃•6H₂O into the Mixed liquid and increase the temperature to 80 °C. Then put the 28%NH₃•H₂O slowly into the Mixed liquid and adjust the PH to10. After that put the 6.4g biological carbon into the Mixed liquid and the preparation of the Fe₃O₄-chitosan-biochar was done. The preparation of the Fe₃O₄-chitosan-biochar was washed by distilled water to clean and stored in the dryer.

2.2.2. Water treatment test. 100mL of slime water and 0.4g nano magnetic composite flocculant put into the beaker are stirred at 300r/min for 30min to coagulate. The coagulation liquid was separated by magnet. COD and turbidity were measured by spectrophotometer in the residual supernatant, and the removal rate was calculated according to the amount of COD and turbidity which are changed in the water treatment.

3. Results and discussion

3.1. Characterization of magnetic nanometer flocculant

3.1.1. 3XRD analysis.
Figure 1. XRD patterns of Fe3O4, Fe3O4 – chitosan-cellulose, Fe3O4 - chitosan-biochar

Figure 1 shows the X-ray diffraction patterns have sharp diffraction peak, shows that after Fe3O4 by chitosan loaded on cellulose and biochar which Fe3O4 crystal structure has not changed and the crystallization effect is very good, corresponding to the Fe3O4 crystal plane of (220), (311), (400), (422), (511) and (440), and 2 theta is 30.1° ,35.5°, 43.0° , 53.3°,57.2° and 62.7°respectively. This indicates that Fe3O4 was successfully encapsulated by cellulose and biochar without structural changed. Figure of Fe3O4- chitosan-biochar map, in 2 theta equals 21.5° biochar character of diffraction peak was appeared.

3.1.2. FT-IR. Figure. 2 is an infrared spectrum of Fe3O4-chitosan, Fe3O4 -chitosan-biochar, and Fe3O4-chitosan-cellulose. Among them, Fe3O4 -chitosan showed an OH vibration peak at 3700 cm-1 and an N-H vibration peak at 3400 cm -1. Compared with the infrared spectrum of Fe3O4-chitosan-biochar and Fe3O4-chitosan-cellulose, the OH vibration peak disappeared at 3700cm-1, and the NH vibration peak which appeared at 3400cm-1 move to 3300cm -1 and 3340cm -1respectively. Explain that Fe3O4 - chitosan-biochar, Fe3O4 -chitosan-cellulose in the preparation process, the NH on the chitosan hydrogen bond with the hydroxyl group on the surface of the supported material, so that the magnetic composite flocculant has a stable structure.

Figure 2. FT-IR patterns of Fe3O4-chitosan, Fe3O4-chitosan-biochar, and Fe3O4-chitosan-cellulose

3.1.3. SEM
Figure 3 is an SEM image of Fe₃O₄-chitosan-biochar, and Fe₃O₄-chitosan-cellulose. The magnification factor is 100,000. From Figure (a), Fe₃O₄-chitosan-biochar composite flocculant has good dispersibility of without too much agglomeration, so it can be better combined with the flocculant matrix biochar. The Fe₃O₄ particles in the field of view are between 30nm, which can ensure the surface of the particles contain hydroxyl groups, so they can be effectively bonded to the biochar with chitosan. It can be seen from Figure. (b) that Fe₃O₄ in Fe₃O₄-chitosan-cellulose composite flocculant has poor dispersibility and partial agglomeration because cellulose is coarser and less adsorbent than biochar, which results magnetic particles collide with each other to cause agglomeration under the action of chitosan adhesion.

3.1.4. Energy spectrum analysis

The energy spectrum analysis mainly judges what elements contained in the flocculant prepared. According to the energy spectrum of the flocculant in Table 1 and Table 2, it is judged that the elements in Fe₃O₄-chitosan-biochar were C, H, O, Fe, Mg, Ca and Cl. Fe₃O₄-chitosan-cellulose contains elements such as C, H, O, Fe and Ca. It can be seen from the ratio of elements in the figure that the element of C in Fe₃O₄-chitosan-biochar is higher than Fe₃O₄-chitosan-cellulose, while the Fe element of Fe₃O₄-chitosan-cellulose is higher than Fe₃O₄-chitosan-biochar, C element mainly comes from the main body of the load including biochar, cellulose, Fe element derived from Fe₃O₄, it can be judged that Fe₃O₄ can be better loaded on biochar than cellulose, which is because voids and specific surface area of biochar are higher than cellulose, so the ability to adsorb Fe₃O₄-chitosan is higher. The O element is mainly derived from chitosan and Fe₃O₄, and the range of variation is not large.

| Table 1. Energy spectrum of Fe₃O₄-chitosan-biochar |
|------|------|------|------|
| element | line style | wt [%] | Sigma | atomic percent |
| C      | K     | 49.39 | 0.49  | 63.83          |
| O      | K     | 31.47 | 0.45  | 30.54          |
| Mg     | K     | 0.44  | 0.07  | 0.28           |
| Cl     | K     | 0.47  | 0.06  | 0.21           |
| Ca     | K     | 0.74  | 0.08  | 0.29           |
| Fe     | K     | 17.47 | 0.38  | 4.86           |
| total: |       | 100   | 100   |                |

| Table 2. Energy spectrum of Fe₃O₄-chitosan-cellulose |
|------|------|------|------|
| element | line style | wt [%] | Sigma | atomic percent |
| C      | K     | 26.84 | 0.79  | 44.36          |
| O      | K     | 33.41 | 0.65  | 41.45          |
| Ca     | K     | 0.49  | 0.12  | 0.24           |
| Fe     | K     | 39.26 | 0.75  | 13.95          |
| total: |       | 100   | 100   |                |
3.2. Slurry effect of treatment
The nano-magnetic composite flocculant prepared according to the test method was used to treat the slime water, and the results are shown in Table 3.

| flocculant             | the removal rate of turbidity [%] | the removal rate of COD [%] | phenomenon                                      |
|------------------------|----------------------------------|----------------------------|-------------------------------------------------|
| Fe₃O₄-chitosan-biochar  | 96.90                            | 78.34                      | Most of the suspended matter is carried out of the water. |
| Fe₃O₄-chitosan-cellulose| 94.05                            | 73.89                      | A large amount of suspended matter is carried out of the water. |

It can be seen from Table 3 that Fe₃O₄-chitosan-biochar exhibits better removal ability for turbidity and COD of coal slurry water, and most of the suspended objects were taken out of the water body, which removal rates were 96.90% and 78.34% respectively. However, the turbidity and COD removal rate of Fe₃O₄-chitosan-biochar on coal slurry water also reached 94.05% and 73.89% respectively. At the same time, a wide range of cellulose sources have also shown great development scenarios.

4. Conclusions
- Preparation of Fe₃O₄-chitosan-biochar and Fe₃O₄-chitosan-cellulose nano-magnetic composite flocculant by sol-gel method. Structural characterization shows that Fe₃O₄ was stably supported on biochar and cellulose respectively.
- Fe₃O₄-chitosan-biochar and Fe₃O₄-chitosan-cellulose were used for the treatment of slime water. The turbidity and COD removal rate of Fe₃O₄-chitosan-biochar on coal slurry water were 96.90% and 78.34% respectively. The turbidity and COD removal rate of Fe₃O₄-chitosan-biochar on coal slurry water were 94.05% and 73.89% respectively. Among them, Fe₃O₄-chitosan-biochar has better treatment effect on slime water.

5. References
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