

# Effect of magnetic starch on the clarification of hematite tailings wastewater

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**Abstract.** The magnetic starch solution, synthesized by mixing the caustic starch, the Fe<sup>2+</sup> solution (in some cases containing the Zn<sup>2+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup> or Mg<sup>2+</sup> ions) and H<sub>2</sub>O<sub>2</sub> solution, was used as the flocculant to investigate its clarification effect on hematite tailings wastewater. Based on the clarification tests and adsorption analysis it was demonstrated that the magnetic starch produced better clarification effect than the caustic starch, and the adsorption of magnetic starch onto hematite tailings particles was also stronger than the caustic starch. AFM found that the magnetic interaction between magnetic seeds and hematite is characteristic of long range force and greatly strengthens the adsorption of magnetic seeds onto fine hematite for agglomeration. FTIR indicates the starch adsorbed onto the surfaces of hematite and magnetic seeds, thus acting as the bridging between hematite particles and magnetic seeds, resulting in an intensified coverage of the starch onto hematite and positive action in the clarification.

## 1. Introduction

Fine or ultrafine minerals of wastewater are difficult for effective clarification, and further study on the clarification of fines has important practical significance. To take hematite tailings as an example, slime in tailings produced during the crushing and grinding of mineral processing contains a large number of fine particles. This high turbidity wastewater has poor self-purification, forms a stable suspension easily with difficult clarification due to its good hydrophobic surface, fine particle size, less momentum, high negative potential, and etc. In order to improve the clarification of mineral slimes, quite a few of settling methods have been proposed. Most of them are based on the addition of various organic and inorganic chemical agents, such as the application of new organic flocculants [1-2], the use of mixed organic flocculants [3], the combined application of surfactants and flocculants [4-6], the combination of inorganic coagulants and organic flocculants [7], the synergies of magnetic seeds and the polyacrylamide [8], the introduction of magnetic field and electric field [9-11], and etc.

As the typical representative of natural organic polymer flocculants, starch containing the caustic starch was universally used for the clarification of wastewater due to its wide source and low cost [12]. However, the natural or caustic starch has an inefficient flocculation ability and is limitedly applied for flocculation in industry recently. To improve its flocculation ability, modified starch flocculants [13] was studied and used well for efficient flocculation, including non-ionic modified starch, cationic modified starch, anionic modified starch and amphoteric modified starch.



As an important supplement to the modified starch, magnetic starch was reported to treat the wastewater containing heavy metal ions via the strong adsorption capacity of magnetic starch microspheres [14-15]. Recently, a new flocculant of magnetic starch solution [16] synthesized by mixing the caustic starch, the  $\text{Fe}^{2+}$  solution (in some cases containing the  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$  or  $\text{Mg}^{2+}$  ions) and  $\text{H}_2\text{O}_2$  solution, can be used for clarification of wastewater, presents a good clarification effect on fine minerals tailings water. In this study, investigation on the clarification of hematite wastewater by the magnetic starch solution was carried out and the mechanism of the magnetic seeding clarification was studied via the size analysis, the adsorption test, AFM and FTIR analysis.

## 2. Materials and methods

### 2.1. Materials

(1) Hematite tailings: obtained from an iron ore mine in Gansu province, China, assaying 32.84% Total Fe and 39.66%  $\text{SiO}_2$  respectively, were used for clarification tests. The X-ray diffraction analysis showed that the slimes was mainly composed of hematite and quartz. Its average particle size was 13.84  $\mu\text{m}$ , and the sample is fine and not suitable for clarification. Pure hematite with an average particle size of 10.11  $\mu\text{m}$  collected from the above ore slimes by high-intensity magnetic separation and gravity separation, was mainly used for the investigation of the mechanism analysis.

(2) Caustic starch: potato starch purchased from Changsha province, China, was conditioned with a ratio of 4 parts starch to 1 part sodium hydroxide by boiling the mixture for about 20 min while stirring at a speed of 300 r/min in the air atmosphere and cooling rapidly (in ice water) to room temperature. The solution, so-called 'caustic starch', was used for clarification tests.

(3) Magnetic starch [16]: synthesized by mixing the caustic starch mentioned above, the  $\text{Fe}^{2+}$  solution (in some cases containing the  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$  or  $\text{Mg}^{2+}$  ions) and a certain concentration of  $\text{H}_2\text{O}_2$  solution with the mixture pH10 ~ 11. Then the mixture was maintained at 85  $^\circ\text{C}$  while stirring at a speed of 300 r/min and was finished after 30 min stirring, and the suspension was kept in store for use, and the average particle size of the magnetic seeds was 100-160 nm.

### 2.2. Methods

#### (1) Clarification tests

The suspension with a 20 g/L concentration of the hematite tailings, with the addition of magnetic (or caustic) starch solution, was conditioned for 3 min in a beaker and then was poured into a cylinder for 7 min sedimentation test. After the sedimentation, a 20 mL sample of the supernatant in the cylinder was transferred to a WZ-200S turbidity meter for turbidity measurement.

#### (2) Laser diffraction for flocs size analysis

The suspension with the 20 g/L concentration of the tailings, with the addition of magnetic starch solution or caustic starch, was conditioned for 3 minutes in the above 1L beaker and then was introduced into a beaker for laser diffraction analysis by the equipment Mastersizer2000.

#### (3) Total Organic Carbon (TOC) analysis for the adsorption

To measure the adsorption density of the starch on hematite tailings or the pure hematite, two groups (caustic starch, magnetic starch) of samples obtained from the supernatant after the sedimentation were centrifuged by a general laboratory centrifuge. Then, a 25 mL aliquot of the supernatant in the centrifuge tube was transferred for TOC analysis and the residual organic carbon concentration of the sample. Finally, the adsorption density was calculated according to the residual and initial carbon concentration, along with the carbon concentration of the starch solution.

#### (4) Atomic Force Microscope (AFM) study for forces

The interaction forces between hematite, quartz and magnetic particles (magnetic seeds) were measured by a Multimode SPM Atomic Force Microscope (AFM). The substrate surface of hematite or quartz with high purity was produced by slicing, lapping, polishing, and then using deionized water, alcohol and deionized water to wash it sequentially, and at last drying the surface by nitrogen. Glass fiber with a 10- $\mu\text{m}$ -diameter magnetic seeding aggregate was manipulated to stick to the tip of the

probe by epoxy resin. Probe with the seed and substrate surface (hematite or quartz) were fixed to the corresponding positions of the AFM. Start button was pushed to make the probe move to, contact with and remove from the substrate surface. Then the result was measured.

#### (5) Fourier transform infrared spectroscopic (FTIR) study

In order to characterize the nature of the adsorption between the starch and minerals (hematite and magnetic seeds), FTIR spectra were obtained with KBr pellets using a Fourier transform infrared spectrometer Nicolet-Thermo 750. Samples of pure hematite (less than 2  $\mu\text{m}$  size) and magnetic seeds conditioned with the starch solution in a thermostatic shaker for 30 min at the temperature of 25  $^{\circ}\text{C}$  were prepared, respectively. After equilibrium, a small sample of the suspension was centrifuged and the sediment was dried. Then, FTIR spectra were measured.

### 3. Clarification tests and measurements

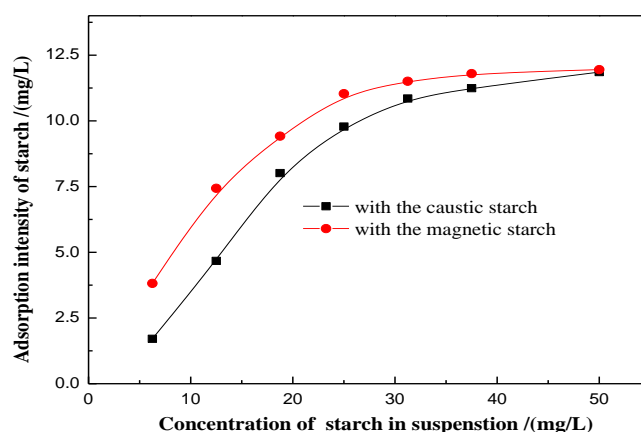
#### 3.1. Clarification tests

Table 1 shows the effect of magnetic starch on the clarification tests of the tailings wastewater. As shown in Table 1, the clarification effect is enhanced with the addition of magnetic starch. The magnetic starch was adsorbed better on fine particles than the caustic starch while also produced larger flocs size, surprisingly exhibits suitable flocculation effect on the wastewater clarification. It can be also inferred from Table 1, Mn-Fe magnetic starch was presented as a best flocculant might be attributed to the strong magnetic property of Mn-Fe ferrite, so the magnetism change of different types of magnetic starch can be utilized to investigate different clarification effects for wastewater.

**Table 1.** Effect of magnetic starch on the clarification tests (starch 300 mg/L, pH 7.8)

Magnetic starch	Clarification turbidity /NTU	Flocs size / $\mu\text{m}$	Starch adsorption /mg/L
Blank - caustic starch	450.81	14.64	110.94
FeO Fe <sub>2</sub> O <sub>3</sub> -starch	277.02	26.93	168.64
Zn <sub>0.5</sub> Fe <sub>0.5</sub> O Fe <sub>2</sub> O <sub>3</sub> -starch	390.22	21.44	163.82
Mn <sub>0.5</sub> Fe <sub>0.5</sub> O Fe <sub>2</sub> O <sub>3</sub> - starch	238.53	25.63	167.02
Cu <sub>0.5</sub> Fe <sub>0.5</sub> O Fe <sub>2</sub> O <sub>3</sub> -starch	349.61	23.97	161.04
Mg <sub>0.5</sub> Fe <sub>0.5</sub> O Fe <sub>2</sub> O <sub>3</sub> -starch	335.56	23.26	163.25

#### 3.2. Adsorption of the magnetic starch onto hematite

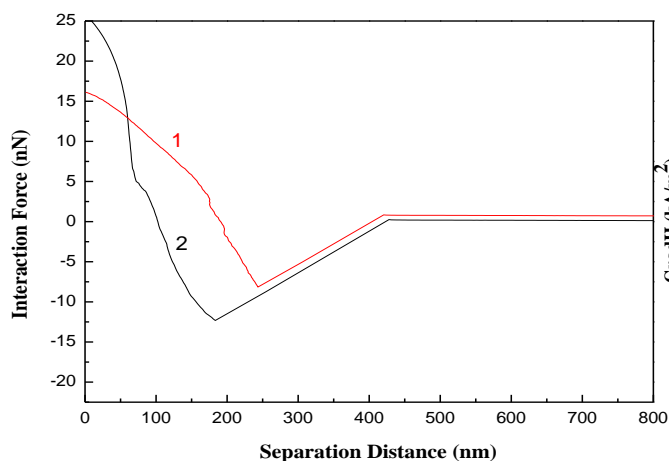


**Figure 1.** Adsorption intensity of magnetic starch onto hematite (natural pH).

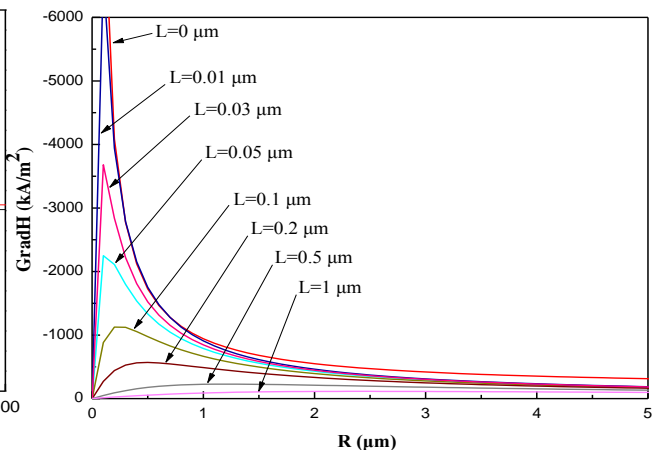
Based on the above clarification tests, the adsorption intensity of magnetic starch onto hematite was investigated and the result was given in Figure 1. It can be found that the adsorption intensity on hematite increases with the increase of the starch concentration, and by contrast the adsorption was strengthened after the addition of the same concentration of magnetic starch. Also according to Figure 1, under the condition of a small starch concentration 25mg/L the adsorption amount increases from 9.78 mg/L to 11.03 mg/L after the addition of magnetic starch, so the stronger clarification effect in the tests should be attributed to the higher adsorption of magnetic starch onto iron minerals.

### 3.3. The interaction force between particles and the magnetic field distribution on the magnetic seed

**3.3.1 The interaction force between particles.** It was performed that the adsorption of magnetic starch onto hematite was higher than the adsorption of caustic starch and the result might be related to the magnetic force between hematite and fine magnetic particles of the magnetic starch. So, AFM was used to investigate the interaction forces, and the forces between the magnetic seed and substrate surfaces (hematite and quartz) were obtained in the dry atmosphere and recorded in Figure 2.



**Figure 2.** Measured force as a function of separation distance between a 10- $\mu\text{m}$ -diameter magnetic seeding aggregate and a flat substrate surface in the dry atmosphere; 1 –the quartz substrate, 2 –the hematite substrate.



**Figure 3.** Effect of the magnetic seed radius on the magnetic field gradient of the seed surface.

As shown in Figure 2, the attractive force can still be measured while the separation distance is more than 200 nm and the maximum value of the attractive force is up to 10 nN. So, this force can be characterized as the long range force due to the high magnetic energy in the presence of the magnetic seed. This long range force would greatly strengthen the adsorption of magnetic particles onto fine minerals, and then enhance the flocculation (or agglomeration). Therefore, it can be also suggested that the flocculation of fine hematite wastewater with the magnetic starch would be stronger in the case of the presence of external magnetic field [8, 17].

**3.3.2 The magnetic field distribution on the magnetic seed surface.** While in presence of the geomagnetic field, an equation to calculate the magnetic field distribution for the fine magnetic seed was proposed [18]:

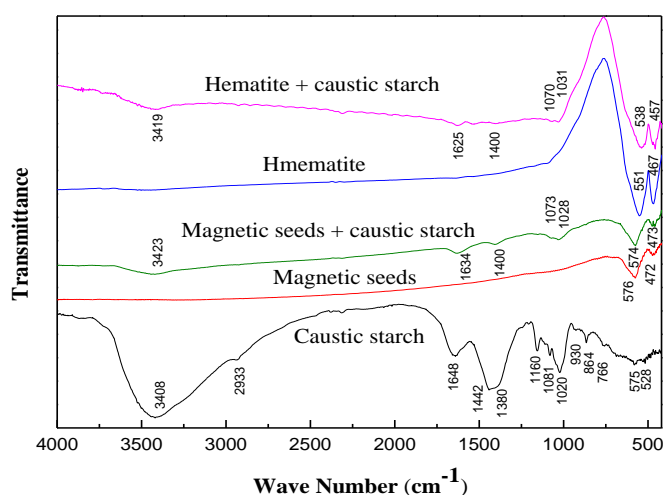
$$\text{grad}H = -\frac{\pi}{3}\sigma\delta\left(30\frac{R^3}{l^4} + 6\frac{R}{l^2}\right) \quad (1)$$

where  $R$  is the radius of magnetic seed,  $l$  is related to the distance between the magnetic seed and the fine mineral particle,  $L$  is the distance from the magnetic seed surface to the fine mineral particle,  $\sigma$  is the density of the magnetic seed, its value  $5 \times 10^3 \text{ kg/m}^3$ ;  $\delta$  is the residual specific magnetization of the magnetic seed with the value  $5 \text{ Am}^2/\text{kg}$ .

Based on the Eq. (1), the magnetic field distribution for magnetic seed was calculated in Figure 3. Figure 3 shows the magnetic field gradient on the magnetic seed increases with the decrease of the magnetic seed radius, especially increases greatly in the case of the presence of  $R$  minus  $2 \mu\text{m}$ , and within the  $0.1 \mu\text{m}$  range around the seed the magnetic force between the seed and fine minerals also increases greatly. So, the decrease of the magnetic seed size produces high magnetic field gradient which is beneficial to the flocculation of the magnetic particles and fine mineral particles.

Thus, the long range force between the magnetic seed and minerals results in a good adsorption of the fine-sized magnetic seeds onto minerals, and then improves the flocculation (or agglomeration).

### 3.4. FTIR spectra of hematite and magnetic seeds conditioned with the starch



**Figure 4.** FTIR spectra of magnetic seeds and hematite conditioned with the starch.

As shown in Figure. 4, in the spectrum of hematite–starch the new band appearing at  $1031 \text{ cm}^{-1}$  is related to C-O stretching and C-OH bending vibration, and the band at  $1070 \text{ cm}^{-1}$  is attributed to the C-H bending vibration, and the  $\text{COO}^-$  asymmetric and symmetric stretching peaks [19] are observed at  $1625 \text{ cm}^{-1}$  and  $1404 \text{ cm}^{-1}$ , and the peak around  $3419 \text{ cm}^{-1}$  is the stretching vibration of O-H group. It can be also found in the spectrum of magnetic seeds-starch, the new bands at  $1634 \text{ cm}^{-1}$  and  $1400 \text{ cm}^{-1}$  due to the  $\text{COO}^-$  asymmetric and symmetric stretching peaks [19], demonstrating the chemisorption of caustic starch onto magnetic seeds, and the C-O stretching and C-OH bending vibration at  $1028 \text{ cm}^{-1}$  and the band at  $1073 \text{ cm}^{-1}$  regarded as the C-H bending vibration are observed. Other peak around  $3423 \text{ cm}^{-1}$  is the O-H stretching vibration. Like the adsorption onto hematite, the starch was also absorbed onto the magnetic seeds through the hydrogen bonding adsorption and chemisorption.

Therefore, the starch was adsorbed onto the magnetic seeds and hematite, and also acts as a bridging media between the two types of particles, leading to an intensified coverage of the starch onto hematite particles and positive action in the flocculation.

#### 4. Conclusions

- (1) The magnetic starch was particularly beneficial to the clarification tests of hematite tailings wastewater, exhibiting a better clarification effect on the target wastewater particles than the caustic starch, and producing a strong adsorption onto hematite minerals.
- (2) Fine particles (magnetic seeds) in the magnetic starch solution exhibits high magnetic field gradient on their surfaces, and the magnetic interaction between magnetic seeds and hematite is characteristic of long range force and greatly strengthens the adsorption of magnetic seeds onto fine hematite for agglomeration.
- (3) The starch adsorbed onto the surfaces of hematite and magnetic seeds, thus acting as the bridging between hematite particles and magnetic seeds, resulting in an intensified coverage of the starch onto hematite and positive action in the clarification.
- (4) Due to its flocculation of the tailings wastewater and strong adsorption onto ion minerals, the magnetic starch can also play its pre-conditioning effect on the next flotation depression for the flocculent underflow. So, in compassion to the caustic starch the magnetic starch is more suitable for the tailings reprocess containing the flocculation and reverse flotation.

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