

Article

# Depressing Iron Mineral by Metallic-Starch Complex (MSC) in Reverse Flotation and Its Mechanism

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Received: 31 January 2018; Accepted: 22 February 2018; Published: 27 February 2018

**Abstract:** A series of metallic-starch complex (MSC) solutions, synthesized by mixing relevant metallic ionic solutions with the caustic starch solution, were used as the flotation depressants to investigate their depressing effects on hematite ore. The MSC is a nano-sized colloidal complex which is configured by hydrophilic metallic hydroxide as the colloidal nucleus on which starch and hydroxyl complex are adsorbed, resulting in a larger molecule than starch itself. The flotation tests showed that the depressing abilities of various MSC ( $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Mg}^{2+}$ ) on the iron minerals were higher than the caustic starch, and the order of depression ability was:  $\text{Zn}^{2+}$ -starch >  $\text{Pb}^{2+}$ -starch >  $\text{Fe}^{3+}$ -starch >  $\text{Mg}^{2+}$ -starch > caustic starch. Based on the adsorption analysis, the high depressing ability of the MSC arose from increasing the adsorption density of starch on iron minerals and slightly reducing the absorption of the collector dodecylamine. Adsorption behaviour also indicated that the adsorption of the MSC on mineral surfaces was thicker than the caustic starch, and among various MSC the adsorption of  $\text{Fe}^{3+}$ -starch exhibited the thickest adsorption layer while that of  $\text{Mg}^{2+}$ -starch the thinnest. Zeta potential indicated that with a weaker electronegativity than the caustic starch, MSC adsorbed onto iron minerals more easily, and the strong electrostatic adsorption with the aid of the hydrogen bonding and chemisorption agreed well with the high depressing ability of the MSC.

**Keywords:** metallic-starch complex (MSC); hydrophilic metallic hydroxyl complex; caustic starch; iron minerals; flotation depressant

## 1. Introduction

As to flotation of iron ores, much attention is attached to the reverse flotation as a significant commercial separation process using polysaccharide as the depressant for iron minerals and amine as the collector for silica [1,2]. Starch and its derivatives are widely used for depressing iron minerals in flotation due to their widespread source and low cost. In principle, starch usually adsorbs onto iron minerals via its active groups forming hydrophilic films, producing its depressing effect on the iron minerals [3]. Furthermore, Xia et al. [4] reported that hydrogen bonding adsorption is considered as a universal adsorption model for starch in the depressing process of the reverse flotation.

There are two main types of starch; amylopectin and amylose. The amylopectin starch usually produces strong depression on the flotation [5,6], and specially exhibits better depressing action on iron minerals. However, starch as the depressant for fine iron minerals is consumed too much due to high specific surface areas of fines. In order to strengthen the adsorption of starch on iron minerals and reduce its consumption in flotation, starch has been modified through different techniques [7,8], such as various chemical, physical, and compound modifications, etc. Among them, the chemical modification is one of the most widely used modification methods, and so are their modified products, such as dextrin, carboxyl methyl starch, the oxidized starch, and phosphate ester starch. These modified starches have been widely reported only for laboratory studies, but industrially caustic starch has

been widely applied in the reverse flotation of iron ore [9–12]. In fact, the causticization technique, on one hand, is to prepare the caustic starch by conditioning the starch with some alkali solution [13,14]; on the other hand, mixtures of carboxylic acids were found in the caustic starch [15]. So besides the hydroxyl groups, the existence of active carboxylic groups could further facilitate the adsorption of starch onto iron minerals and metallic hydroxide colloids concerned in this study.

There are various active groups in caustic starch. Therefore, some new techniques derived from caustic starch could be introduced into the reverse flotation for iron ores. Yue and Wu [16] recently claimed a marked technique called as “magnetic seeding depression (MSD)” for fine flotation, i.e., adding organic depressant (such as caustic starch) and magnetic seeds and applying a low field intensity pre-magnetization for depressing target minerals in the reverse flotation. This technique was reported to have a strong depressing ability in flotation of hematite ore slimes via the chemical interactions between the magnetic seeds and caustic starch, along with the magnetic interactions between the magnetic seeds and minerals, might be also named as a compound depressor (magnetic starch). In view of this, Wu [17,18] patented a new series of depressants based on the caustic starch composed of metallic hydroxide colloids and starch, known as the metallic-starch complex (MSC) solutions. As a type of nano-sized colloid, MSC synthesized by mixing relevant metallic ionic solutions with the caustic starch solution, could be used as the flotation depressant for iron minerals, producing efficient depressing ability on target minerals with a relatively low consumption of starch. In this study, the flotation of hematite ore in the presence of the metallic-starch complex (MSC) solution was investigated and the mechanism of the strong depression was studied via various measurements.

## 2. Materials and Methods

### 2.1. Materials

The sample (86.34% less than 74  $\mu\text{m}$ ) used for flotation tests and adsorption analysis was obtained from an iron ore mine in Shandong province, China, and contained 51.55% Fe (Total), 69.06% hematite, and 19.35%  $\text{SiO}_2$  respectively. Pure hematite (containing 98.02% hematite) with an average size of 17.11  $\mu\text{m}$  was obtained from an iron ore mine by high-intensity magnetic separation and gravity separation, being mostly used for the mechanism analysis.

Caustic starch was conditioned with a ratio of 4 parts starch (potato starch, commercial product) to 1 part sodium hydroxide by using deionized water and boiling the mixture for about 20 min while stirring in the atmosphere. The solution, so-called “caustic starch”, was prepared as a 0.02 g/mL concentration (pH 13.27) for use. In flotation the dodecylamine (DDA,  $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$  > 99.7% purity) was prepared into a solution of 0.05 g/mL concentration. The DDA solution (used as the collector) with a 1:1 mole ratio of dodecylamine to acetic acid was conditioned in the deionized water by stirring for certain time.

Metallic-starch complex (MSC) solution [17,18] was synthesized by mixing the 0.02 g/mL caustic starch solution mentioned above with relevant metallic ionic solution (such as  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Mg}^{2+}$  ions), using corresponding soluble salts of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ , and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , respectively. Then, the mixture conditioned with a ratio of 1 part soluble salt to 2 parts starch was maintained at 20 °C and pH 13.27 while stirring for about 20 min. Therefore, the starch in the MSC solution can be calculated as a 0.013 g/mL concentration here. Finally, the suspension (a nano-sized colloid, as confirmed in Table 1) with good dispersion was obtained for use.

### 2.2. Methods

#### 2.2.1. Reverse Cationic Flotation Tests

For each test sample, 180 g hematite ore sample was dispersed with tap water and conditioned for 3 min in a 0.5 L flotation cell with the pulp of 28.13% solids by weight, and stirred for 5 min after

adding moderate depressant. Following the depressant (using caustic starch or the MSC here), collector of dodecylamine (DDA) was introduced into the pulp and conditioned for 3 min. Then, the reverse flotation test was carried out. Finally, the target mineral hematite was depressed as a sink product, and the flotation recovery was calculated from the assaying results.

### 2.2.2. Total Organic Carbon (TOC) Analyses for Adsorption

In order to determine the amount of starch adsorption onto the particles, the supernatant solutions after conditioning the pulp with the reagents for some time according to the flotation tests were further centrifuged by a general laboratory centrifuge equipment. Then, a 25 mL aliquot of the supernatant in the centrifuge tube was taken for TOC analysis. Finally, the adsorption amount was calculated according to the residual and initial carbon concentration in the solution, as presented in Equation (1) for starch and Equation (2) for DDA, respectively.

$$\Gamma_{starch} = (C_{is} - \frac{C_{TS}C_{OS}}{C_{CS}}) / M \quad (1)$$

$$\Gamma_{DDA} = (C_{iD} - \frac{(C_{TD} - C_{TS})C_{OD}}{C_{DDA}}) / M \quad (2)$$

where  $\Gamma$  represents the adsorption amount (mg/g),  $C_{is}$  or  $C_{iD}$  is the initial concentration (mg/L) of the starch (432 mg/L) or DDA (225 mg/L) added in the suspension,  $C_{OS}$  or  $C_{OD}$  is the concentration (mg/L) of the initial starch ( $2 \times 10^4$  mg/L) or DDA ( $5 \times 10^4$  mg/L) solution,  $C_{TS}$  or  $C_{TD}$  is related to the TOC analysis value (mg/L) of the centrifugal supernatant after the conditioning with the starch or DDA,  $C_{CS}$  or  $C_{DDA}$  (mg/L) is regarded as the TOC analysis value of the initial starch or DDA solution,  $M$  (g/L) refers to the concentration of hematite ore sample (actual value is about 360 g/L).

### 2.2.3. Adsorption Behaviour of the Metallic-Starch Complex (MSC) on Minerals

The adsorption behaviour study of the metallic-starch complex (MSC) on mica surface was scanned by a Multimode SPM Atomic Force Microscope (AFM) via the Tapping Mode, combined with the Contact Mode. Prior to the measurements, a 120 mg/L concentration of the MSC solution was prepared firstly, and then a fresh mica plate was placed in the solution for 30 min. Finally, the mica plate conditioned with the MSC was blow-dried slightly by the nitrogen and measured by the AFM.

### 2.2.4. Zeta Potential Measurements

Zeta potentials of hematite and the hematite in the presence of the MSC were measured using a Coulter Delsa-440SX zeta potential analyzer (Brookhaven Corporation, Long Island, NY, USA). To prepare samples for analyses, 0.03 g pure hematite (less than 5  $\mu\text{m}$ ) was dispersed in a 50 mL  $10^{-3}$  mol/L KCl solution by an ultrasonic cleaner, and then stirred at room temperature for 2 min. Then, the reagents were added to the suspension. The mixed suspension was conditioned for 20 min for pH adjustment using HCl or NaOH. Finally, the equilibrium pH was recorded, and a small aliquot of the supernatant in the suspension was transferred to the sample cell of the analyzer for zeta potential measurements, and the average potential values were recorded. In addition, the MSC depressant itself with its concentration of 0.013 g/mL was also analyzed for zeta potentials after pH adjustment.

### 2.2.5. Fourier Transform Infrared Spectroscopic (FTIR) and X-ray Diffraction (XRD) Studies

To study the adsorption characteristics of the MSC and hematite-MSC, the FTIR analysis of the samples was measured via the transmission method using an IRAffinity-1 spectrometer (Shimadzu Corporation, Kyoto, Japan). Firstly, the pure hematite ( $\sim 2 \mu\text{m}$ ) was conditioned with the MSC solution in a thermostatic shaker for 20 min at 25  $^{\circ}\text{C}$ . Then, a small part of the suspension was collected for centrifugation, and the precipitate was dried at 55  $^{\circ}\text{C}$  using a vacuum drying oven, and was used

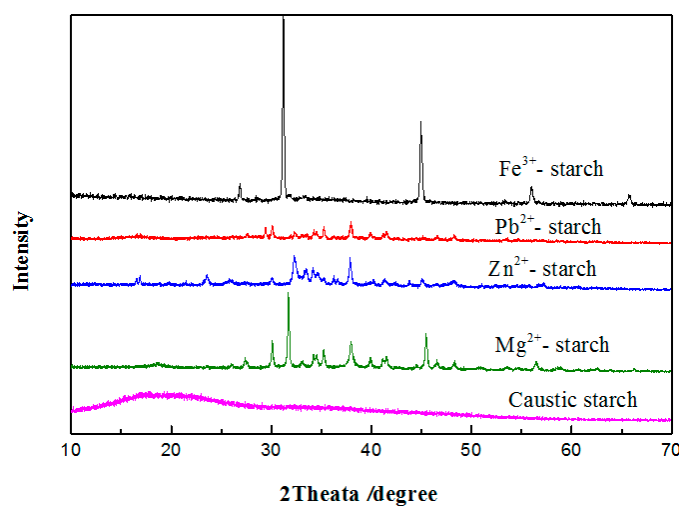
for the FTIR analysis. In addition, to understand the characteristics of the MSC, the X-ray diffraction (XRD) studies along with the FTIR measurements of the MSC were performed by crystallizing the MSC solution directly at 55 °C, and then the crystal was ground to less than 5 µm for measurements.

### 3. Results and Discussion

#### 3.1. Characterization of the Metallic-Starch Complex (MSC)

Based on the preparation method of the MSC, it can be inferred that metallic ions ( $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Mg}^{2+}$ ) could be transformed into corresponding hydrophilic metallic hydroxides and hydroxyl complexes under the strong alkali condition ( $\text{pH} > 13$ ). In order to characterize the MSC, X-ray diffraction, FTIR, turbidity analysis, and nano-particle size testing techniques were used to understand the properties of metallic starch complexes (MSC).

Figure 1 shows the XRD spectra of the MSC and caustic starch. It can be seen that the caustic starch presents an amorphous state. In the  $\text{Fe}^{3+}$ -starch spectrum the diffraction peaks nearing  $26.78^\circ$  and  $55.95^\circ$  can be attributed to the characteristic of  $\beta\text{-FeOOH}$  [19], indicating the presence of  $\beta\text{-FeOOH}$  crystal structure in the  $\text{Fe}^{3+}$ -starch. Then, in the spectrum of  $\text{Pb}^{2+}$ -starch, the characteristic diffraction peak of  $(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2$  and the peak of  $\text{Pb}_2\text{O}_3$  were observed at  $34.18^\circ$ ,  $26.78^\circ$  and  $55.95^\circ$ , respectively, and these might be due to the decomposition of  $\text{Pb}(\text{OH})_2$  and its reaction with  $\text{CO}_2$  during the crystallization of the  $\text{Pb}^{2+}$ -starch. However, there are no characteristic peaks of  $\text{Zn}(\text{OH})_2$  found in the  $\text{Zn}^{2+}$ -starch spectrum; only two characteristic peaks at  $36.25^\circ$  and  $36.53^\circ$  of  $\text{ZnO}$  were observed. Finally, it was found in the  $\text{Mg}^{2+}$ -starch spectrum, the bands around  $38.04^\circ$  and  $58.76^\circ$  can be assigned as the characteristics of  $\text{Mg}(\text{OH})_2$ , and  $\text{MgCO}_3$  was confirmed at  $33.15^\circ$  and  $46.53^\circ$ . These suggested that some metal oxides or carbonates were created during the crystallization of the MSC, indirectly reflecting the possible presence of metallic hydroxides or hydroxyl complexes in the MSC.



**Figure 1.** XRD spectra of the metallic-starch complex (MSC) and caustic starch.

Figure 2 presents the FTIR result of the  $\text{Fe}^{3+}$ -starch. It can be inferred that peaks at  $1645\text{ cm}^{-1}$  and  $1016\text{ cm}^{-1}$  can be assigned as the  $\text{C}=\text{O}$  stretching vibration and the  $\text{O}-\text{H}$  bending vibration, respectively, and the bands around  $1160\text{ cm}^{-1}$  and  $1081\text{ cm}^{-1}$  are attributed to the  $\text{C}-\text{O}$  stretching vibration, demonstrating the characteristics of starch. Then, the peak of  $\text{Fe}-\text{O}$  stretching vibration [10], which was found at  $905\text{ cm}^{-1}$ , might be due to the adsorption band of  $\beta\text{-FeOOH}$  [20]. Meanwhile, in contrast to the FTIR spectrum of  $\text{Fe}(\text{OH})_3$  colloids seen in Figure 2, it was found that the  $\text{Fe}(\text{OH})_3$  could not represent the characteristic component of the  $\text{Fe}^{3+}$ -starch. These highlighted the presence of the hydrophilic metallic hydroxide ( $\beta\text{-FeOOH}$ ) which agreed with the XRD results in Figure 1.

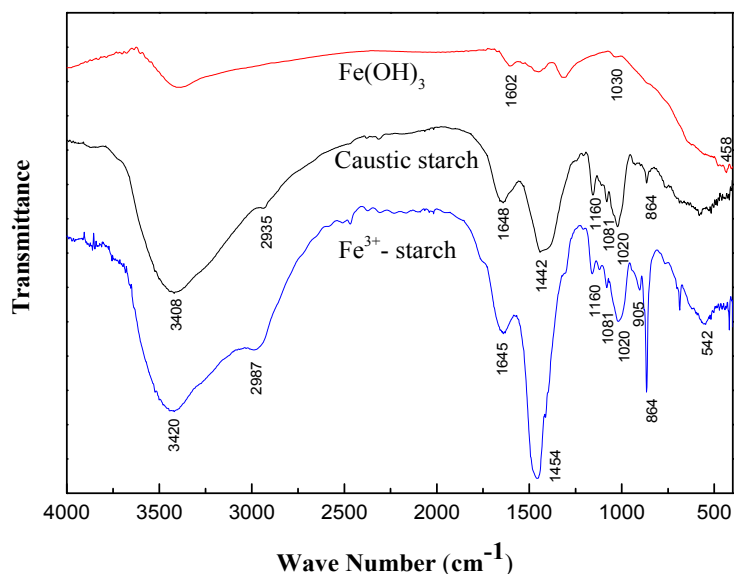


Figure 2. FTIR spectra of  $\text{Fe}^{3+}$ -starch.

Figure 3 shows the FTIR spectra of the MSC. It is seen from the spectrum of  $\text{Zn}^{2+}$ -starch that peaks of  $475\text{ cm}^{-1}$  and  $406\text{ cm}^{-1}$  can be attributed to the adsorption band of  $\text{Zn-O}$  [21], and bending vibrations of the hydroxyl of  $\text{Zn(OH)}_2$  were found around the peak  $1087\text{ cm}^{-1}$ ,  $1037\text{ cm}^{-1}$  and  $768\text{ cm}^{-1}$ . Then, in the spectrum of  $\text{Pb}^{2+}$ -starch the band nearing the  $1382\text{ cm}^{-1}$  is the O-H bending vibration of the  $\text{Pb(OH)}_2$ , and the stretching vibration of  $\text{Pb-O}$  can be also observed at  $461\text{ cm}^{-1}$ . As shown in the  $\text{Mg}^{2+}$ -starch spectrum, peaks of  $565\text{ cm}^{-1}$  and  $447\text{ cm}^{-1}$  can be considered as the adsorption band of  $\text{Mg-O}$ . Due to the high alkali pH of the MSC preparation, hydrophilic metallic hydroxides (such as  $\text{Fe(OH)}_3$  or  $\beta\text{-FeOOH}$ ,  $\text{Zn(OH)}_2$ ,  $\text{Pb(OH)}_2$  and  $\text{Mg(OH)}_2$ ) could be dissolved into corresponding hydrophilic metallic hydroxyl complexes on their surfaces (such as  $[\text{Fe(OH)}_4]^-$ ,  $[\text{Zn(OH)}_4]^{2-}$ ,  $[\text{Pb(OH)}_4]^{2-}$  and  $[\text{Mg(OH)}_4]^{2-}$ ).

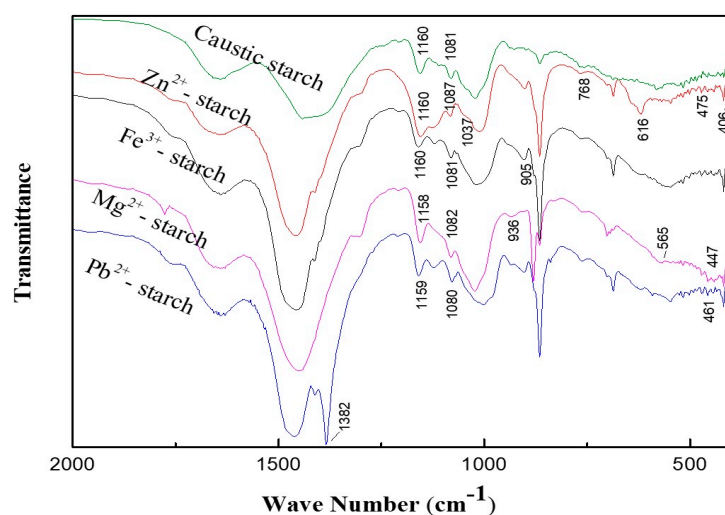


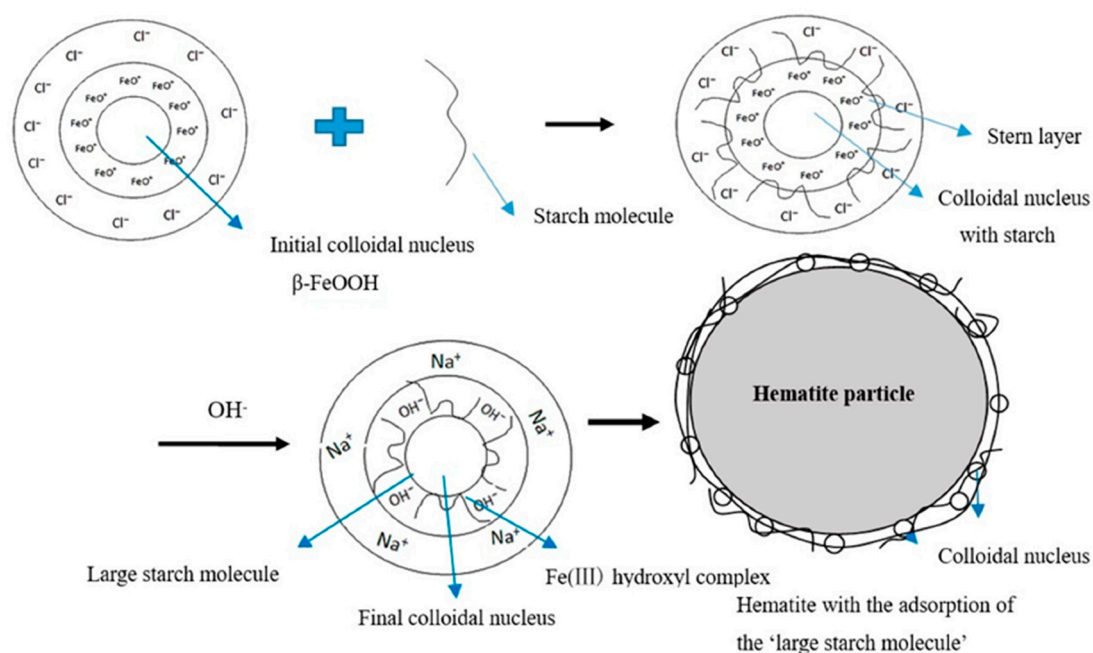
Figure 3. FTIR spectra of MSC.

Table 1 listed the turbidity and size of the MSC. As shown in Table 1, MSC exhibits a larger size than the caustic starch, and the size (1–1000 nm) order of them could be given as follows:  $\text{Mg}^{2+}$ -starch >  $\text{Zn}^{2+}$ -starch >  $\text{Pb}^{2+}$ -starch >  $\text{Fe}^{3+}$ -starch > caustic starch. Meanwhile, the low turbidity of the MSC reveals a high degree of dispersion as a stable solution (or colloid).

**Table 1.** Turbidity and average size of the MSC at pH 13.27 (NTU: Nephelometric Turbidity Unit).

MSC	Caustic Starch	Fe <sup>3+</sup> -Starch	Zn <sup>2+</sup> -Starch	Pb <sup>2+</sup> -Starch	Mg <sup>2+</sup> -Starch
Turbidity/NTU	28.32	144.21	230.63	187.41	346.83
Average size/nm	97.47	202.22	464.34	326.70	645.18

Based on the analyses mentioned above, a molecular model could be proposed as follows. To take the Fe<sup>3+</sup>-starch as an example, starch molecules adsorbed initially on the colloid nucleus ( $\beta$ -FeOOH), resulting in a stable “compound molecule” composed of the nucleus and covering of hydrophilic metallic hydroxyl complexes, together with the starch molecules. The colloid nucleus exhibited a low concentration of FeO<sup>+</sup> ions on its surface at low alkali pH, and then grew into a larger nucleus at high alkali pH. Therefore, some OH<sup>-</sup> and starch molecules would adsorb into the stern layer of the colloid nucleus, forming a “large starch molecule”, surprisingly leading to a particular adsorption effect on iron particles with the aid of the bridging adsorption of the starch and the H-bonding adsorption of the hydrophilic metallic hydroxyl complexes. The proposed model of the MSC (Fe<sup>3+</sup>-starch) is given in Figure 4.

**Figure 4.** The proposed molecular model of the MSC (such as the Fe<sup>3+</sup>-starch).

### 3.2. Reverse Cationic Flotation Tests

The effects of the metallic-starch complex (MSC) on the flotation performance of hematite ore were investigated at 625 g/t DDA, and the results are seen in Figure 5 and Table 2.

Figure 5 and Table 2 indicated that the flotation recovery of iron minerals increased with the increasing depressant dosage, but the iron recovery of depressant MSC was obviously higher than the caustic starch while adding the same concentration of starch. The flotation recovery using MSC as the depressant was slightly better than that using the same dosage of caustic starch, demonstrating the depressing ability of MSC (Fe<sup>3+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> and Mg<sup>2+</sup>) on the iron minerals were higher than the caustic starch, and amongst them, the order of depressing ability was summarized as: Zn<sup>2+</sup>-starch > Pb<sup>2+</sup>-starch > Fe<sup>3+</sup>-starch > Mg<sup>2+</sup>-starch > caustic starch. In addition, it was also found that the Fe<sup>3+</sup>-starch displayed the best flotation selectivity among the MSC depressors.

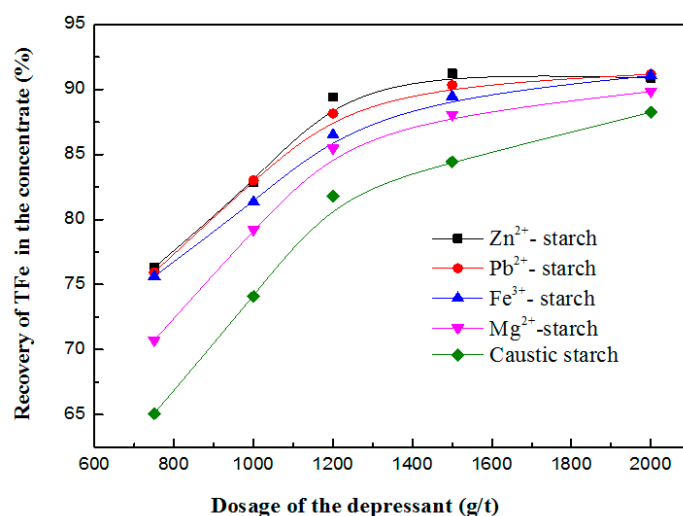


Figure 5. Effect of depressant dosage on the flotation recovery at pH 7.5 (DDA 625 g/t).

Table 2. Effect of MSC on the flotation performance (depressant 1200 g/t, DDA 625 g/t, pH 7.5).

Depressant	Mass Recovery/%	Grade Total Fe/%	Recovery of Total Fe/%
Caustic starch	72.55	58.11	81.79
Fe <sup>3+</sup> -starch	76.65	58.18	86.50
Zn <sup>2+</sup> -starch	80.16	57.49	89.40
Pb <sup>2+</sup> -starch	78.70	57.74	88.15
Mg <sup>2+</sup> -starch	76.02	57.96	85.47

### 3.3. Adsorption Amount of Reagents onto Iron Minerals in Flotation

Measurements of the adsorption amount of depressant and collector onto mineral particles in flotation pulp were carried out, and the results are presented in Table 3.

Table 3. Effect of MSC on the adsorption of flotation reagents (depressant 1200 g/t, DDA 625 g/t, pH 7.5).

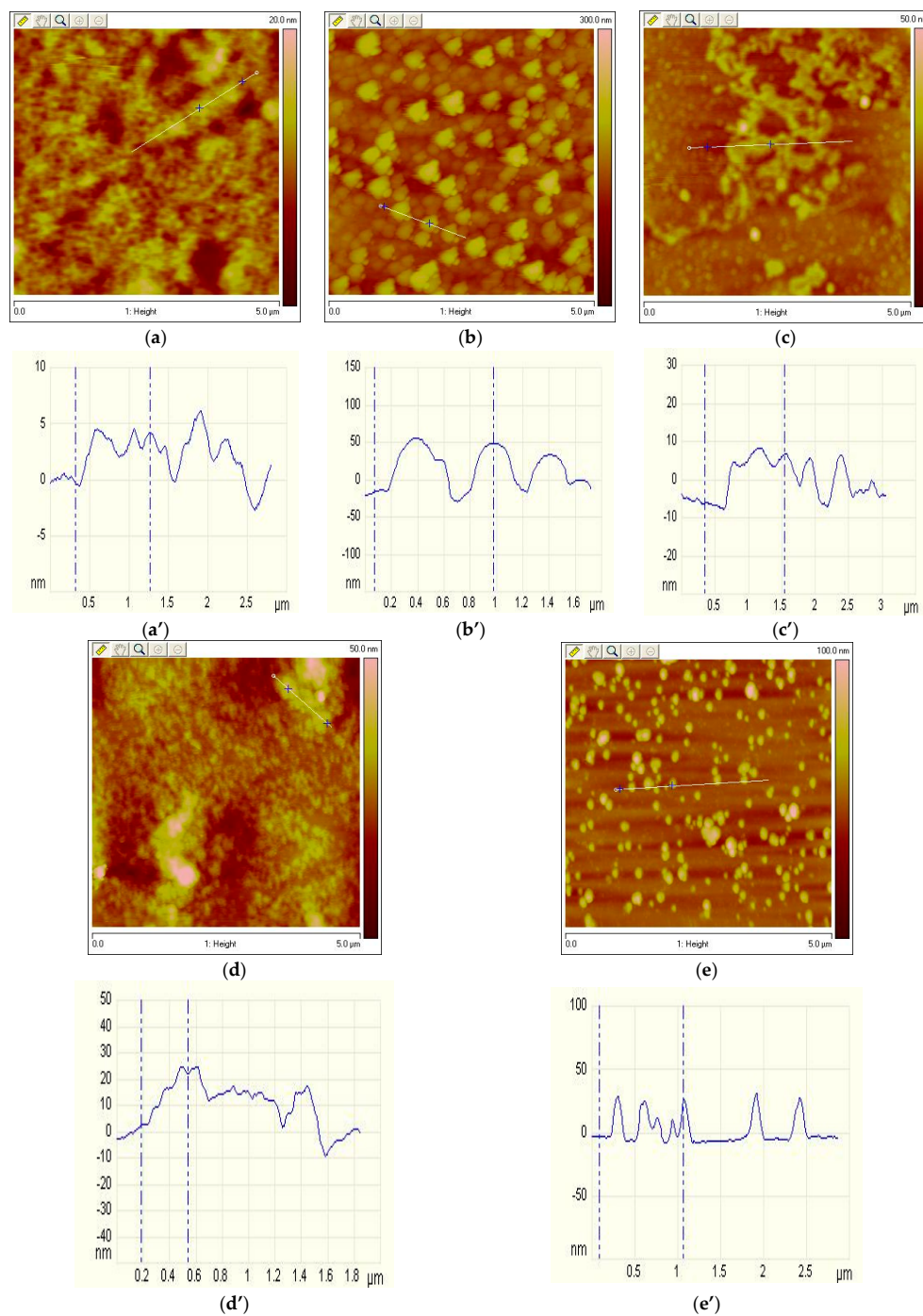
Depressant	Recovery of TFe/%	Adsorption of Starch/mg/g	Adsorption of DDA/mg/g
Caustic starch	81.79	0.2105	0.2317
Fe <sup>3+</sup> -starch	86.50	0.2496	0.2187
Zn <sup>2+</sup> -starch	89.40	0.3103	0.2206
Pb <sup>2+</sup> -starch	88.15	0.2788	0.2216
Mg <sup>2+</sup> -starch	85.47	0.2598	0.2253

Table 3 shows that the MSC adsorbed more on the particles than the caustic starch while slightly reducing the absorption of the collector (DDA), and among them, the Fe<sup>3+</sup>-starch exhibited a high adsorption of starch and relatively low adsorption of DDA. It can be also inferred that the adsorption abilities of the MSC agreed well with the flotation results in Table 2. Therefore, based on the adsorption analysis, it was confirmed that the MSC produced a high depressing ability through increasing the adsorption amount of starch on iron minerals and slightly reducing the absorption of the collector.

### 3.4. Adsorption Characteristics of the MSC onto Mica

Figure 6 shows the adsorption behaviour of various MSC on mica surface. It can be seen from Figure 6a that the adsorption effect of the caustic starch was especially weak on the mica surface with a sparse adsorption layer of only 5 nm. However, the Fe<sup>3+</sup>-starch exhibits up to 50 nm thick and

a uniform adsorption layer in Figure 6b. In addition, Figure 6c shows the adsorption behaviour of  $Zn^{2+}$ -starch onto mica with a moderate adsorption of 10–15 nm thickness, and in Figure 6d,e both the  $Pb^{2+}$ -starch and  $Mg^{2+}$ -starch display the adsorption coverage with about 10 nm thickness on the mica surface. It could be demonstrated that all the depressants of the MSC created a higher adsorption thickness on the minerals than the caustic starch, and especially the  $Fe^{3+}$ -starch displayed a thicker and smoother adsorption coverage than the other MSC. Therefore, the adsorption difference of the MSC from the traditional caustic starch could partly explain the flotation depressing gap between the two.



**Figure 6.** Effect of 120 mg/L MSC on the adsorption characteristic: (a,a') caustic starch; (b,b')  $Fe^{3+}$  starch; (c,c')  $Zn^{2+}$  starch; (d,d')  $Pb^{2+}$  starch; (e,e')  $Mg^{2+}$  starch.



### 3.5. Zeta Potential Measurements

Zeta potential measurements of the MSC and hematite in the presence of the MSC were carried out, and the results are shown in Figures 7 and 8, respectively.

As shown in Figure 7, both the MSC and caustic starch were negatively charged at neutral and alkali pH, but the MSC presents a weaker electronegativity than the caustic starch at the same pH value, and amongst the results of the MSC, the  $\text{Fe}^{3+}$ -starch exhibits the lowest negative charge while the  $\text{Zn}^{2+}$ -starch displays the largest negative charge. Therefore, it can be also revealed that the MSC (especially the  $\text{Fe}^{3+}$ -starch) could adsorb onto iron minerals more easily than the caustic starch while in some cases iron minerals were negatively charged. Figure 8 found that the iso-electric point (iep) of hematite is around pH 6.5 and the hematite has a negative potential at neutral and alkali pH. Meanwhile, the absolute value of hematite potential was raised after adding a certain concentration of caustic starch, however, was weaker by using the  $\text{Fe}^{3+}$ -starch. In this case, therefore, the adsorption of  $\text{Fe}^{3+}$ -starch on hematite could facilitate agglomeration of particles more easily than the caustic starch, resulting in a good flotation effect.

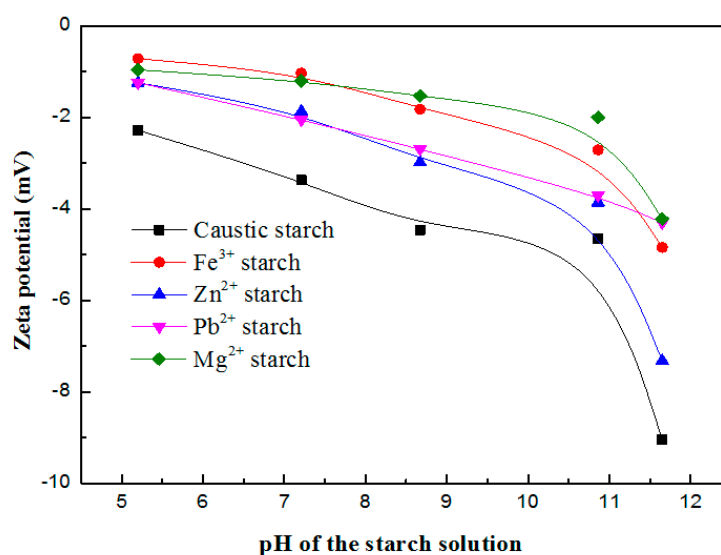


Figure 7. Zeta potential of various depressoants (0.013 g/mL) as a function of pH.

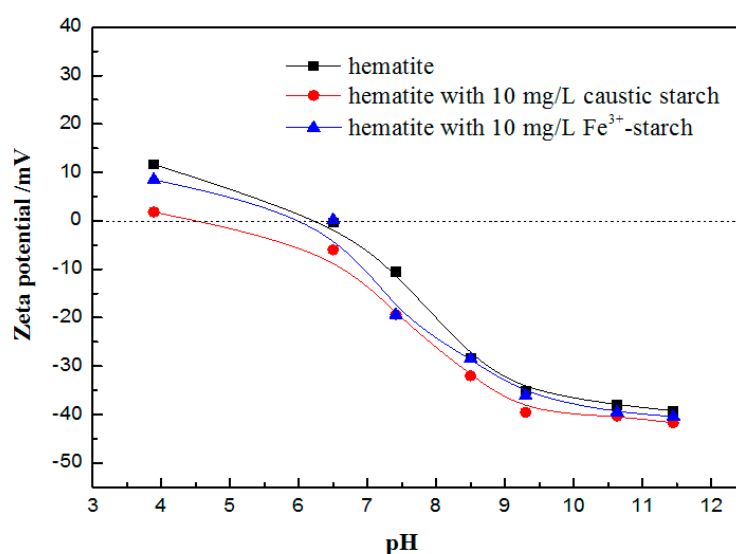


Figure 8. Zeta potential of hematite in the presence of the  $\text{Fe}^{3+}$ -starch as a function of pH.

### 3.6. FTIR Spectra of the Hematite Conditioned with the MSC ( $\text{Fe}^{3+}$ -Starch)

Figure 9 shows the FTIR spectra of hematite in the presence of the MSC ( $\text{Fe}^{3+}$ -starch). It can be observed in the spectrum of hematite conditioned with the  $\text{Fe}^{3+}$ -starch that the adsorption peak around  $1031\text{ cm}^{-1}$  is due to the C–O stretching and C–OH bending vibration, and the small adsorption at  $1070\text{ cm}^{-1}$  can be attributed to the C–H bending vibration, and then the  $\text{COO}^-$  asymmetric and symmetric stretching bands [10] are also found nearing  $1625\text{ cm}^{-1}$  and  $1404\text{ cm}^{-1}$ . The band at  $3420\text{ cm}^{-1}$  can be considered as the stretching vibration of O–H group, suggesting the presence of hydrogen adsorption on the hematite. In addition, the adsorption bands around  $561\text{ cm}^{-1}$  and  $467\text{ cm}^{-1}$  are shifted to  $538\text{ cm}^{-1}$  and  $457\text{ cm}^{-1}$ , respectively, indicating the hematite–starch interaction. Therefore, the  $\text{Fe}^{3+}$ -starch adsorbed onto the hematite through the hydrogen bonding adsorption and chemisorption, however, the adsorption characteristic of  $\beta\text{-FeOOH}$  in that spectrum was not found at  $905\text{ cm}^{-1}$  probably due to its low concentration in the mixture of the hematite- $\text{Fe}^{3+}$  starch.

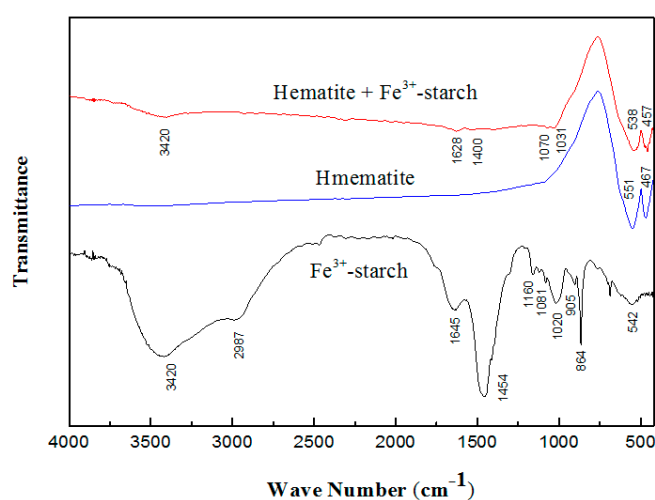


Figure 9. FTIR spectra of hematite conditioned with the  $\text{Fe}^{3+}$ -starch (MSC).

## 4. Conclusions

The MSC is a type of nano-sized colloidal complex which is configured by hydrophilic metallic hydroxide as the colloidal nucleus on which starch and hydroxyl complex are adsorbed, resulting in a larger molecule than starch itself. Amongst the MSC colloids, the  $\text{Fe}^{3+}$ -starch presented its specific characteristics using  $\beta\text{-FeOOH}$  as the colloid nucleus while the other MSC colloid nuclei are synthesized by the corresponding metallic hydroxides (such as  $\text{Pb}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ ).

MSC produced higher depressing ability on the flotation of iron ores than the caustic starch, and different types of the MSC showed some different depressing ability as follows:  $\text{Zn}^{2+}$ -starch >  $\text{Pb}^{2+}$ -starch >  $\text{Fe}^{3+}$ -starch >  $\text{Mg}^{2+}$ -starch > caustic starch, and the  $\text{Fe}^{3+}$ -starch displayed the best flotation selectivity among the MSC depressors.

The high depressing ability of the MSC arose from increasing the adsorption density of starch on iron minerals and slightly reducing the absorption of the collector (DDA). All the MSC depressants created a thicker adsorption layer on the minerals than the caustic starch, and especially the adsorption of the  $\text{Fe}^{3+}$ -starch displayed a thicker and smoother adsorption layer than the other MSC depressants. The strong adsorption ability of the MSC lies in the fact that the MSC exhibited a weaker electronegativity than the caustic starch, therefore leading to a better adsorption result of the starch onto iron minerals. In addition, the absolute value of hematite potential was raised after adding a certain concentration of caustic starch but it was, however, lowered by using the  $\text{Fe}^{3+}$ -starch.

**Acknowledgments:** The authors would like to acknowledge the financial support from the National Natural Science Foundation of China (No. 51274256).

**Author Contributions:** Xiqing Wu and Tao Yue conceived and designed the ideas; Tao Yue performed the experiments; Xiqing Wu and Tao Yue analyzed the data; Xiqing Wu and Tao Yue contributed reagents/materials/analysis tools; Tao Yue and Xiqing Wu wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

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