Ultrasonic treatment improves the performance of starch as depressant for hematite flotation

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ABSTRACT
In this study, ultrasonic treatment was introduced to enhance the depressive performance of starch in the reverse flotation separation of fine hematite from quartz. It was found that after ultrasonic treatment, starch was not only able to impart a higher surface wettability of hematite, but also better reduced the degree of entrainment of fine hematite, both of which alleviated the loss of hematite to the froth. Flocculation tests together with starch property characterization were conducted to understand the underpinning mechanism. It is interesting that ultrasonic treatment of starch led to stronger and more selective flocculation of hematite, which accounted for the reduced entrainment loss of fine hematite and benefited the concentrate Fe grade. It was also found that ultrasonic treatment enhanced the dissolution and acidity of starch with a simultaneous increase in the content of amylose, which in turn could contribute to the improved depression and selective flocculation of hematite.

1. Introduction

With depletion of high quality iron ores, the mineral processing industry starts to process an increasing amount of low grade and difficult ores. To achieve good liberation of iron-bearing minerals from their associated gangue in low grade ores, ultrafine grinding is required [1]. As a result, a large amount of fine and ultrafine particles is generated. The majority of Earth’s iron resources are in the fully oxidized hematite form [2] and reverse flotation is known as the most efficient method to separate fine iron oxide from gangue impurities [3]. In flotation, while the recovery of hydrophobic particles to the froth through bubble–particle collision and attachment is defined as true flotation, entrainment is a process by which particles suspended in the pulp are mechanically pushed up into the froth by the ascending bubbles without attaching to the air bubbles [4]. Unlike true flotation, entrainment is non-selective because both hydrophobic and hydrophilic particles can be transported to the froth via entrainment [5]. The finer the particles, the more likely they are to remain suspended in the inter-bubble water and to be recovered via entrainment [6].

In reverse flotation practice of iron oxide, depressants are introduced to render the surface of iron-bearing mineral hydrophilic, while ideally having a minimal adsorption on the gangue (Silicates) surfaces [3]. Starch, which belongs to the natural polysaccharide depressant family, is consisting of two major components, amylose (a helical polymer made of α-D-glucose units) and amylopectin (a branched polymer in which the main chain is linked to the branches) [7]. When introduced to the iron ore reverse flotation systems, starch can not only render the iron oxide surface hydrophilic as a depressant, but also flocculate the fine iron oxide to form larger sized flocs as a flocculant [1,8]. While the former inhibits the true flotation of iron oxide, the latter reduces the loss of iron to the froth through entrainment [1]. The dual function and high availability of starch make it the most widely used depressant for iron ore flotation. However, the increasing mineralogical complexity and fine nature of the low grade iron ore flotation feed mean that more starch is required to depress the flotation and entrainment of iron oxides, which at the same time may lead to the depression of silica. Depressed silicate gangue flotation caused by an excessive dosage of starch has been reported by Pavlovic and Brandao [9] and by Kar, et al. [10]. In addition, it was suggested that starch as a flocculant could result in the entrapment of gangue particles in the hematite flocs [1,11], diluting the iron ore concentrate grade. Hence, it is important to improve the efficiency and selectivity of starch in iron ore flotation.

Before being used in iron ore flotation, starch is normally treated by alkali and/or thermal gelatinization to enhance their dissolution [12] and there is a strong correlation between starch solubility and its depressing ability [7]. Hence, starch dissolution could be critical in...
improving its performance in flotation. In the literature, there are several physical and chemical methods available for the dissolution of starch, including high pressure microwave vessel method and oxidation, etc. The former method requires harsh dissolution conditions (such as high pressure and high temperature) to obtain complete dissolution of starch [13], while the latter produces a large amount of NaCl during the oxidized modification process in the wastewater with high treatment difficulty [14]. It is worth noting that recently, Fletcher, et al. [15] reported that starch after oxidation allowed greater recovery of chalcopyrite in the presence of graphite or copper-activated pyrite as gangue, pointing to selectivity potential.

Ultrasound is an effective and environmentally friendly technology which has been widely applied in the modification of physicochemical properties of starch, such as solubility [16,17] and swelling power [18,19]. To date, however, there is no report on the use of ultrasound for the gelatinization/dissolution of starch under the flotation context. Therefore, the objective of this study was to investigate the effect of ultrasound treatment on the properties of starch and its performance in the flotation separation of fine hematite and quartz. The experimental results are expected to provide a valuable reference for dealing with other fine minerals such as talc and graphite when using starch as depressant.

2. Experimental

2.1. Materials

The coarse crystalline mineral samples having a pure and compact appearance was obtained from Guangdong province, China. The Fe$_2$O$_3$ content of the hematite sample was 97.4% and the SiO$_2$ content of the quartz sample was 99%. The elemental analysis, except for Fe, for the samples were performed using X-ray fluorescence spectrometry (ARL PERFORM’X, Thermo Fisher, USA) and the results are shown in Table 1. Total iron and ferrous iron contents were determined with the standard titrimetric method which uses potassium dichromate as titrant after reduction of the iron (III) by tin (II) chloride and/or titanium (III) chloride (ISO 2597–1) [20,21]. The two mineral samples were then carefully ground to very fine sizes. Particle size distributions of the ground hematite and quartz were determined by laser diffraction (Malvern Mastersizer 2000), and their D90s were found to be 19.55 and 25.27 μm, respectively.

Commercial corn starch was supplied by Weihaiwei Food (China). Deionized water (DI water) with an electrical conductivity less than 5 μS/cm was used in all the experiments in this study. Caustic digested starch (CS) solution (0.5 wt%) was prepared by mixing 2.5 g starch with 0.25 g NaOH in a beaker containing 500 mL DI water, followed by heating in a water bath at 95 °C with stirring for 1 h. All starch solutions were prepared fresh on the day of testing. I$_2$ and KI (analytical grade) was purchased from Jinbei Chemical (China) and Dodecylamine (DDA) with a purity of 98% by Energy Chemical (China). Hexane and acetic acid (analytical grade) were purchased from Sinopharm Chemical (China).

2.2. Methods

2.2.1. Ultrasonic treatment

A 3.8 L ultrasonic cleaner (DS150-XN1, Fuzhou Desen Precision, China) was selected for ultrasonic treatment. To prepare ultrasonic modified starch (MS) samples, 50 mL CS solutions were placed in a beaker and then sonicated in the water bath for various times (5, 10, 15, 20, and 30 min) at room temperature and an ultrasonic frequency of 40 kHz and power of 150 W. During treatment, the increase in the temperature of the water bath was within 10 °C.

2.2.2. Micro-flotation and batch flotation test

Micro-flotation tests of single minerals were conducted in an XFGC laboratory flotation machine with a 50 mL plexiglass cell and at an impeller speed of 1800 rpm. CS and MS were used in parallel in the study. For each test, the mineral suspension was prepared by adding a 3.0 g hematite or quartz and 40 mL DI water into the flotation cell. The pulp was pre-mixed for 2 min and its pH was adjusted to ~ 10.5 using NaOH, followed by conditioning with CS or MS for 5 min and DDA (2 × 10$^{-4}$ M) for another 2 min. After that, flotation was commenced and operated for 3 min. The concentrates and tailings were oven dried and weighed for mineral flotation recovery calculation.

Batch flotation of hematite and quartz mixture using CS or MS as depressant was conducted in a XFD 0.5 L laboratory flotation cell. For each test, 25 g hematite together with 25 g quartz were added to the cell which was then filled with DI water to make up the flotation pulp. The pulp pH was adjusted to ~ 10.5 so that surfaces of both minerals were negatively charged and the initial heterocoagulation was minimized by electrostatic repulsion [1]. The pulp was pre-mixed for 2 min and then conditioned successively with 125 g/t sodium silicate and varying dosages of CS or MS for 2 and 5 min, respectively. After further conditioning with DDA for 2 min, flotation was operated at an air flow rate of 0.17 m$^3$/h and impeller speed of 1800 rpm. In flotation, four concentrates were collected after cumulative times of 1, 2.5, 4, 7 min. Flotation concentrates and tailings were weighed wet and dry to determine water recovery and the dried concentrates and tailings were further analyzed for Fe content.

2.2.3. Surface wettability characterization

The surface wettability of hematite with and without depressant was characterized using a simple solvent extraction method that based on the principle of oil agglomeration flotation [1]. Briefly, a 50 mL suspension containing 0.5 wt% hematite was placed in a beaker and mixed by a magnetic stirrer at 800 rpm. The pH of the suspension was adjusted to the flotation pH (~10.5) using NaOH. For each test, 20 mL hematite suspension was firstly pipetted into a glass bottle with a volume of approximately 50 mL, followed by the addition of CS or MS and DDA of desired concentrations. After that, 10 mL hexane (660.6 kg/m$^3$) was added to the glass bottle as the extracting solvent and the rest of the experiment was conducted following the procedure described elsewhere [1]. Each test was repeated three times and the average result was reported.

2.2.4. Flocculation procedure

Flocculation tests were carried out in a self-made 500 mL graduated cylinder [22]. For each test, 15 g of hematite and quartz mixture (at a mass ratio of 1:1) was dispersed in a beaker with 350 mL of DI water by stirring with a magnetic stirrer for 2 min and the pH of the resultant slurry was adjusted to ~ 10.5 by adding NaOH. A desire amount of CS or MS was then added, followed by 5 min of mixing. After thorough mixing, the slurry was washed into the cylinder with 150 mL of DI water, the pH of which was pre-adjusted to 10.5. The cylinder was turned upside down five times and then placed on a solid, flat surface with no further disturbances permitted. After that, the mixture was allowed to settle for 30 s and the supernatant (upper 50% part) was released via the outlet port.

| Mineral | TFe | FeO | SiO$_2$ | Al$_2$O$_3$ | MgO | CaO | P | S |
|---------|-----|-----|---------|------------|-----|-----|---|---|
| Hematite | 68.19 | 0.14 | 1.03 | 0.31 | 0.34 | 0.09 | 0.039 | 0.002 |
| Quartz | 0.08 | 0.00 | 99.38 | 0.02 | 0.04 | 0.02 | 0.003 | 0.007 |

Table 1

Elemental composition of the mineral samples.
in the cylinder wall. Finally, the supernatant and sediment (concentrate) were dried, weighed and analyzed for Fe content. Each test was repeated thrice to ensure the repeatability of the data obtained.

The selectivity of flocculation was assessed by calculating the separation index (SI) [11], which considers both grade and recovery and is defined as:

\[
SI = \frac{\% \text{ valuable minerals recovered in concentrate} - \% \text{ gangue minerals recovered in concentrate}}{100}
\]

A SI of unity corresponds to complete separation of the valuable and gangue minerals and a value close to zero corresponds to no separation [11].

### 2.2.5. Solubility and swelling power

Solubility and swelling power were determined based on the method described by Hong, et al. [23] with a slight modification. 500 mL of CS solution of 1 wt% starch was prepared following the same starch to NaOH ratio and procedure as 0.5 wt% CS solution. After cooling down, 50 mL of the CS solution was ultrasonically treated for different times to obtain MS samples. 10 mL of CS or MS sample was then transferred to a centrifugal tube and centrifuged at 3000 rpm for 30 min. The supernatants were collected and dried at 105 °C until a constant weight \((W_1)\) reached, and the sediments were weighed wet \((W_2)\) and dry \((W_3)\). The following Eq. (2) and (3) were used to calculate the solubility and the swelling power:

\[
\text{Solubility} \% = \frac{W_2}{W_1 + W_3} \times 100% \tag{2}
\]

\[
\text{Swelling power (g/g)} = \frac{W_2}{W_1} \tag{3}
\]

### 2.2.6. Zeta potential measurement

Zeta potentials of CS samples (0.5 wt%) with and without ultrasonic treatment were measured by a zeta potential analyser (Malvern Zetasizer Nano ZS90). For each test, 5 mL of the CS solution was withdrawn and diluted to 100 mL with a 10⁻³ mol/L NaCl solution [24]. The pH of the diluted suspension was adjusted using HCl or NaOH, and a small aliquot of the suspension was transferred to the sample cell of the ZS90 for zeta potential measurements.

### 2.2.7. Rheology measurement

A 5 wt% CS solution (500 mL) was prepared following the same procedure as described above. Rheology measurements on CS samples (5 wt%) without and with ultrasonic treatment of different times were performed with a Physica rheometer (Anton Paar MCR 301) at room temperature (25 °C). For each test, approximately 20 mL of CS or MS sample was transferred to a Couette geometry with a rotating inner cylinder and a stationary outer cylinder by using a 50 mL syringe while the slurry was being stirred by a magnetic stirrer. The rheometer was then operated under controlled shear rate mode where the shear rates were pre-set (0.1–1000 s⁻¹).

### 2.2.8. Measurement of iodine absorption spectra

Iodine absorption spectra of CS samples (0.5 wt%) ultrasonically treated and untreated was determined based on the method of Li, et al. [25]. In each test, to a 0.3 mL aliquot of the starch solution, 0.25 mL of acetic acid and 0.5 mL of iodine solution (1% w/v KI + 0.1% w/v I₂) were added, and the solution was diluted to 25 mL with DI water. After shaking, the solution was kept at room temperature for 1–2 h. The absorbance was then measured at 450–800 nm by UV–VIS spectrophotometry (Shimadzu UV-2550) where the blank control was iodine reagent.

### 3. Results and discussion

#### 3.1. Micro-flotation of single minerals

Flotation recovery of single quartz or hematite in the presence of 30 mg/L CS with various lengths of ultrasound time is shown in Fig. 1. As can be seen, while ultrasonic treatment of CS had no effect on its depressing ability on quartz flotation, the hematite recovery in the presence of CS decreased with increasing ultrasonic time and reached a minimum at 20 min, suggesting that the depressing ability of CS on hematite flotation was increased after ultrasonic treatment. For instance, 20 min ultrasonic treatment of CS resulted in a hematite recovery of 15.6%, which is 31.1% lower than that obtained without ultrasonic treatment. However, since further increase in the ultrasonic time (>20 min) did not give lower hematite recovery, 20 min ultrasonic time was selected when preparing MS in subsequent investigations.

Fig. 2 shows the flotation recovery of single quartz or hematite in the presence of CS or MS at various concentrations. It can be seen that while the quartz recovery was not influenced by either CS or MS addition, the hematite recovery declined with increasing concentration of CS or MS. The results of CS are in agreement with the literature [1,26], which showed that CS can selectively depress hematite flotation while having no obvious effect on quartz flotation. More importantly, at a same concentration, the depressing effect of starch on hematite flotation was more pronounced in MS form than in CS form. For instance, at a concentration of 30 mg/L, the hematite recovery decreased from 46.7% to 15.6% when CS was replaced by MS. Overall, the micro-flotation results demonstrated that ultrasonic treatment of CS significantly enhanced its efficiency in depressing hematite flotation without altering its impact on quartz flotation. It was anticipated that the difference in hematite flotation recoveries using these two depressants could be contributed by

![Fig. 1. Micro-flotation recoveries of quartz and hematite in the presence of 30 mg/L CS with various lengths of ultrasound time.](image-url)
two reasons: (1) MS imparted higher surface wettability of hematite than CS, and (2) MS could better reduce the recovery of fine hematite via entrainment [1,8].

3.2. Surface wettability characterization

The surface wettability of hematite with and without depressant was firstly characterized using a solvent extraction method adapted from Wang and Liu [1]. The weight percentage of solids in the oil phase which is indicative of the surface hydrophobicity of hematite particles was measured in the absence and presence of CS or MS [1]. As illustrated in Fig. 3, 61.3% of hematite moved up and retained in the oil phase in the presence of DDA alone, indicating the high hydrophobicity of hematite surface without depressant. In contrast, when 30 mg/L CS was added prior to DDA, the percentage of hematite remained in the oil phase reduced to 31.4%, and it further dropped to 21.5% when a same amount of MS was used. These results were in line with the micro-flotation results that when used at the same concentration, MS was more capable of reducing the surface hydrophobicity of hematite than CS, resulting in a more hindered true flotation of hematite.

As mentioned earlier, in addition to surface wettability, the observed lower recovery of fine hematite in the micro-flotation using MS could also be caused by a reduction in the entrainment of hematite. To justify this and examine the effect of ultrasonic treatment on the performance of CS in the mixed minerals flotation systems, batch flotation of hematite and quartz mixture was studied in the next section (3.3).

3.3. Batch flotation of hematite and quartz mixture

Fig. 4 shows the cumulative Fe recovery into the froth as a function of water recovery using CS or MS at the dosages of 300 and 600 g/t, respectively. It can be observed that regardless of the type and amount of depressant used, there existed an almost linear relationship between Fe recovery and water recovery. The slopes of these linear relationships can be approximated as entrainment factor or otherwise known as the degree of entrainment (ENT) [1,8]. The value of ENT normally lies in the range between 0 and 1 and is indicative of the severity of entrainment [27–29]. Regression analysis of the cumulative Fe recovery as a function of water recovery in batch flotation were then conducted using the classic model of Warren [6] and the fitting results are summarized in Table 2:

$$R_M = F_M + ENT_R$$

where $$R_M$$ is the overall recovery of mineral; $$F_M$$ represents the recovery by true flotation and $$R_R$$ is the recovery of water.

As can be seen from Table 2 that the values of $$F_M$$ which represented the true flotation were relatively small in the presence of depressants, suggesting that the primary mechanism for the transfer of hematite into the froth phase was entrainment [1,8]. Importantly, compare to batch flotation using CS, lower ENTs were observed when MS were used at the same dosages. For instance, when 300 g/t MS was used, an ENT of 0.67 was obtained as compared to 0.96 at 300 g/t CS. Further increasing the CS dosage from 300 to 600 g/t reduced the ENT to 0.82, whereas MS at 600 g/t resulted in an ENT of 0.68. Apparently, compare with CS, MS was more effective in reducing the ENT of hematite. In other words,
ultrasonic treatment of CS improved its ability to reduce the carryover of hematite into the froth product by entrainment.

### 3.4. Selective flocculation

It is well known that the coarse particles tend to have a lower ENT since they drain more readily in the water between the bubbles than the fine particles [4] and recently, Wang and Liu [1] studied the influence of aggregation/dispersion state of a hydrophilic mineral (hematite) on its entrainment in the reverse flotation separation of hematite from quartz and found that unlike dextrin (another typical polysaccharide depressant), starch was more capable of initiating the aggregation of fine hematite particles in suspension and thus better reduced their recovery via entrainment. To understand the reason for the reduced entrainment of fine hematite using MS, particle size distribution measurements and flocculation tests were conducted.

Fig. 5 shows the size distributions of quartz and hematite without and with the addition of 30 mg/L CS or MS. It is evident from Fig. 5a that size distribution of quartz particles was not influenced by either CS or MS addition, indicating that the presence of starch dispersants had little impact on the aggregation/dispersion state of quartz particles. In contrast, the addition of both CS and MS shifted the size distribution curve of hematite particles to the right (Fig. 5b), suggesting an enhanced aggregation of hematite particles. This is in line with the literature [1,26], which has reported that starch did not flocculate quartz but was able to flocculate hematite. Interestingly, at the same concentration, the flocculating ability of starch was more pronounced in MS form than in CS form as suggested by the further enrichment of hematite particles in the coarser fraction in the presence of MS (Fig. 5b).

Fig. 6 shows the flocculation results of hematite-quartz mixture (3 wt %) in the absence and presence of 10 mg/L CS or MS. As can be seen, after 30 s of settling, the Fe recovery increased from 73.2% without starch to 77.9% in the presence of 10 mg/L CS, while the Fe grades were similar in these two cases, being approximately 35%. The use of 10 mg/L MS further increased the Fe recovery to 92.1% with an improved Fe grade (38.6%). The value of SI which can be used as an indicator of the selectivity of flocculation was then calculated using Eq. (1) [11]. While the SIs without starch and with 10 mg/L CS were low, being 0.05 and 0.06, respectively, the SI increased to 0.22 when 10 mg/L MS was added. The size distribution results in Fig. 5b suggest that CS did flocculate of the hematite particles, thereby the relatively lower SI when using CS could be resulted from the entrapment of fine quartz particles in the hematite flocs [1,11]. In contrast, the greater SI when CS was replaced by MS indicates that MS was able to flocculate the hematite particles more selectively in the presence of fine quartz than CS. Based on the size distribution and flocculation results, it can be concluded that ultrasonic treatment improved both the ability and selectivity of CS in flocculating
hematite. While the improved flocculating ability accounts for the alleviated entrainment carryover (loss) of fine hematite to the froth product (Tailing) in flotation using MS, the latter should be beneficial for improving the concentrate Fe grade with less quartz entrainment.

The beneficial effect of improved selective flocculation using MS on concentrate Fe grade was supported by the results from batch flotation of hematite-quartz mixture as shown in Fig. 7. It is clear that at a given Fe recovery in the concentrate, higher Fe grade would be obtained when MS was used as compared with CS. For example, if the required recovery is 85%, the Fe grade is approximately 50% in the presence of 300 g/t MS, which declined to less than 40% in the presence of 300 g/t CS. Moreover, the comparative curves of Fe grade versus Fe recovery obtained with MS are always above those obtained with CS at a same concentration, indicating that CS after ultrasonic treatment always produced better flotation results in the mixed minerals flotation systems.

3.5. Effect of ultrasonic treatment on the properties of CS

The improved performance of CS after ultrasonic treatment as a hematite depressant could be attributed to variations in its physicochemical properties. It was reported that the depressing ability of starch on hematite was strongly related to its solubility [7]. Therefore, the effect of ultrasound treatment on the solubility and swelling power of CS was firstly examined and the results are presented in Table 3. The solubility and swelling power of untreated CS were 43.9% and 26.5 g/g, respectively, suggesting that the typical alkali and thermal gelatinization was not able to reach a high degree of dissolution of corn starch used in this study. Hence, the relatively poor performance of CS without ultrasonic treatment in depressing hematite flotation could be explained by its low dissolution extent [7]. By contrast, after 10 min ultrasonic treatment, the solubility and swelling power of CS jumped to 87.3% and 30.4 g/g, respectively, which further increased to 97.3% and 35.9 g/g, respectively, after treated for 20 min. These increases which indicate higher degrees of gelatinization after ultrasonic treatment could be caused by the break of the crystalline molecular structure of starch and the bonding of water molecules to the free hydroxyl groups of amylose and amylopectin by hydrogen bonds [17,30]. Similar observations have previously been reported by Sujka and Jamroz [17] and Jambrik, et al. [18] who subjected starch to ultrasonic action. The improved gelatinization/dissolution might in turn accelerate the leaching out of short-chain amylose and amylopectin chains from starch granules [31,32] and hence, their adsorption on the surface of hematite as suggested by hematite surface wettabily results (Fig. 3) as well as the more depressed flotation of hematite.

In addition to dissolution, the more depressed flotation of hematite using MS could also be related to a variation in the acidity of CS after ultrasonic treatment. It has been proposed that acid-base interaction/chemical interaction is the main mechanism with which polysaccharide adsors onto mineral surfaces [33,34]. In this view, (1) the polysaccharide acts as an acid and interacts with hydroxylated metallic ion impurities at the mineral surface which act as a base [35], and (2) the higher the acidity, the stronger will be the interaction, and vice versa [34]. Fig. 8 shows the zeta potentials of CS with and without ultrasonic treatment as a function of pH. As can be seen, without ultrasonic treatment, the isoelectric point (IEP) of CS was about 3.2, close to that reported by Tang and Liu [24]. Meanwhile, ultrasonic treatment shifted the IEP of CS towards more acidic pHs, from about 3.2 before treatment, to about 2.4 after treated for 5 min, and to about 1.5 for 10 min, indicating the formation of more acidic groups on the starch after ultrasonic treatment [24]. Similar decreases in the IEP of CS with increasing concentrations of NaOH has been previously reported by Tang and Liu [24]. It is known that in the preparation process of CS, the starch granules go through swelling and deformation, and eventually the breaking of the long polymer chains [36], which exposes more “open areas” of starch granules to dissolved oxygen, and produces various oxidation products (organic acids) on the starch chains [24]. The subsequent ultrasonic treatment of CS might assist the oxidation of CS with an increased acidity [37], which in turn facilitated the adsorption of starch on the surface of hematite.

The curves of shear stress-shear rate for CS dispersions (5 wt%) before and after ultrasonic treatment are shown in Fig. 9. The untreated CS dispersion exhibited shear-thinning behaviour. Similar pseudoplastic behaviour in heat-gelatinized starch was recently reported by Ang, et al. [38]. In contrast, after treated for 10 and 20 min, the samples approached Newtonian behaviour, suggesting an increased degree of starch disassembly [38]. This rheological change has been attributed to the fragmentation of amylose chains and debranching of amyllopectin molecules caused by the effect of ultrasound waves in C–O–C linkages.

Table 3

| Ultrasonic time (min) | Solubility (%) | Swelling power (g/g) |
|-----------------------|---------------|---------------------|
| 0                     | 43.9 ± 0.7    | 26.5 ± 1.1          |
| 10                    | 87.3 ± 1.9    | 30.4 ± 1.8          |
| 20                    | 97.3 ± 0.7    | 35.9 ± 2.2          |

Fig. 8. Zeta potentials of CS before and after ultrasonic treatment for 5 and 10 min as a function of pH.

Fig. 9. Rheograms of CS dispersions (5 wt%) before and after ultrasonic treatment for 10 and 20 min.
The increased degree of starch dissolution and disassembly after ultrasonic treatment may lead to a variation in the content of amylose. Fig. 10 gives the snap shots and spectral patterns of starch–iodine complexes of CS dispersions (0.5 wt%) before and after ultrasonic treatment. Although the iodine content in the three samples was low, the bule color differences produced were detectable with the naked eye. These differences are known to be due to the formation of amylose–iodine complex and suggest that ultrasonic treatment altered the amylose content of CS [39,40]. The variation in the amylose content after ultrasonic treatment was also confirmed by UV–VIS spectrophotometry (Fig. 10). As has been widely reported, the spectra of amylose–iodine complex for all three samples exhibits a broad and asymmetric absorption peak, with its maximum near 600 nm. Moreover, the spectra gradually shifted to higher levels of absorbance as the ultrasonic time increased, indicating that ultrasonic treatment of CS led to an increase in its amylose content [41]. Increased amylose content of corn starch after ultrasonic treatment has also been reported by Li, et al. [25] and it was suggested that a partial depolymerization of amylose might occur during ultrasonic treatment, which in turn increased the number of linear chains and the amylose content of corn starch.

In a previous study, Weissenborn [42] compared the behavior of amylopectin and amylose components of starch in the selective flocculation of ultrafine iron ore and concluded that when combined with amylopectin, amylose slightly enhanced the selective flocculation of hematite. In light of this, the selective flocculation of fine hematite using MS was likely contributed by the increase in amylose content after ultrasonic treatment shown in Fig. 10. Detailed correlation between amylopectin to amylose ratio in MS and its performance in the selective flocculation is under investigation.

4. Conclusion

The current study found that the use of ultrasound-treated starch in the flotation separation of fine hematite and quartz better alleviated the loss of hematite to the froth products by, (1) imparting higher surface wettabilitly of hematite, and (2) reducing the degree of entrainment of hematite. It was also revealed that ultrasonic treatment of starch resulted in stronger and more selective flocculation of hematite. While the improved flocculating ability was responsible for the reduced hematite entrainment, the enhanced selectivity benefited the concentrate Fe grade. Lastly, after ultrasonic treatment the dissolution and acidity of starch was enhanced along with an increase in amylose content, which could contribute to the improved depression and selective flocculation of hematite.

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CRediT authorship contribution statement

Ming Zhang: Conceptualization, Methodology, Resources, Supervision, Project administration, Writing – review & editing. Zeping Xu: Methodology, Investigation, Data curation, Writing – original draft. Lei Wang: Methodology, Data curation, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Fig. 10. Snap shots and spectral patterns of starch–iodine complexes of CS dispersions (0.5 wt%) before and after ultrasonic treatment (blank control was iodine reagent without starch).
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