CAUSTIC-DIGESTED STARCH AND ITS ADSORPTION ON HEMATITE

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Abstract: Adsorption characteristics on hematite of caustic-digested starch by sodium hydroxide or potassium hydroxide were investigated through a series of tests, like adsorption tests, paste titration and zeta potentials measurement, scanning electron microscope measurement (SEM) and Fourier transform infrared spectroscopic analysis (FTIR) as well. An attempt was made in order to identify the possible effects of starch digested with alkali at different concentrations on its adsorption on mineral surfaces. All results pointed out that a different amount of carboxyl groups in the starch gel were harvested from alkali-digestion as a function of concentrations of sodium hydroxide or potassium hydroxide; more acidic groups were produced if higher concentrations of alkali were added. These carboxyl groups may contribute the acid/base interaction of the caustic-digested starch on hematite. Also, different concentrations of sodium hydroxide to digest starch seem to induce different degrees of its gelatinization from the SEM results, partially attributing to a wide range of its adsorption capacities on mineral surfaces. The optimum adsorption density of the caustic-digested starch on mineral surfaces, 9.87 mg/g hematite for sodium hydroxide and 10.51 mg/g hematite for potassium hydroxide, respectively, was achieved at the weight ratio of starch to sodium/potassium hydroxide as 1:2.

Keywords: starch; digestion; alkali; carboxylic groups

Introduction

The common methods to prepare starch solution for its use in mineral flotation are alkali digestion at room temperature, or its combination with heating-treatment as shown in Table 1 (Khosla et al., 1984; Pinto et al., 1992; Wessenborn et al., 1995; Peres and Correa, 1996; Pavlovic and Brend, 2003; Rocha et al., 2010; Turrer at el., 2010). A wide range of separation results were achieved for fine hematite by using caustic-digested starch. This indicates that dosages of alkali or temperature may play an important role in the flocculation of starch on mineral surfaces, other than pulp pH, types of collector and particle size.

Table 1. Some applications of alkali or heating digested starch as a flocculants on fine iron oxides

Minerals depressed	Starch digestion methods	pH	Separation Results	References
Iron oxide	Caustic-digested starch with 1/2N NaOH.	6.0	magnitudes of adsorption are only 12–46% and the maximum is 1.75×10^{-3} g/g hematite when using 200 ppm starch	Khosla et al. (1984)
Iron ore tailings	Unknown	10.5	64.8% grade and 80% recovery of Fe	Rao and Narasimhan, 1985
Hematite	Starch/amylsoe/amlopectin were prepared at a constant 4:1 NaOH/polysaccharde ratio	10.0	Less than 10% floatability of hematite when 10 mg/L starch (amylose/amylopectin ~40/80)	Pinto et al.(1992)
Hematite	0.10mol/1 NaOH at 90-95°C	10.5	0.077 peak area for wheat starch adsorbed on hematite by chemical interaction	Weissenborn et al. (1995)
Hematite	Starch : NaOH weight ratio is = 4:1	11.0	Less than 5% floatability of hematite using 2:1 weight ratio of starch to amine	Peres and Correa, 1996
Hematite	Causticized starch (amylose, amylopentin, glucose)	10.5	10% floatability of hematite using 10 mg/t caustic digested starch	Pavlovic and Brandao, (2003)
Iron ore slimes	Unknown	10.7	80.5% recovery of Fe and 23.9 of Gaudin's selectivity index	Rocha et al., (2010)
Iron oxides ore	Starch/NaOH weight ratio is 5:1	9.5–10.5	More than 65% Fe recovery at a less than 1% silica using about 180 g/t starch	Turrer and Peres, (2010)

According to the previous researches reported by Roberts and Cameron (2002), starch granules can swell rapidly at room temperature to form a gel in the presence of sodium hydroxide and the remnants of the starch granules can become smaller, more dispersed and homogenous with increasing concentrations of sodium hydroxide. That may be in accordance with the founding by Erguoerlang (1980), who indicated that alkali can destroy hydrogen bonding between starch and water, inducing its irreversible swelling and gelatinizing at room temperature. But this may not occur unless starch granules adsorb 40–60% water, allowing the intrusion of small-molecular inorganic ions. And the major variables of this process are the ratio of starch/caustic soda and the gelatinization time (Peres and Correa, 1996). An investigation of Viana and Souza (1988) showed that for a starch/soda ratio of 4:1 the gelatinization of conventional corn starch (99% passing 44 μm) requires 3 to 4 minutes. For the same starch/soda ratio a coarser one (100% passing 1 mm) is solubilized within 20 min. However, industrial gelatinization times of at least 30 min are recommended for starches having this kind of size distribution. Also temperature is another key factor for starch gelatinization during alkali-digestion. For example, the

paste temperature of starch digested with a concentration of 0.2% ranges at 56–70°C, which drop to 49–65°C if its alkaline concentration is up to 0.3% found by Li (2004).

Moreover some new chemical species produced during alkali-degradation of starch were observed in food or agricultural areas (Isbell et al., 1969; De Wit et al., 1979; Liu et al., 2002). For example, Niemela (1990) investigated a starch treated with 1M and 3 M sodium hydroxide at 175°C and found that mixtures of carboxylic acids, up to 40–60% of the original mass of the starch, were produced. Jebber et al. (1996) reported that various carboxylic acids (formic, acetic, glycolic, lactic, 2-hydroxybutanoic, 2-hydroxy-2-methylpropanoic, and 2-hydroxypentanoic acids) were isolated from alkali-degraded starch. Also Tang and Liu (2012) found a very small amount of carboxylic groups from the diluted starch solution in the presence of sodium hydroxide in 2012.

What happen to starch after alkali-digestion may influence its adsorption on mineral surfaces? Various adsorption mechanisms of starch onto mineral surfaces have been presented in recent years (Koral et al., 1958; Wassenborn et al., 1995; Ma and Pawlik, 2005), like hydrogen bonding, electrostatic interaction, hydrophobic bonding and ionic interactions. Ravishankar et al. (1995) suggested that both of chemisorption (acid/base interaction) between O–H groups from starch granules and the Fe_2O_3 surface and electrostatic interactions were involved during its adsorption on iron oxide in 1995. Also a few researches mentioned that acid/base chemisorption of starch onto mineral surfaces regardless of its digestion methods (Ravishankar et al., 1995; Liu et al., 2000; Laskowski et al., 2007). However, the explanation about what type and amount of acidic groups was produced from starch gel after alkali-digestion and how these acidic species influence starch adsorption on mineral surfaces is limited. Since alkali-digestion seems to induce some different physical or chemical changes on starch granules, like degree of its swelling or gelatinizing, different amounts of new products resulted from alkali-digestion and etc. Those changes definitely contribute different flocculation selectivity and capacity of starch on mineral surfaces. In this study, the adsorption characteristics of starch digested with different types/concentrations of alkali on its adsorption on hematite are investigated with the objective of identifying the possible effects on the adsorption of the caustic-digested starch on hematite.

Experimental

Materials

Corn starch, with a product number S-4180, was purchased from Sigma-Aldrich. It was found to contain 12.3% moisture. Sodium hydroxide (96.0%), 081120, was purchased from Fengchuan Chemical Reagent Company, Tianjin of China and potassium hydroxide (85%), 0100121, was also purchased from Fengchuan Chemical Reagent Company. Potassium chloride (99.4%), P217-500, hydrochloric acid (36.5–38%) and sulfuric acid (96.8%) were purchased from China Medicine Company,

Beijing. The powder of iron (III) oxide (hematite) (>99%, <5 μm), CAS 1309-37-1, was purchased from Sigma-Aldrich. Nitrogen was from Meisaier Co. Kunming.

Methods

Zeta potential measurement

The zeta potentials of starch were measured with the use of a ZetaPALS zeta potential and particle size analyzer manufactured by Brookhaven Instruments Corporation, USA. The technique is based on electrophoretic light scattering (ELS), also known as Laser Doppler Velocimetry (LDV). To prepare samples for the zeta potential measurements, a 100 cm^3 0.5% (5 g/L) starch suspension was mixed with 100 cm^3 of 0.5% sodium/potassium hydroxide solution (the NaOH/starch or KOH/starch weight ratio was 1) or 100 cm^3 distilled water at room temperature. The mixed suspension was stirred at room temperature for 30 min. 5 cm^3 of the mixed suspension was withdrawn and diluted to 100 cm^3 with a 10–3M NaCl/KCl solution. The pH of the diluted suspension was adjusted using HCl or NaOH/KOH, and a small aliquot of the suspension was transferred to the sample cell of the ZetaPALS for zeta potential measurements.

Paste titration

The carboxyl content of causticized starch was determined according to the procedure of Mattisson and Legandrev (1952) and Chattopadhyay (1997) after slight modifications. Starch was causticized with a given concentration of sodium hydroxide, and the suspension was filtered to collect the starch as a filter cake. The concentration of sodium hydroxide was chosen such that it did not cause complete digestion of the starch. Half a gram (0.5 g) of the collected starch cake was mixed with 25 cm^3 of 0.1M HCl in a 150 cm^3 beaker at room temperature with magnetic stirring for 30 min. The slurry was filtered through a 150 cm^3 medium porosity fritted glass funnel, and a fine stream of distilled water from a wash bottle was used to transfer the sample from the beaker. The sample was washed with 400 cm^3 of distilled water in order to completely remove the chloride ions. The starch cake was then transferred to a 500 cm^3 beaker with the aid of distilled water, and the slurry was diluted to approximately 300 cm^3. The slurry was heated in a boiling water bath with continuous stirring for 15 min to ensure complete gelatinization. The hot starch solution was adjusted to approximately 450 cm^3 with boiling distilled water and immediately titrated to pH 8.3 with standardized 10–3M sodium hydroxide with stirring. The amount of the 10–3M sodium hydroxide used in cm^3 was recorded. The original untreated starch sample was used as control blank to correct for any possible inherent acidic substances in the starch. For the control blank titration, instead of stirring with 0.1M HCl, 1 g of untreated starch was stirred with 25 cm^3 of distilled water for 30 min, and the remainder of the procedures was the same as above. The acidity and carboxyl content of the starch were calculated from the following equations:

$$meq \frac{acidity}{100 \; starch} = \frac{(cm^3 \; NaOH \; for \; sample - cm^3 \; NaOH \; for \; blank) \cdot Normality \; of \; NaOH \cdot 100}{Sample \; weight \; (dry \; basis) \; in \; g}, \quad (1)$$

Apparent % carboxyl (% dry basis or % d = meq of acidity of 100 g starch · 0.045. (2)

Scanning Electron Microscope measurement

The samples of caustic-digested starch with sodium hydroxide at different concentrations were analyzed with Scanning Electron Microscope (Quanta 200 FEG, manufactured by FEI Company, USA). To prepare samples for the SEM measurements, a 100 cm^3 0.5% (5 g/dm^3) starch suspension was treated by sodium hydroxide at a range of concentrations in the distilled water for half an hour. Then the suspension was filtered to collect the starch as a filter cake.

Adsorption tests

To measure the adsorption density of the starch digested with sodium/potassium hydroxide or boiling distilled water on mineral surfaces, 100 cm^3 0.5% starch suspension was causticized with 100 cm^3 of a sodium hydroxide solution at a sodium hydroxide concentration of 1.5, 1.75, 2, 2.25, or 2% of potassium hydroxide, or boiling distilled water. The mixed suspension was stirred at room temperature for 30 min, and then 20 cm^3 of the suspension was withdrawn and diluted to 200 cm^3 with distilled water. 50 cm^3 of the 0.025% starch solution was adjusted to pH 7 and mixed with 50 cm^3 2% hematite suspension (containing 1 g of hematite) that was also adjusted to pH 7. The mixture was shaken in a thermostated circular shaker for 30 min. The temperature was maintained at 25±1 °C. After equilibrium, the pH of the suspension was measured again, and a small sample of the suspension was centrifuged for 10 min by Sorvall GLC-4 General Laboratory Centrifuge (G~325N). The supernatant was assayed for starch following the phenol-sulfuric acid method, developed by Dubois et al. (1956).

Fourier transform infrared spectroscopic (FTIR) analysis

The FTIR spectra of several samples were recorded by a Nicolet-Thermo 8700 Fourier transform infrared spectrometer in the range from 4000 cm^{-1} to 400 cm^{-1} at a resolution of 4 cm^{-1}. The powdered samples were prepared in the form of KBr pellets containing 10–15 mg powder samples and 200 mg KBr, which were mixed and ground in an agate mortar, and pressed into pellets. The measured samples included native starch, the starch digested with 0.15 or 0.25%, sodium hydroxide, hematite after equilibration with caustic-digested starch, and the precipitate obtained from mixing Fe(III) chloride and caustic-digested starch. To prepare the precipitation sample between Fe(III) and caustic-digested starch, 100 cm^3 0.5% (5 g/dm^3) starch suspension was caustic-digested with 100 cm^3 of a sodium hydroxide solution at a sodium hydroxide concentration of 2% (therefore the NaOH/starch weight ratio was 4). The starch-NaOH suspension was stirred at room temperature for 30 min, and then 20 cm^3 of the suspension was withdrawn and diluted to 200 cm^3 with distilled water. 50 cm^3 of the 0.025% starch solution was adjusted to pH 7 and mixed with 50 cm^3 0.054%

FeCl$_3$·6H$_2$O suspension (containing 0.002M of Fe(III)) that was also adjusted to pH 7, so that the final concentration of ferric ion was 0.001 M and that of starch was 125 ppm. The mixture was shaken in a thermo-stated circular shaker for 30 min. The temperature was maintained at 25±1 °C. After conditioning, a small sample of the suspension was centrifuged for 10 min by Sorvall GLC-4 General Laboratory Centrifuge (G~325 N) and the sediment was dried at <40 °C.

Results and discussion

Zeta potentials of caustic-digested starch

Figure 1 provides the zeta potentials of starch digested with alkali, i.e. 0.25% NaOH, or 0.25% KOH in room-temperature water. As can be seen, KOH-digestion at 0.25% concentration shifted the isoelectric points of the starch towards more acidic pH than NaOH-digestion at same concentration. The isoelectric point of starch suspended in water was about 5, by extrapolation. However, it shifted to about 3.3 after digestion with 0.25% NaOH, and about 2.8 after digestion with 0.25% KOH. It may be explained well by dissociation of surface functional groups for starch digested with NaOH/KOH at same concentration, such as carboxylic (R-COO$^-$), surface charge arises from the protolysis of these functional groups. The acid dissociation constant pKa of the hydroxyl groups in starch is about 12 (Oosten, 1990), so that it is unlikely that the hydroxyl groups could dissociate at the acidic pH between 3 and 4. Comparing the results of zeta potentials of starch digested with hydroxides, high ionic strength (the concentration of Na$^+$ or K$^+$ is about 0.015 M in the caustic-digested starch suspension) may contribute to the increase of zeta potentials for starch digested with alkali (Oosten, 1990; Ma, 2006). Since K$^+$ has water-structure breaking capacity while Na$^+$ has water-structure making capacities, which may play different roles in gelatinizing starch (Ma and Pawlik, 2005).
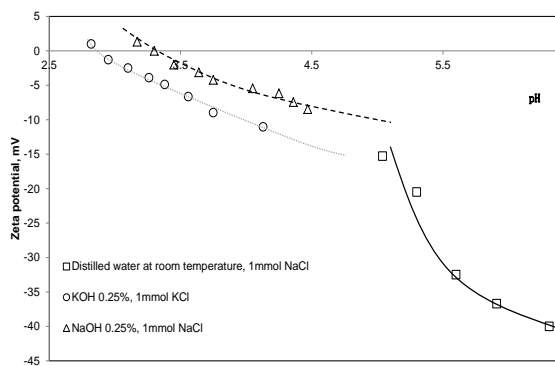
Fig. 1. Zeta potential of starch digested with sodium hydroxide or potassium hydroxide at 0.25% concentration as a function of pH

Carboxyl contents of caustic-digested starch

Table 2 shows the contents of carboxyl groups generated on starch remnants when a 0.5% starch suspension (5 g/dm^3) was digested with KOH or NaOH at different concentrations. It can be seen that more amount of carboxyl groups were produced in the starch gel if higher concentrations of sodium hydroxide were added. When the weight ratio of NaOH to starch was about 1, the amount of carboxyl groups reached 0.0342%db. And it can be expected that more carboxyl groups will be generated at these higher weight ratios, for example 0.513%db by extrapolation at a 2 ratio of NaOH to starch. But the titration tests were not performed at higher NaOH and starch weight ratios because of the difficulty in harvesting the treated starch remnants for titration. Comparing the carboxyl contents of starch treated with 0.25% NaOH and 0.25% KOH, it can be explained well that more acidic groups was resulted from the starch digested with KOH than NaOH at same concentration, triggering a more acidic zeta-potential shift of starch as shown in Fig. 1. Those acidic species on starch remnants produced from alkali-digestion would enhance the acid/base interaction on mineral surfaces.

Table 2. Carboxyls content and isoelectric point of starch digested
with different concentrations of sodium hydroxide, 0.25% potassium hydroxide

	Methods	Acidity of carboxyl content of caustic-digested starch, %db
KOH	0.25%	0.027
NaOH	0.075%	0.0099
	0.25%	0.0162
	0.50%	0.0342
	2% (by extrapolation)	0.513

SEM images of caustic-digested starch

Figures 2a-2d present the comparison of the SEM images of the starch digested with sodium hydroxide at a concentration of 0, 0.125, 0.25 and 0.5% (the weight ratio of starch to sodium hydroxide is 1:1). Native starch granules observed from the images magnified by 3000 and 10000 in Fig 2a change little after digesting in the water at room temperature, mostly dispersing without any swelling. These granules begun to degrade from their hilum by using only 0.125% sodium hydroxide, substantially distorted by further increasing alkaline concentration to 0.25%, and eventually those original granules structures disappeared and turned into some small pieces of the gel remnants at a 1:1 weight ratio of starch to sodium hydroxide as shown in Figs 2c and 2d.
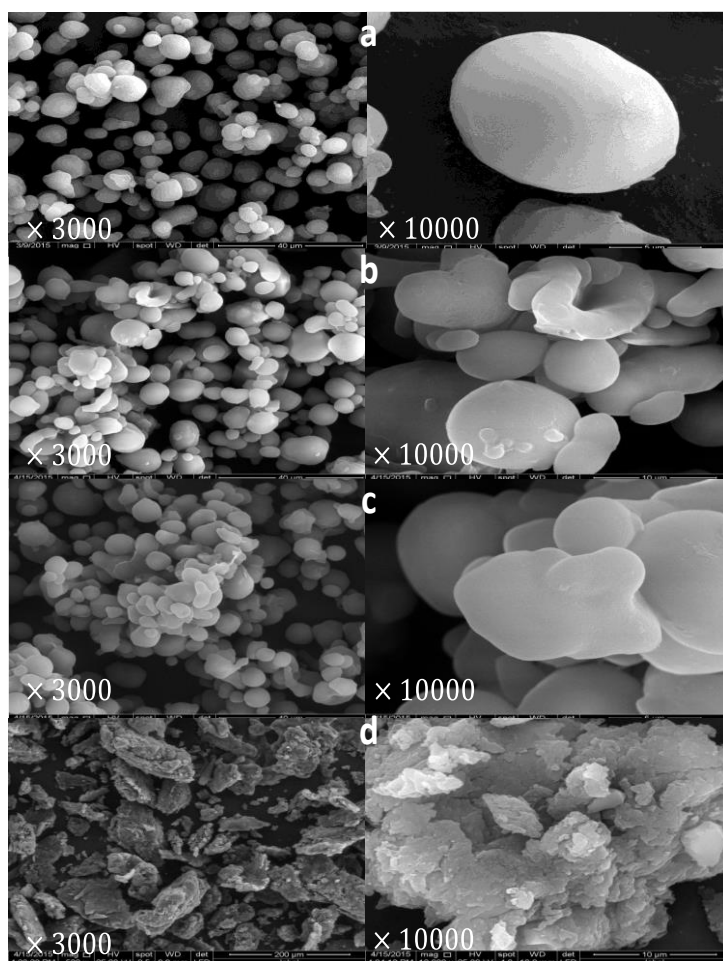
Fig. 2. SEM images (magnified 100000) of the caustic-digested starch with sodium hydroxide at different concentrations at room temperature: a) native starch granules, b) at a concentration of 0.125% sodium hydroxide, c) 0.25% sodium hydroxide, d) 0.5% sodium hydroxide)

As can be seen, native starch granules exposed to massive water at room temperature firstly absorbed a certain amount of water and then lead to a limited and reversible swelling. This swelling may begin in the least organized, amorphous, inter-crystallite regions of these granules, slightly exerting a tension on neighboring crystallites and tending to distort those (French, 1984). And the total length of the swollen granules remains more or less constant, for the molecules of the inner core aligned along the long axis of the granules may not be distorted at this range of temperatures. Those granules substantially degraded in the presence of sodium hydroxide, even at a low concentration. And this process accelerated and induced an internal longitudinal splitting, probably beginning in the central part as shown as Fig

2c (image magnified by 10000) by increasing alkaline concentration. Eventually further adding alkaline and hydration weaken the granule to the point where it can no longer resist mechanical or thermal shearing, and a good gel is resulted. Gelatinizing of starch granule may start from its hilum according to previous researches by Gough and Pybus (1971), but it is not the same case if ions were involved. And paste temperature of starch may depend on type and concentration of ions. Strong alkali can degrade starch at room temperature and it starts at an adsorption density of 0.4 mg/g sodium hydroxide on corn starch based on the adsorption formula of Freundlich. And spinodal decomposition of starch begins at a critical concentration of alkali and immediately all granules turn into a statement of micro-phase separation found by Feke and Prins (1974).

Adsorption on hematite of caustic-digested starch

Fig. 3 compares the adsorption densities of starch digested with different methods on hematite, i.e., boiling water only and sodium hydroxide or potassium hydroxide at different concentrations at room temperature. About 9.87 mg/g hematite for starch treated by 2% NaOH, 10.51 mg/g hematite for starch treated by 2% KOH and 6.2 mg/g hematite by boiling water only were observed from Fig. 3. These results seem to be in accordance with the former researches (Schulz and Cooke, 1953; Khosla et al., 1984; Patridge and Smith, 1971), which were reported that typical adsorption amount for starch on hematite had been investigated to be 2-18 mg/g hematite or 0.3-2.6 mg/m^2 for alkali-digestion and about 6 mg/g hematite for heating (Khosla et al., 1984). More acidic groups on the starch remnant was harvested from KOH-digestion at a concentration range of more than 1.9% than by NaOH-digestion at same concentration ranges or by heating-treatment only. That could be well accordance with zeta-potential results in Fig. 1and the carboxyl content of the caustic-digested starch in Table 2 (0.0270 db% for starch digested with 0.5% KOH and 0.0162 db% for starch digested with 0.5% NaOH).

Also it can be seen from Fig. 3 that there was a similar trend for the caustic-treated starch digested with sodium hydroxide or potassium hydroxide at different concentrations on hematite surfaces. The maximum amount of starch adsorbed on hematite was 9.87 mg/g hematite at a NaOH concentration of near 2%, but 11.12 mg/g hematite at a KOH concentration of near 2.25%; a sharp drop of the adsorption density of the caustic-digested starch occurs if over 2% of NaOH or 2.25% of KOH was added. Because starch granules swelled rapidly at room temperature to form a gel in the presence of sodium hydroxide and the starch granules became smaller, more dispersed and more homogenous with increasing concentrations of sodium hydroxide according to the previous literatures (Somasundarum and Wang, 1985; Wooton and Ho, 1989; Tomasik and Schilling, 2004; Cao et al., 2009). Much smaller and homogenous short-chain granules resulted from alkali-digestion at a higher concentration range of NaOH or KOH may weaken the flocculating capacity of the

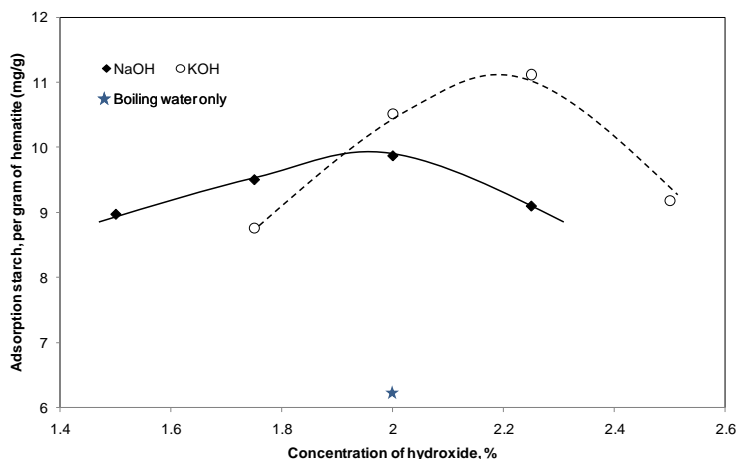caustic-degraded starch on hematite and lead to the decreasing of the adsorption density.

Fig. 3. Adsorption densities on hematite of the starch digested with sodium hydroxide or potassium hydroxide at different concentrations, or boiling distilled water only

FTIR spectra of Fe (III) or hematite by using caustic-digested starch

Figure 4 presents the Fourier transform infrared (FTIR) spectra of pure hematite, a mixture of hematite and the caustic-digested starch at a 2 weight ratio of sodium hydroxide to starch or Fe (III) and the caustic-digested starch at a 2 weight ratio of sodium hydroxide to starch. It shows that overtone and combination bands of Fe–O stretching vibrations near 1110 and 1020 cm^{-1} for pure hematite disappear and –CO and C–OH stretching vibrations of starch near 1130~1010 cm^{-1} arise when caustic-digested starch adsorbed on hematite. This means the assignment of infrared adsorption bands for hematite before and after adsorption with the caustic-digested starch (Casu and Reggiani, 1966; Wessenborn et al., 1995; Hadjiivanov and Vayssilov, 2002; Pavlovic and Brando, 2003; Wen et al., 2006). Comparing the FTIR spectra of pure hematite, COO^{-} asymmetric stretching and COO^{-} symmetric stretching occur near 1620 and 1450~1340 cm^{-1} when co-precipitation between Fe(III) and the caustic-digested starch. FTIR measurements were not performed at higher NaOH/starch ratios as the higher concentration of NaOH could cause the hydrolytic cleavage of the starch molecules and result in the formation of smaller, more water soluble compounds (Germann et al., 1963).

It is worthy to be noticed that a typical acid/base interaction happens between hematite and the caustic-digested starch due to a certain amount of carboxylic groups resulted from alkali-digestion. According to the previous research by Ravishankar et al. (1995), the polarized oxygen from O–H groups on starch granules involved the acid/base interaction with Fe$_2$O$_3$ surfaces. Since the acid dissociation constant pKa of

the hydroxyl groups in starch is about 12 (Oosten, 1990), so that it is more likely that a small amount of the carboxyl groups in the starch gel produced from alkali-digestion contribute to this interaction than these hydroxyl groups.
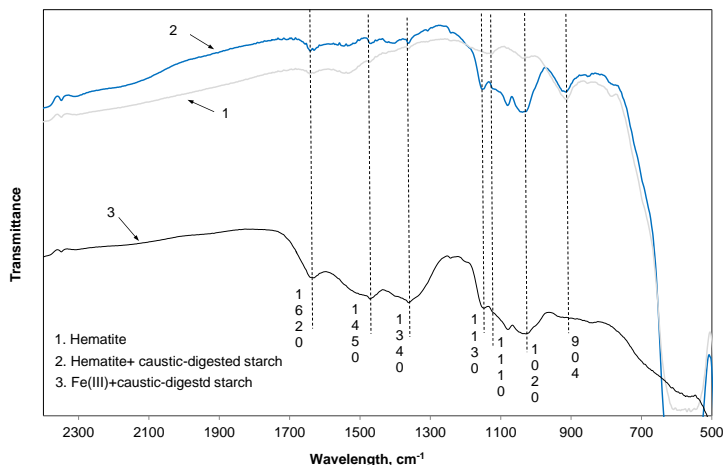

Fig. 4. FTIR spectra of pure hematite, a mixture of hematite and the caustic-digested starch at a 2 weight ratio of sodium hydroxide to starch or Fe(III) and the caustic-digested starch at a 2 weight ratio of sodium hydroxide to starch

Conclusions

It was shown that the corn starch digested with sodium hydroxide or potassium hydroxide at different concentrations at room temperature only possessed different carboxyl contents, isoelectric points and adsorption characteristics on mineral surfaces. A certain concentration (a weight ratio of NaOH to starch of about ~2% for sodium hydroxide or 2.25% for potassium hydroxide) can harvest the maximum adsorption density on hematite of the caustic-digested starch, accounting for 9.87 mg/g hematite for sodium hydroxide and 10.51 mg/g hematite for potassium hydroxide, respectively. And its FTIR spectra all indicate the presence of interaction of the carboxylic groups with the hematite surfaces. Also the SEM images of the caustic-digested starch show that a severe degradation of starch granule seems to start from its hilum and immediately form a gel if alkaline concentration reach a critical point. The gel from alkali-digestion may account for the increase in its adsorption on mineral surfaces.

Acknowledgements

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