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FLOCCULATION/DISPERSION OF HEMATITE WITH CAUSTIC DIGESTED STARCH

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Abstract: Selective flocculation of hematite with starch is a process well-known in practice. However, the separation of hematite from other minerals depends strongly on the methods of starch digestion performed either as heating-digestion or alkali-digestion (different type and dosage of alkali). The purpose of this study is to identify possible influence of the alkali-digested starch on flocculation of ultra-fine hematite when the starch was digested at different concentrations of sodium hydroxide at room temperature. Adsorption of starch digested with sodium hydroxide at different concentration on hematite was investigated by abstraction and co-precipitation tests. Turbidities tests, settling rates, flocculation/dispersion measurement and Fourier transform infrared spectroscopic analysis (FTIR) have also been conducted. Based on the results of the above mentioned tests it is suggested that the flocculating power of caustic digested starch towards fine particles may be significantly weakened, while its dispersing ability starts to play a role instead, if the concentration of sodium hydroxide is high enough in starch digestion. When the weight ratio of NaOH /starch is lower than 2, incomplete gelatinization of starch granules may lead to coagulation of fine particles of hematite mostly due to non-selective electrostatic attraction. The weight ratio of NaOH /starch from 2 to 4 helps to flocculate mineral surfaces selectively and efficiently, assuring a complete digestion of starch granules and a small amount of acidic functional products on the starch chain. However, much smaller and homogenous short-chain granules resulting from higher concentration of sodium hydroxide (the weight ratio of NaOH /starch is more than 4) used to digest starch may weaken the flocculating capacity of the caustized starch for hematite and lead to its dispersion.

Keywords: *starch, alkali-digestion, flocculation, dispersion*

Introduction

The common methods to prepare starch solution for use in mineral flotation are alkali-digestion using sodium hydroxide at room temperature (Iwasaki and Lai, 1965; Peres and Correa, 1996; Pavlovic and Brandao, 2003; Tomasik and Schilling, 2004) and heating-digestion at certain temperature (Afenya, 1982; Khosla et al., 1984;

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Subramanian and Natarajan, 1988). Table 1 provides the application of starch as flocculant in flotation of hematite, indicating that selective flocculation on fine iron oxides is obtained with starch digested using traditional methods like alkali or heating, which may contribute to different flocculating results partly even under similar reagent condition and particle size.

Table 1. Selected literature data on application of starch as a flocculant for hematite

Mineral depressed	scale	Reagents, pH	Separation results	Reference
Hematite	Lab	Polyacrylic acid as flocculants; pH=3-9	Selective flocculation	Drzymala and Fuerstenau, 1981
Iron ore tailings	Lab	Starch as flocculants; Sodium silicate or sodium hexametaphosphate as dispersant; pH=10.5	64.8% grade and 80% recovery of Fe	Rao and Narasimhan, 1985
Hematite	Lab	Starch/amylose/amylopectin as flocculants; pH=10.0	Less than 10% floatability of hematite when 10 mg/l starch (amylose/amylopectin ~40/80)	Pinto et al., 1992
Ultrafine Hematite	Lab	Wheat Starch as flocculants; pH=10.5	Selective flocculation	Weissenborn et al., 1994; Weissenborn et al., 1995
Fine hematite	Lab	Sodium oleate as collector; Starch as depressant; pH=9-9.5	60%recovery with adding 1 $\times 10^{-4}$mol/dm^2 oleate	Shibata and Fuerstenau, 2003
Fine hematite	Lab	Tetradecylammonium chloride as collector; Starch as depressant; pH=7.5	80%recovery of hematite when adding 7.0$\times 10^{-4}$M collector.	Montes and Atenas, 2005
Iron ore slimes	Pilot	Amine as collector; Starch as depressant; pH=10.7	80.5% recovery of Fe and 23.9 of Gaudin's selectivity index	Rocha et al., 2010
Hematite in waste-water	Lab	Polyalumiun chloride (PAC)/ferric chloric (FA)=3:7 as coagulant; Polyacrylamide (PAM) as flocculant; pH=10.45	Decrease the turbidity from 13530 NTU to 12 NTU	Yang et al., 2010
Hematite <100µm	Lab	N-laure-1,3-diaminopropane as collector; Starch as depressant; pH=7.27	58.45% grade and 86.93% recovery of Fe from a 2:3 ratio of hematite: quartz mixture containing 28% grade of Fe	Liu et al., 2011

Previous investigations were focus on the physicochemical effects of concentration of sodium hydroxide on starch degradation used mostly in food or agriculture industries. Roberts and Cameron (2002) and Wootton and Ho (1989) indicated that during gelatinization of starch in the presence of sodium hydroxide it can swell rapidly at room temperature, and the granules can become smaller and more dispersed as well as homogenous with increasing the dosages of NaOH. It was observed by Maher and Peoria (1983) that the alkali/starch weight ratio can determine the degree of gelatinization. Also there are some investigations which explain chemical changes induced by NaOH-degradation of starch suspension and affected of the concentration of NaOH. Sheng et al. (2011) found that a certain amount of NaOH at 100 ^{o}C for 3 hours during starch digestion can harvest desirable water-soluble oxidized starch with carboxyl content of 3.6 g/100 g, indicating that the amount of sodium hydroxide can influence the oxidation of native starch. Niemela (1990) investigated a starch treated with 1 M and 3 M sodium hydroxide at 175 ºC 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 the alkali-degraded starch. Tang and Liu (2012) found that a few acidic carboxyl groups produced during alkali-degradation of starch were observed.

Although the use of alkali-gelatinized starch in mineral processing is well established, the effects of concentration of sodium hydroxide on starch adsorption on mineral surfaces are not sufficiently understood. Different concentrations of NaOH in starch digestion may lead to changes of starch granule structures, size of remnant chains and the amount of new functional groups on the chains. Those may enhance or weaken its adsorption on the surfaces of minerals. In this study, the possible functions, flocculation or dispersing, of hematite by starch digested with NaOH at different concentrations at room temperature were studied. The objective was to determine the flocculating power of caustic digested starch.

Experimental

Materials

Corn starch S-4180, containing 12.3% moisture, was purchased from Sigma-Aldrich. Sodium hydroxide S318-1, assaying 98.8%, was from Fisher Scientific. Sulfuric acid (96.8%) was used as a pH modifier and was purchased from Fisher Scientific. Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99.8%), 188-510, was purchased from Fisher Scientific and used in co-precipitation tests. The powder of iron(III) oxide (hematite, CAS 1309-37-1, 99+ %, < 5 μm) was purchased from Sigma-Aldrich.

Methods

Turbidity measurement

The turbidities of starch suspensions were measured by turbidity meter 66120-200, manufactured by VWR Scientific. To prepare the starch suspensions for the turbidity measurements, 50 cm^3 of a 0.5% (5 g/dm^3) starch suspension was digested with either 50 cm^3 sodium/potassium hydroxide solutions at different concentrations or distilled water at different temperatures for 30 min, then a small volume of the digested starch suspension was diluted twice with distilled water and used for turbidity measurement.

Paste titration

The carboxyl content of caustized starch was determined according to the procedure of Mattisson et al. (1952) and Chattopadhyay et al. (1997) after slight modifications. Starch was caustized 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 0.1 M HCl in a 150 cm^3 beaker at room temperature with a magnetic stirrer 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 volume was adjusted to approximately 450 cm^3 with boiling distilled water and immediately titrated to pH 8.3 with standardized 10^{-3} M sodium hydroxide with stirring. The amount of the 10^{-3} M sodium hydroxide used in cm^3 was recorded. The original untreated starch sample was used as a blank test to check potential presence of any possible inherent acidic substances in the starch. For the control blank titration, instead of stirring with 0.1 M HCl, 1 g of untreated starch or starch digested with only boiling water 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 (Chattopadhyay et al., 1997):

$$\frac{\text{meq acidity}}{\text{100g starch}} = \frac{(\text{mL NaOH for sample} - \text{mL NaOH for blank test}) \cdot \text{Normality ofNaOH} \cdot 100}{\text{Sample weight (dry basis)in g}} \qquad (1)$$

$$\frac{\text{apparent \%}}{\text{Carboxyl (\% dry basis db)}} = \text{meq of acidity of 100g starch} \cdot 0.045 \qquad (2)$$

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 caustized 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. Fifty 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±1ºC. After reaching 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~ 325 N). The supernatant was assayed for starch following the phenol-sulfuric acid method developed by Dubois et al. (1956).

Co-precipitation tests

A certain amount of ferric chloride solution was adjusted to pH 7 to form hematite and then mixed with the caustized starch solution digested with sodium hydroxide at different concentrations which also was adjusted to pH 7 before mixing, 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 thermostated circular shaker for 30 min. The temperature was maintained at 25±1ºC. After conditioning, a small sample of the suspension was centrifuged for 10 min by Sorvall GLC-4 General Laboratory Centrifuge (G~ 325 N). The supernatant was then sampled to assay for the residual concentration of starch. Blank tests for starch were also conducted.

Settling rate measurements

To measure the settling rate of the flocs resulting from the adsorption of caustized starch on hematite, 100 cm^3 0.5% (5 g/dm^3) starch suspension was caustized with 100 cm^3 of a sodium hydroxide solution at a sodium hydroxide concentration of 1.25%, 1.5%, and 2%. 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. One hundred cm^3 of the 0.025% starch solution was adjusted to pH 7 and mixed with 100 cm^3 2% hematite suspension (containing 1 g of hematite) that was also adjusted to pH 7. The mixture was shaken slightly in a thermostated circular shaker for 30 min. The temperature was maintained at 25±1ºC. After conditioning, the settling tests were performed using a 250 cm^3graduated glass cylinder (280 mm high and 40 mm in diameter).

Flocculation/dispersion measurements

The degree of flocculation/dispersion of mineral suspension was measured by a Photometric Dispersion Analyzer (PDA2000) manufactured by Rank Brothers Inc. In the test, 0.5g hematite (-5 µm) and 50 cm^3 water were agitated using a magnetic stirrer in a 250- cm^3 beaker and circulated through the flow cell of the PDA 2000 using a peristaltic pump. The magnetic stirring bar was 50 mm long and the stirring speed was fixed at 300 rpm. The Ratio output as a function of time was recorded by a computer connected to the PDA2000. The flocculation/dispersion state of the suspension was monitored in real time following the addition of starch to the circulating suspension.

Results and discussion

Carboxyl contents of starch digested sodium hydroxide

Table 2 shows the contents of carboxyl groups generated on starch when a 0.5% starch suspension (5 g/dm^3) was digested with different concentrations of sodium hydroxide. It can be seen that with increasing concentrations of sodium hydroxide, more carboxyl groups were produced. Although the NaOH-to-starch weight ratios were less than 1, some amounts of carboxyl groups were detected. In practice, starch is usually digested with more sodium hydroxide, with NaOH-to-starch weight ratios ranging from 2 to 4. It can be expected that more carboxyl groups will be generated at these higher weight ratios. The titration tests were not performed at higher NaOH to starch weight ratios because of the difficulty in harvesting the treated starch granules for titration.

Table 2. The carboxyl content and isoelectric point of starch digested with different concentrations of sodium hydroxide

Concentration of NaOH, %	IEP of starch after digestion, pH	Acidity of carboxyl content of caustized starch, %db (dry basis)
0.075	3.80	0.0099
0.250	3.25	0.016
0.500	2.95	0.034
1.000	2.89	0.14

Flocculation/dispersion measurement with PDA

Figure 1 shows the images (1:1) of starch solution digested with 2%, 2.5% and 3% NaOH after settling. As can be seen, the size of flocs for starch remnants became smaller and smaller with increasing the concentration of NaOH, indicating that the higher concentration could lead to breakdown of the starch chain rapidly, lowering its flocculating power and playing its dispersing role on hematite to some degree. These results are in agreement with the results from flocculation/dispersion measurement with PDA as shown in Fig. 1. It can be observed that the ratio of ultra-fine hematite (-5µm) reduced significantly from 7 to 2~3, suggesting that the initial fluffy aggregated hematite particles induced by their electrostatic attractions were not flocculated, but dispersed when adding starch digested with 2.5% NaOH.

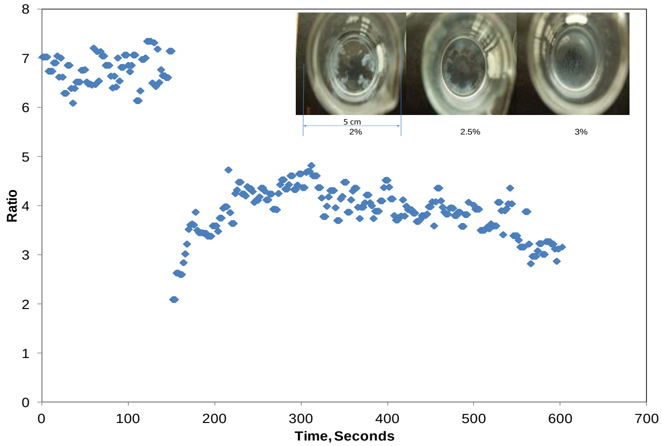

Fig. 1. Effect of starch digested with 2.5% NaOH on the flocculation/dispersion of hematite (particle size of hematite: -5µm, pulp density: 1%, pH=7, hematite: 1%, starch: 500 ppm)

Adsorption on hematite and co-precipitation with Fe (III) of caustized starch

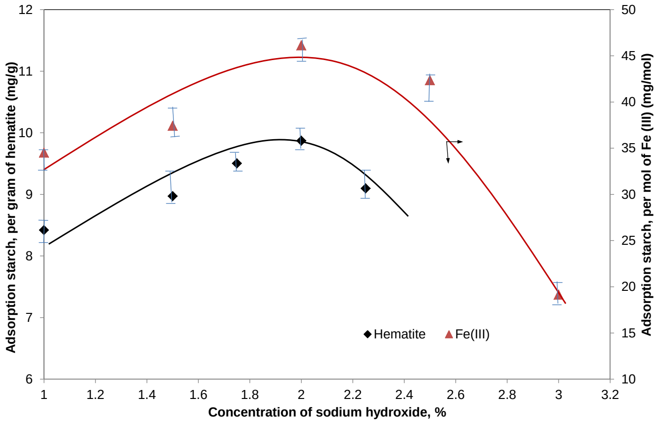

Fig. 2. Adsorption of starch on either hematite or Fe(III) for with different concentrations of sodium hydroxide used for digestion

It can be seen in Fig. 2 that there was a similar trend of adsorption of caustized starch on both co-precipitated Fe(III) and hematite for different concentrations of NaOH used for digestion. The maximum amount of starch co-precipitated with Fe(III) (46.13 mg/mol Fe(III)) and adsorbed on hematite (9.87 mg/g hematite) occurred for about 2% NaOH. The small number of carboxyl groups resulted from alkali-digestion may help flocculation according to the results shown in Table 2. However, a decrease in the amounts of starch absorbed on either hematite or Fe (III) might be related partly to the changes of sizes of the remnants granules, inducing mostly short-chain granules from caustic starch digestion using more than 2% NaOH. This is based on the results shown in Fig. 1 and previous literature (Casu and Reggiani, 1964; Liu et al., 2002). Much smaller and homogenous short-chain granules resulted from higher concentration of NaOH used to digest starch may weaken the flocculating capacity of the caustized starch on hematite and Fe(III) leading to a decrease in the adsorption density.

Settling behaviors of -5 µm hematite treated with caustized starch by visual observations

As can be seen in Fig. 3, with increasing concentration of sodium hydroxide used to digest the starch, the settling rate of a -5 µm hematite sample was increased when it was treated with starch. The initial settling rate increased from $3.7 \cdot 10^{-5}$ m/s when the sodium hydroxide concentration was 1.25%, to $6.9 \cdot 10^{-5}$ m/s, when the sodium hydroxide concentration was 2.0%. The results are in a good agreement with the pictures taken at same time intervals during settling rate measurement of hematite treated by caustic starch, indicating that much faster settling rate was found for hematite treated by starch digested with 2.00% than with 1.25%. In view of the results shown in Fig. 1, complete digestion and dissolution of starch was achieved at a sodium hydroxide concentration of 1%. A further increase occurring for higher sodium hydroxide concentration may not be the result of better dissolution. A higher sodium hydroxide concentration induces two changes that have opposite effect on the settling behavior of hematite. On one hand, it generated acidic groups on the starch which may promote its adsorption on hematite. On the other hand, the higher concentration could lead to breakdown of the starch chain (Khosla et al., 1984), lowering its flocculation power. In the sodium hydroxide concentration range tested, it can be seen that the increasing concentration caused an increase in the settling rate. This is most likely the result of increasing adsorption density that was caused by the acidic groups of carboxylic acid. Figure 2 indicates that the adsorption density of starch was higher at higher sodium hydroxide concentrations that were used to digest starch. The acidic groups may provide more “anchor” sites for starch on the surface of hematite. It was reported by Weissenborn et al. (1995) that starch prepared with sodium hydroxide solution (weight ratio of starch/NaOH was 1: 0.4) at 85 ^{0}C could produce large and fast settling aggregates during adsorption on hematite.

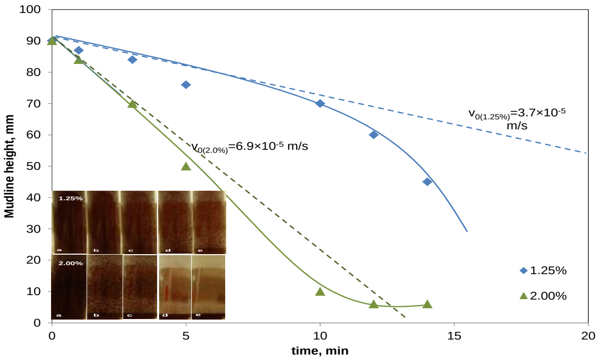

Fig. 3. Settling curves and pictures of -5 µm hematite treated by starch digested with 1.25% and 2.00% NaOH. Interval of settling pictures was: a.0 s, b. 30 s, c. 60 s, d. 120 s and e. 180 s. The two dashed lines were drawn in a tangential direction from two settling curves, respectively

FTIR spectra of starch digested sodium hydroxide

Figure 4 shows the Fourier transform infrared (FTIR) spectra of pure hematite, hematite mixed with starch digested with 2% NaOH and Fe(III) ions mixed with starch digested with 2% NaOH. It has been observed that the overtone and combination bands of Fe-O stretching vibrations near 1,110 and 1,020 cm^{-1} for pure hematite disappeared, and –CO and C-OH stretching vibrations of starch near 1,130~1,010 cm^{-1} arose when caustized starch was reacted with hematite. Those results are well in agreement with the previous research published by Tang and Liu in 2012, who found that two new small peaks, at 1,558 cm^{-1} and 1,548 cm^{-1} for the 0.3% NaOH, and 1,552 cm^{-1} and 1,544 cm^{-1} for the 0.5% NaOH, appeared for the alkali digested starch compared with the native starch, indicating the presence of carboxyl groups. However, these peaks were small meaning that the concentrations of the carboxyl groups are not very high. This is consistent with the titration results shown in Table 2. The low carboxyl contents may be a result of the relatively low NaOH to starch ratio (0.6 and 1.0). Also it can be seen that the COO$^-$ asymmetric and symmetric stretching occurred near 1,620 cm^{-1} for the caustized starch adsorbed on the hematite, and at 1,450 and 1,340 cm^{-1} in the precipitates obtained after reacting Fe(III) chloride ($FeCl_3\cdot6H_2O$) with the caustized starch. Those results are in accordance with the previous literature (Gersmann et al., 1963; Casu and Reggiani, 1964; Wootton and Ho, 1989; Nakazawa and Wang, 2003; Somasundaran and Wang, 2006; Cao et al., 2009), indicating that there were indeed carboxylate groups that were involved in the interaction between the iron oxide/hydroxide species and the caustized starch.

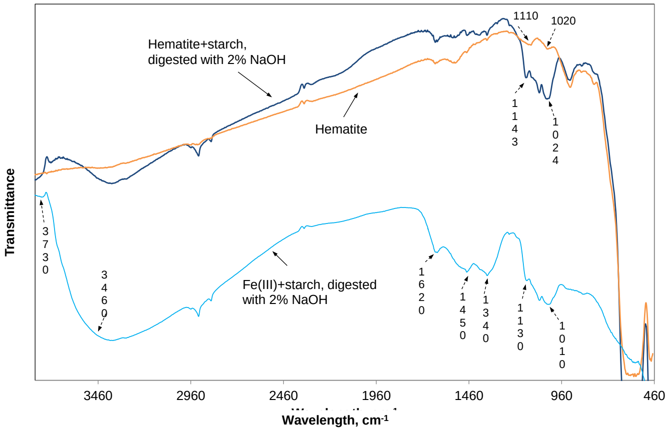

Fig. 4. FTIR spectra of starch digested with 2% sodium hydroxide adsorbed on hematite and Fe(III)

Possible model of flocculation/dispersion of caustic digested starch onto mineral surfaces

Figure 5 presents the possible model for starch, digested with NaOH of different concentrations, adsorbed on hematite. It is hypothesized that there may be four scenarios for adsorption of digested starch on mineral surfaces: no aggregation of native starch and particles, coagulation at a very low concentration, flocculation at suitable concentration, and finally dispersion at higher concentrations. Based on the data of turbidity and paste titration tests, when the weight ratio of NaOH/starch is near 4, the turbidity of the starch suspension is <10 NTU and the DS of carboxylic acids on the granules' remnants is up to 0.5/100ATU, very good gel of starch occurs which may achieve the maximum adsorption between starch and hematite due to acid-base interaction. In that case, the size of the starch remnants may provide suitable container for the flocculation of hematite. Meanwhile, the new acidic groups may provide more "anchor" sites for starch on the surfaces of minerals. However, the selective dispersion of starch occurs when the concentration of NaOH is greater than 2%. Because small short-chain starch granules cannot interact with ultra-fine particles effectively, it leads to a lower efficiency of flocculation of hematite and starts to show its dispersion to some degree. The results from Table 2 and Figs 1- 4 are in accordance with this hypothesis. Of course, the high ionic strength of the starch suspension resulting from the high concentration of NaOH during flocculation of starch and hematite cannot be ignored (Ma and Bruckard, 2010).

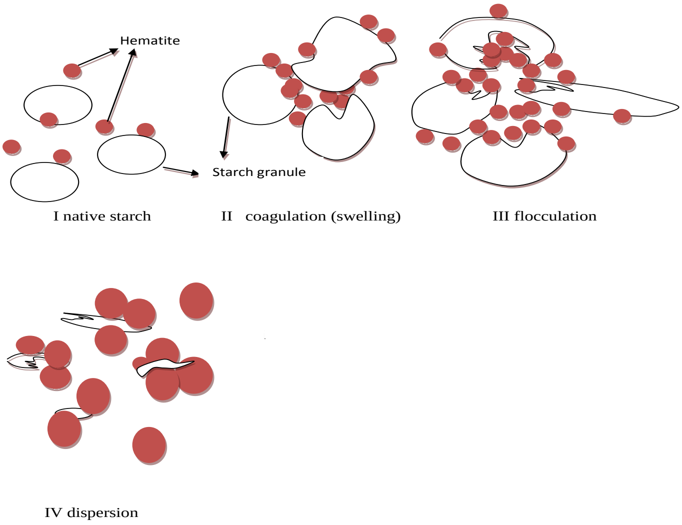

Fig. 5. Macro-model for adsorption of starch digested with increasing concentration of NaOH on hematite

Conclusions

The optimum NaOH:starch ratio equal to about 4 used for starch digestion was found to ensure maximum adsorption efficiency of 9.87 mg/g hematite on the mineral surface of hematite. It is hypothesized that there may be four possible scenarios during of starch and mineral interactions based on flocculating or dispersing mechanism. The “fluffy” flocks and open crystal areas of the granules’ remnants, as well as a small amount of carboxyl groups resulting from suitable alkali-digestion, may enhance the adsorption of starch on hematite. On the other hand, too short chains of the granules may cause dispersion of hematite fines causing difficulties in settling.

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