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XPS study on the mechanism of starch-hematite surface chemical complexation

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ABSTRACT

Polysaccharides are some of the most widely employed flotation reagents in the mineral processing industry. Among several, starch is of particular importance for reverse flotation of iron ores. It is known to behave as an efficient depressant for hematite and, therefore, its interaction is of great relevance. In this paper, we investigate the surface chemistry of starch adsorbed onto hematite by means of X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. Our results indicate that starch undergoes an important oxidation process under industrial gelatinization conditions, which favors the binding of starch molecules. Meanwhile, the oxide surface is subjected to full hydroxylation, leading to strong polysaccharide-metal hydroxide interaction. Previously proposed starch interaction mechanisms are discussed, and the importance of acid-base interactions is underscored.

1. Introduction

Adsorption of specific molecules on metal oxide and hydroxide surfaces is of significant importance in a variety of fields, ranging from catalysis to corrosion science and semiconductor manufacture (Shrimali et al., 2016). Applications involving separation of minerals by flotation are particularly relevant for this paper (Araujo et al., 2005). In this field, a metal oxide surface immersed in aqueous solution undergoes several reactions at acid-base sites, including the formation of surface hydroxyl groups and eventual adsorption of organic molecules, resulting in hydrophobicity or hydrophilicity. The adsorbed species can interact upon the oxide surface in different ways, such as through electrostatic or hydrophobic interactions and chemical complexation, depending on the choice of appropriate aqueous solution conditions. Therefore, a significant step toward understanding their chemical interaction can be made by investigating surface composition and associated changes (Laskowski et al., 2007; Liu et al., 2000; Filippov et al., 2013).

In this study, we focus on the interaction between iron oxide (hematite) and cornstarch, one of the mostly widely used organic depressants. Adsorption of starch on iron oxides has been widely investigated and debated in the literature as it represents a relatively inexpensive and environmentally-friendly separation agent, besides acting as a very effective depressant (Laskowski et al., 2007; Liu et al., 2000; Weissenborn et al., 1995; Kar et al., 2013; Tang and Liu, 2012; Pavlovic and Brandao, 2003; Martins et al., 2012). Moreover, the starch adsorption mechanism is of major importance not only for the separation of iron ores, but also because it is largely employed for a number of other minerals, including sulfide and phosphate ores (Laskowski et al., 2007; Liu et al., 2000; Filippov et al., 2013; Raju et al., 1997; Leal Filho et al., 2000).

In short, the separation process is based on the adsorption of starch molecules onto iron oxide, which renders the surface hydrophilic, preventing, at the same time, the adsorption of hydrophobic amine molecules present in the aqueous solution. In earlier studies, non-selective hydrogen bonding and electrostatic forces were proposed as the primary adsorption mechanism for carbohydrate molecules, mainly because of the large number of hydroxyl groups on both starch and oxide surfaces (Balajee and Iwasaki, 1969). Later investigations suggested, however, that polysaccharide molecules might preferably adsorb through acid-base interactions, as discussed by Laskowski et al. in a recent review article (Laskowski et al., 2007). Current research on starch adsorption addresses the important role of metal-hydroxylated oxide surface, supported by a number of studies using

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infrared spectroscopy and adsorption curves, in particular the one by Weissenborn et al. (1995), Pavlovic and Brandao (2003), Tang and Liu (2012), Subramanian and Natarajan (1988), Lima and Brandao (1999). These studies suggest that shifts in the infrared vibrational bands are related to the glucopyranose ring, and C—H deformation occurs due to the attachment of two carbon atoms to an oxygen-terminated hematite surface. This model is consistent with the one previously proposed by Liu et al. (2000), Ravishankar and Pradip (1995), in which a polysaccharide metal ring complex formed between the organic molecule and the oxide surface. Actually, this acid-base interaction is likely to occur; however, evidence of whether this chemical interaction is weak or strong and of its bonding nature is lacking in the literature.

To assess these mechanisms and to improve our understanding of chemical complexation, we investigated natural hematite (Fe_2O_3) surfaces after alkali treatment (pH 10.5) and starch adsorption, using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and X-ray photoelectron spectroscopy (XPS). Through surface-sensitive chemical characterization, we found compelling evidence of iron oxyhydroxide formation under alkaline conditions and spectral signatures of starch oxidation followed by strong surface complexation of iron polysaccharide.

2. Experimental design

2.1. Materials

Natural hematite (Fe_2O_3) powders (5–150 µm) were used. The samples were dry-ground and wet-sieved. Fraction sizes around 150 µm were used for XPS while those below 20 µm were used for DRIFTS and zeta potential measurements. The obtained fractions were washed with Milli-Q water.

The chemical composition of the samples, determined by X-ray fluorescence (XRF) and inductively coupled plasma optical emission spectrometry (ICP-OES), is summarized in Table 1. The results indicate that the major components are Fe with minor to trace amounts of Ti, Cr, Al, Si, Ca, and Mn. Scanning electron microscopy images and energy-dispersive spectroscopy analyses (data not shown) also indicate microparticles in the samples are mostly composed of iron oxide with only trace amounts of other elements. The high-grade cornstarch employed in this study was supplied by VETEC Ltda.

Three experimental tests were performed under the following conditions: (1) pure hematite, (2) hematite stirred in water at pH 10.5 and, (3) hematite stirred in gelatinized starch solution at pH 10.5. The conditions strongly dictates the adsorption of starch molecules onto the hematite surface and the chosen pH value is known to effectively boost flotation. Ultrapure deionized water was used for the preparation of all samples under the same ionic conditions (NaCl 10^{-3} M). Hydroxylated hematite was prepared by stirring the particulate samples in analytical grade NaOH solution at pH 10.5 for 60 min at room temperature. The gelatinized starch was prepared by adding NaOH and starch at a 5:1 ratio and the starch solution was designed to yield an optimal concentration of 550 mg/L, just as employed industrially (Ma et al., 2011). For the starch-adsorbed samples, hematite was conditioned with a gelatinized starch suspension for 60 min at pH 10.5. The suspensions were filtered and dried in a vacuum desiccator for approximately 12 h at room temperature and later loaded into an ultra-high vacuum chamber for XPS or FTIR analysis.

Table 1
X-ray fluorescence and inductively coupled plasma optical emission spectroscopy (XRF and ICP-OES) of natural hematite.

Element	Chemical analysis (%)	
	XRF	ICP
Fe	67.60	64.80
Ti	0.66	0.64
Si	0.15	0.10
Cr	0.21	0.15
Al	0.14	0.15
Mn	< 0.10	0.14
Mg	< 0.10	0.036
Ca	< 0.10	0.076
Na	–	0.062

2.2. X-ray photoelectron spectroscopy measurements

The experiments were performed using a SPECS UHV system (base pressure of 1×10^{-9} bar) equipped with a PHOIBOS 150 hemispherical electron analyzer using monochromatic Al-Kα radiation. The spectra were recorded with pass energy of 50 or 20 eV for surveys and high-resolution measurements, respectively. The spectrometer was previously calibrated using the Au $4f^{7/2}$ peak (84.0 eV), resulting in a full width half maximum (FWHM) of 0.7 eV for a sputtered metallic gold foil. The sample surface contained substantial amounts of adventitious carbon, but the samples were not sputtered, since preferential sputtering of oxygen over iron is known to reduce oxidation of original surface species (Biesinger et al., 2011). The binding energies were referenced by setting the adventitious carbon C 1s peak to 284.6 eV for hematite, Na 1s peak at 1071.5 eV for starch or the Fe 3p 56 eV for hematite after starch adsorption (Biesinger et al., 2011; Shchukarev and Korolkov, 2004). The high-resolution spectra of Fe 2p, O 1s, and C 1s regions were fitted using CasaXPS with a Shirley background and a Gaussian/Lorentzian line shape.

2.3. Infrared Fourier transform spectroscopy measurements

For IR spectral studies, DRIFTS and attenuated total reflectance (ATR) were employed using an IRPrestige-21 Shimadzu spectrophotometer at a resolution of 4 cm^{-1}. DRIFTS and ATR measurements were employed to investigate the vibrational bands present in starch powder and in gelatinized starch film after alkali treatment. Further analyses were performed using DRIFTS to investigate hematite powder samples diluted to 10% by mass in a KBr matrix. Spectral changes were better visualized in the difference spectra by subtracting the bare hematite spectrum from the conditioned hematite one, as indicated in the Results section.

2.4. Zeta potential measurements

Zeta potential measurements as a function of pH were obtained at constant ionic strength using the Malvern-Zetasizer system (Malvern Instruments, UK). The samples were thoroughly equilibrated for 60 min at each pH and the measurements were recorded in a dilute suspension of 1% solids by weight. NaCl (10^{-3} M) was used as an indifferent electrolyte and pH was adjusted using diluted HCl and NaOH solutions.

Since electrokinetic studies are performed in liquid, the direct measurement of hematite in suspension with adsorbed starch was performed after adsorption tests. This technique requires dilute solutions; therefore, starch concentrations used in these tests were 12 mg/L, 25 mg/L (previously determined in studies to determine the best conditions), and 550 mg/L for comparison.

3. Results

3.1. Zeta potential measurements

Fig. 1 depicts the zeta potential curves for gelatinized starch, pure hematite, and hematite after starch adsorption at different concentrations. The curve profile indicates that the gelatinized starch surface is negatively charged for the entire pH range, approaching a potential equal to zero between pH 3 and 1, but it was not possible to observe its isoelectric point (IEP). According to a previous study by Tang and Liu