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Research Article

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Spectroscopic characterization of phosphate adsorption on hematite Effects of pH and foreign ions

Lamia Boukemara^{1*}, Chahrazed Boukhalfa¹, Laurence Reinert² and Laurent Duclaux²

¹Chemistry Department, Laboratory of Pollution and Water Treatment, University Constantine, Algeria ²University of Savoie, Laboratory of Molecular chemistry and Environment, 73376 Le Bourget du lac, France

ABSTRACT

In the present work, the phosphate sorption on hematite in the absence and in the presence of foreign ions is studied as function of pH by DRIFT analyses. The obtained results show that in single system, the phosphate interaction with hematite surface depend on pH. At very acidic pH, the formation of inner sphere monodentate complex is observed. As pH increases, the interaction seems to be mainly electrostatic. In the presence of sulfate, chromate and oxalate, phosphate is adsorbed as outer sphere complexes. The interaction of phosphate with hematite in the presence of zinc, cadmium and copper is characterized by the formation of inner sphere complexes at pH 6 for the three metals and only for zinc and cadmium at pH 4.

Key words: Hematite; Phosphate; Sorption; Competitive ions; DRIFT

INTRODUCTION

Phosphorus is an essential element for all living organisms. It is a part of a large number of biological systems and is the main constituent of fertilizers used in agriculture [1]. However excess discharge of phosphorus in aquatic systems causes eutrophication [2, 3]. Sorption reactions onto common soil minerals, such as iron and aluminum oxyhydroxides regulate the bioavailability and the mobility of phosphorus and can retard significantly its dissemination in natural waters. Identifying phosphorus species at oxide/solution interfaces is thus crucial for predicting accurately its geo-cycling [4]. Hematite (α Fe₂O₃) is an abundant mineral in nature. It is the thermodynamically most stable iron oxide. Several FTIR studies are found about the adsorption of anions on hematite such as sulfate [5, 6, 7], chromate [8, 9], oxalate [10] and phosphate [11, 12]. However, few studies are found about the competitive effects of various ions. About phosphate adsorption on hematite, only the effects of cadmium (II) and iron (II) have been studied [13, 14].

The objective of the present study is the characterization of phosphate uptake by hematite in the presence of sulfate, chromate, oxalate, copper, zinc and cadmium.

EXPERIMENTAL SECTION

Hematite (α -Fe₂O₃) preparation and phosphate adsorption experiments have been described in a previous paper [15]. To achieve the spectroscopic analyses, the hematite samples recuperated by filtration after phosphate adsorption in the absence and in the presence of the competitive ions are dried. The DRIFT spectra are registered in the 4000 to 400 cm⁻¹ range by using a Thermo Scientific Nicolet iS10 DRIFT Spectrometer and KBr as reference. The obtained infrared spectra are described in Kubelka–Munk function: K/S= $(1-R_{\infty})^2/2 R_{\infty}$

Where K is the absorption coefficient (a function of the frequency ν); S is the scattering coefficient and R_{∞} is the reflectivity of a sample of infinite thickness (measured as a function of ν). If the scattering coefficient does not

depend on the infrared frequency, the Kubelka–Munk function transforms the measured spectrum $R\infty$ (v) into an absorption spectrum [16].

RESULTS AND DISCUSSION

In the IR studies, the symmetry has been generally used in the interpretation of bonding features of phosphates rather than direct peaks-position comparison [17, 18, 6] because these latter shift differently with environmental factors. If the symmetry reduction is caused only by protonation, as would be the case for outer-sphere adsorption, the vibration should appear at similar wavenumbers as the dominant phosphoric acid species [19]. The presence of absorption bands at around 900 cm⁻¹-1000 cm⁻¹ and 1200-1250 cm⁻¹ characterize P-OH and P=O stretching bands respectively. P-O stretching bands encountered in PO_4^{3-} are often identified in the range 990 cm⁻¹-1100cm⁻¹ [20].

The **Figure 1** shows the DRIFT spectra (1200 cm⁻¹-900 cm⁻¹) of hematite after phosphate adsorption in single system in the pH range 4-6. At pH 4.4, three bands are observed at about 1138 cm⁻¹, 1044 cm⁻¹, and 1000 cm⁻¹ corresponding to the formation of a monodentate complex with symmetry C_{3v} . As pH increases to pH 5.4 and pH 6.2, only two bands are observed at 1154 cm⁻¹, 1056 cm⁻¹ and at 1158 cm⁻¹ and 1044 cm⁻¹ respectively. These changes with pH suggest different phosphate species coordinated as a function of pH. In the spectra obtained for phosphate adsorption on hematite, Persson and coauthors [12] have observed two bands at around 1025 cm⁻¹ and 1120 cm⁻¹ at pH 5. They also identified a predominant surface phosphate species with a strong broad band centered around 1100 cm⁻¹ at pH 1.5–3.0.

The IR bands experimentally observed in this study are different from those found by Elzinga and Sparks [11] in a study on phosphate adsorption on hematite. They observed three bands at 1120 cm^{-1} , 1010 cm^{-1} , and 970 cm^{-1} at pH 3.5 and additional frequencies appear at 1000 cm^{-1} , as pH increased.

The increase in intensity of the IR absorbance with the decrease in pH is in a relation to the increase of phosphate sorption observed in macroscopic result where the phosphate sorption rate was maximal at pH < 5 [15].



Figure 1: Infrared spectra of hematite after phosphate adsorption - Effect of pH (Hematite dose: 2g/l; phosphate concentration: 1mM)

At pH 5, the DRIFT spectra of hematite after phosphate adsorption at initial concentrations greater than 1mM, show the three bands characteristics of C_{3v} complex (**Figure 2**). As the concentration increased from 1.25mM to 3mM, the intensities of the IR bands increase. This is in direct relation to the phosphate adsorbed quantities. A displacement of the third band to lower wavenumber is observed for the most elevated concentration. As phosphate concentration increases in the range (5–500 μ M) at pH 4, Elzinga and Sparks [11] showed also an increase in the intensity of in situ ATR-FTIR bands of hematite after phosphate adsorption. It should be mentioned that the two bands (1115 cm⁻¹ and 1010 cm⁻¹) found in this study are not similar to those detected in the present work.



Figure 2: Infrared spectra of hematite after phosphate adsorption-Effect of phosphate concentrations (Hematite dose: 2g/l; pH~ 5)

Effect of competitive anions

In the presence of sulfate ions, no new peaks are observed (Figure 3). At pH4, only two bands (1138 cm⁻¹, 1044 cm⁻¹) appear, showing the effect of sulfate and the formation of outer sphere complex. When the pH increases, the band at 1138 cm⁻¹ shifts to 1132 cm⁻¹. From macroscopic experiments [15], it was observed that the presence of sulfate ions has a significant effect on phosphate adsorption on hematite in the pH range (3-6). The interference between the peaks attributed to phosphate ions and those assigned to sulfate ions in the region (900 cm⁻¹-1250 cm⁻¹) make difficult the interpretation of the obtained spectra. Hug [5] shows that the DRIFT spectra of sulfate adsorbed onto hematite between pH 5 and 3 contain three bands between 950 cm⁻¹ to 1131 cm⁻¹.



Figure 3: Infrared spectra of hematite after phosphate adsorption in the presence of sulfate ions (Hematite dose: 2g/l; phosphate concentration: 1mM; anion concentration: 1Mm)

The hematite DRIFT spectra obtained in the presence of chromate ions at different pH are presented in **Figure 4**. Whatever the pH, phosphate forms outer sphere complex. The effect of chromate is more important at pH 4 and pH 5 where only a band is observed at 1167 cm⁻¹. However, at pH 6, two bands at 1155 cm⁻¹ and 1049cm⁻¹ are observed implying less effect at this pH. The macroscopic results showed that the presence of chromate ions has a strong effect on the removal of phosphate by hematite [15].



Figure 4: Infrared spectra of hematite after phosphate adsorption in the presence of chromate ions (Hematite dose: 2g/l; phosphate concentration: 1mM; anion concentration: 1Mm)

In the DRIFT spectra obtained in the presence of oxalate ions (**Figure 5**) tow bands appear at 1140 cm⁻¹ and 1003 cm⁻¹ at pH 4.7. As pH increases, the bands shift to lower wavelength and a shoulder at 1050 cm⁻¹ is observed implying the formation of inner sphere complex with C_{3v} symmetry. The peaks observed at 1309 cm⁻¹; 1420 cm⁻¹; 1710 cm⁻¹ (data not shown) are assigned to oxalate ions [21, 22, 23]. Quantitatively, the presence of oxalate ions has no effect on phosphate adsorption by hematite [15].



Figure 5: Infrared spectra of hematite after phosphate adsorption in the presence of oxalate ions (Hematite dose: 2g/l; phosphate concentration: 1mM; anion concentration: 1Mm)

Effect of competitive cations

The DRIFT spectra of hematite after phosphate adsorption in the presence of cations, obtained at pH 4 and 6 are illustrated in Figure 6 and Figure 7.

At pH 4, the three studied metals have different effects on phosphate retention by hematite. As it can be shown in Figure 6, three bands are observed at 1154 cm^{-1} , 1058 cm^{-1} and 1042 cm^{-1} in the presence of zinc, and at 1151 cm^{-1} 1042 cm⁻¹ and 1004 cm⁻¹ in the presence of cadmium, and only one band at 1158 cm⁻¹ in the presence of copper. Consequently, phosphate ions are adsorbed as inner sphere complexes in the presence of zinc and cadmium and as outer sphere complex in the presence of copper. At pH 6 (Figure 7), a monodentate inner sphere complex is formed at the hematite surface in the presence of the three metals.



Figure 6: IR spectra of hematite after fixation in the presence of phosphate ions and metal cations at pH ~ 4. (Hematite dose: 2g/l; phosphate concentration: 1mM; cation concentration: 1Mm)



Figure 7: IR spectra of hematite after fixation in the presence of phosphate ions and metal cations at pH ~ 6 (Hematite dose: 2g/l; phosphate concentration: 1mM; cation concentration: 1mM)

In a study on copper and cadmium adsorption on hematite, it has been found that they are mainly adsorbed as innersphere complexes and that the presence of phosphate reduces the inner-sphere sorption sites inducing a decrease in the metals adsorption on hematite at higher pH [24]

CONCLUSION

The interaction of phosphate on hematite in aqueous solution is related to pH and the presence of other ions. Phosphate ions are more available as pH increases at low concentration and in the presence of chromate and copper ions.

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