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Characterization of Phosphate Adsorption on Goethite Macroscopic and Spectroscopic Analyses

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Abstract

The present study describes phosphate adsorption on goethite. Macroscopic experiments were carried out in order to study the effects of contact time, pH, phosphate concentration and competitive ions. Infrared analyses were performed to characterize the phosphate interaction with the goethite surface in the absence and in the presence of competitive ions. The evolution of phosphate sorption with time is characterized by two steps. In first, the rate of phosphate removal is rapid then, a slower process is observed. The kinetics can be described by the pseudo second order model. The presence of oxalate ions implies a decrease in phosphate sorption in acidic pH. However, no competitive effect is observed in the presence of sulfate ions. Phosphate removal increases in the presence of lead and decreases in the presence of cadmium and copper. At pH > 4, spectroscopic analyses show the formation of monodentate inner sphere surface complex in the absence of competitive ions and in the presence of lead, chromate and sulfate. However, in the presence of oxalate, copper and cadmium, the phosphate surface complex converts to outer sphere complex.

Keywords: goethite, phosphate, sorption, kinetics, isotherm

1. Introduction

Phosphorus is of central concern to a wide variety of biological and chemical processes in natural waters. It is often the growth-limiting factor for biomass production. It is the least available of the major nutrients due to the large reactivity with numerous soil constituents such as mineral surfaces, clays, dissolved metal ions and organic material [1]. Phosphorus is not toxic, but it has been recognized as one of the main species responsible for eutrophication of fresh water bodies [2]. The evaluation of the bioavailability of several ions in aquatic and terrestrial environments required an understanding of their interactions with the common mineral phases found in soils and sediments. Iron oxyhydroxides are important in controlling phosphorus in the environment. In industrial and engineering processes, iron-based adsorbents are useful for the removal of phosphorus due to their economic and safety merits [1]. Goethite (α-FeOOH) is a frequent and abundant form of iron oxide in soils and sediments [3, 4]. It is the most common iron oxy-hydroxides in natural environment. It has been used in many adsorption studies. However, in our knowledge there is no work in the literature concerning macroscopic and spectroscopic studies of phosphate uptake by goethite in the presence of foreign ions with the same experimental conditions.

2. Experimental

2.1. *Reagents*

All chemicals used in this study were of analytical grade reagent and no purification was used. The iron oxyhydroxyde was prepared from $Fe(NO_3)_3.9H_20$ solution. Phosphate solutions were prepared by dissolving

KH_2PO_4. The pH was adjusted by adding NaOH solution prior to each experiment. pH measurements were calibrated to 0.01 pH units using radiometer analytical buffer solutions. Competitive ions were used as the corresponding sodium salts for anions and nitrates salts for cations.

2.2. *Goethite preparation and characterization*

Goethite was synthesized according to the method of Cornell and Schwertmann [5]. Briefly, a solution freshly prepared by dissolving $Fe(NO_3)_3.9H_20$ in distilled water was mixed with KOH solution and diluted with distilled water. The suspension was then held in a closed polyethylene bottle at 70 °C for 60 h. The precipitate recuperated after filtration was rinsed several times with distilled water and dried.

The particles morphology was examined with ZEISS-Ultra+ Scanning Electron Microscope (SEM). The BET surface area of the synthetic goethite was measured by N2 adsorption using ASAP 2020 Micromeritics adsorption instrument. The zero point of charge was evaluated by the titrate method. The granulometry was measured with a Mastersizer S granulometer (Malvern Instruments). Thermogravimetry analyse was performed under air with a heating rate 4°C/min using a thermobalance conceived in laboratory. The infrared spectra were recorded in the 4000 to 500 cm^{-1} range using IR Thermo Scientific NICOLET iS10 Smart diffuse reflectance. X-ray powder diffraction was recorded from 5 to 60° 2θ with a scanning speed of 0.05° 2θ step size by using a Thermo Electron ARL'XTRA diffractometer employing Cu-Kα radiation.

2. 3. *Adsorption Experiments*

All sorption experiments were conducted in batch. The effects of contact time, pH and phosphate concentration were evaluated. To examine the effect of foreign anions at different pH, experiments were performed in the presence of sulfate, chromate and oxalate ions as anions and copper, cadmium and lead as cations. The formed suspensions were agitated, the equilibrium pH was measured using a pH meter M210 equipped with a combined glass electrode then the suspensions were centrifuged at 2000 rpm for 15 min. Residual phosphate concentrations were measured by the molybdenum blue method using UV-1650PC Shimadzu spectrophotometer.

Preliminary experimental results have shown that the phosphate adsorption increased rapidly with increasing the amount of goethite (data not shown). For the initial phosphate concentration used, the increase of goethite dose from 2 $g.L^{-1}$ did not affect the phosphate uptake. Consequently, this dose was used in subsequent adsorption tests.

3. Results and discussion

3.1. *Characterization of the prepared Goethite*

The SEM photography (Figure 1) shows uniform elongated needles of micrometric size which corresponds to goethite morphology [6, 7].

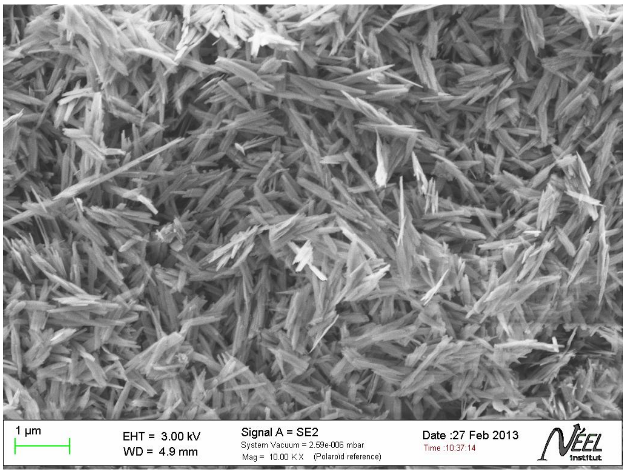

Figure 1: Scanning Electron Micrograph of the prepared goethite

The comparison of the obtained IR spectrum (Figure 2) with that given by Cornell and Schwertmann [5] reveals that is typical of goethite. The absorption band at around 897 cm^{-1} is attributed to δ-OH deformation in plane, those at 793 cm^{-1} and 646 cm^{-1} are due to δ-OH deformation out of plane. The broad band at 3127 cm^{-1} is assigned to stretching of goethite hydroxyls ($\nu_{(O\text{–}H)}$). The XRD spectrum (Figure 3) is also identified as that of goethite, characterized by the intense XRD peaks observed at 0.448, 0.254, 0.281 and 0.177nm.

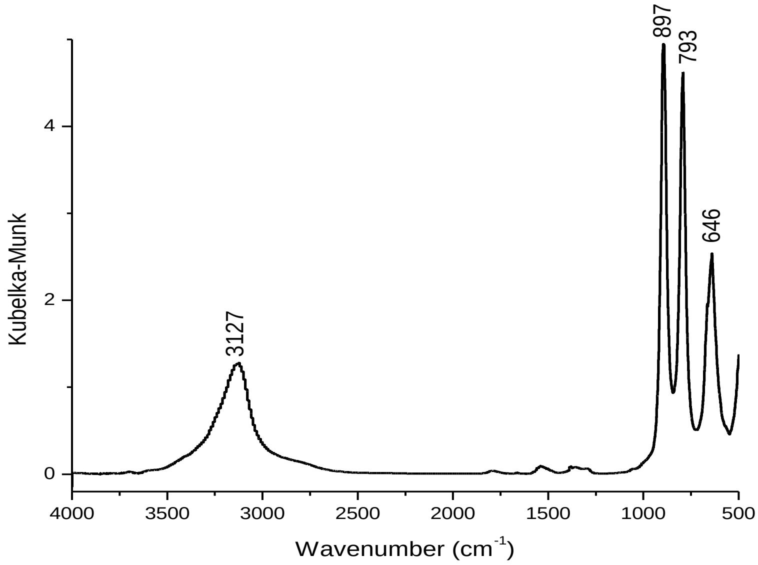

Figure 2: Diffuse reflectance FTIR spectrum of the prepared goethite

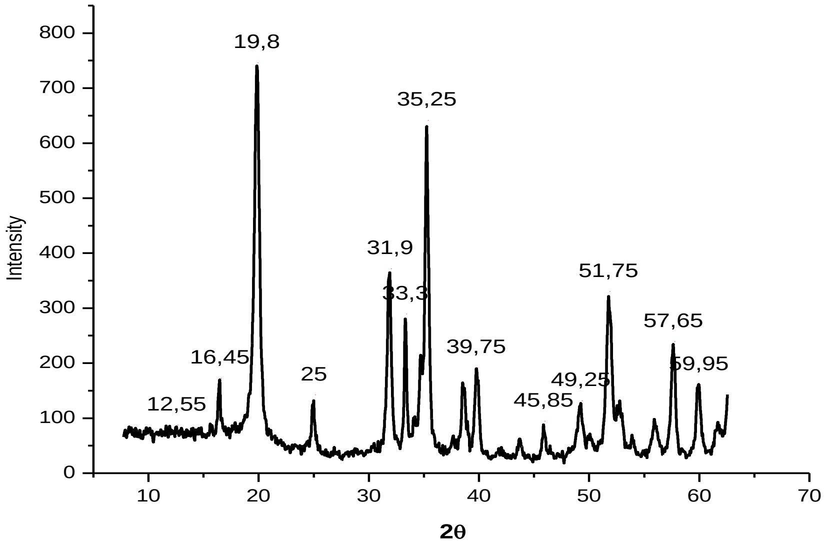

Figure 3: X-ray diffraction pattern of the prepared goethite

The specific surface area of the synthesized goethite is 29.6m^2/g. A value of 33.5 was reported by Gao and Mucci [8]. However, greater values were found in other studies [2, 3, 7, 9, 10]. It has been suggested that the difference between these values reflects different rates of base addition in the goethite preparation [6]. The adsorption-desorption isotherms (Figure 4) show the presence of hysteresis in the range of high pressure, indicating the presence of mesoporous. The zero point of charge (pH_{ZPC}) determined by titration method is about 8.2. It coincides with the one reported by Luengoa and coworkers [2]. Generally, the pH_{ZPC} values reported in the literature are included in the range 7.8 to 8.9 [9, 11, 12].

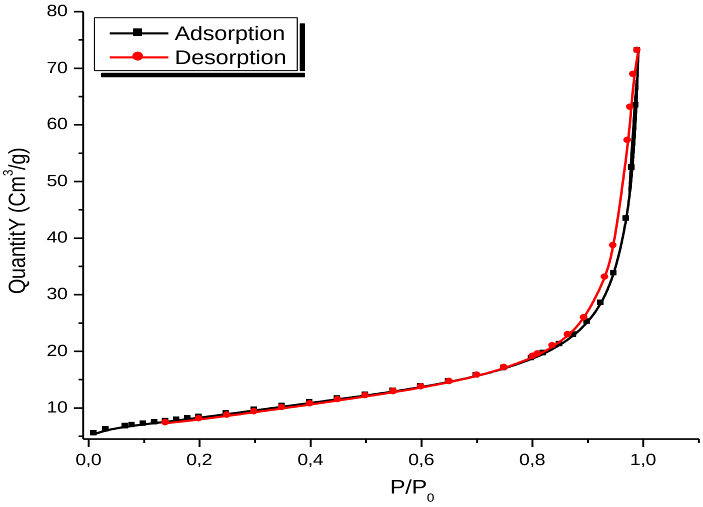

Figure 4: N_2 adsorption-desorption isotherms of the prepared goethite

The plot of the particles size distribution (Figure 5) shows three maxima centered at ~ 0.62, 2.48 and 39.94 µm respectively. The first two maxima are attributed to the finer particles and the third to the micron-sized particles.

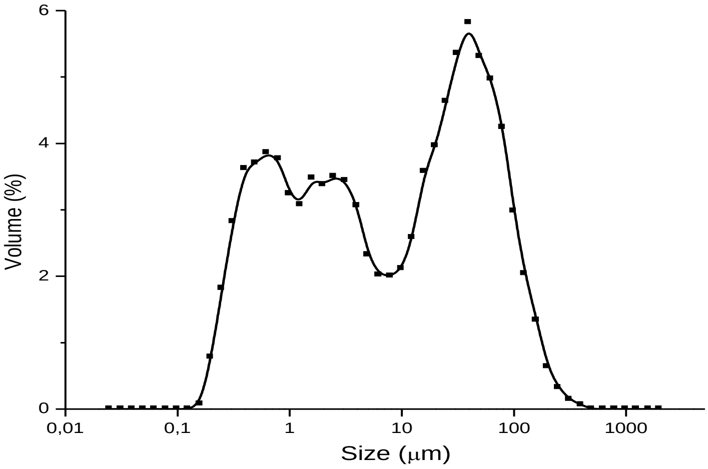

Figure 5: Particles size distributions of the prepared goethite

The total weight loss measured by TGA at 1200°C is about 28% (Figure 6). The weight loss occurred at below 400°C is attributed to sorbed surface water (11%) and dehydration (16%). It was reported that the dehydration temperature of pure goethite is 238 °C [13]. At higher heat temperature, a loss of only 1% is observed.

3.2. *Phosphate adsorption – macroscopic analyses*

3.2.1. *Adsorption kinetics*

The evolution of phosphate uptake is illustrated in Figure 7. Important and fast adsorption is observed in the first five minutes flowed by a slower adsorption at longer times. It has been suggested that the initial fast adsorption process corresponds to an adsorption reaction, whereby dissolved phosphate species bind rapidly and directly surface groups at the goethite surface [14]. Elsewhere, it has been reported that phosphate adsorption takes place only on the surface implying a fast rate of adsorption. However, in the slower stage, diffusion into pores and precipitation has been proposed [1]. The phosphate adsorption kinetics data are fitted with several kinetics models. The first order model and the parabolic diffusion model are ruled out; the obtained linear correlation coefficients are too small. The second order model provides satisfactory fitting of the experimental kinetics data. The predicted adsorbed mass at equilibrium agrees with the experimental data (Figure 7) suggesting a chemical adsorption.

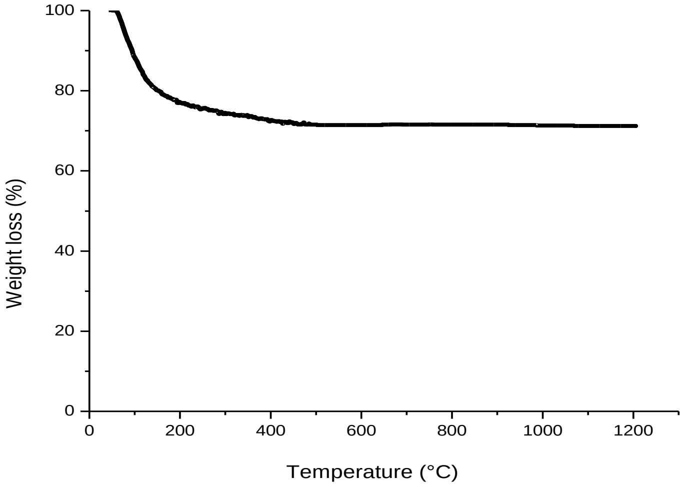

Figure 6: TGA curve of the prepared goethite

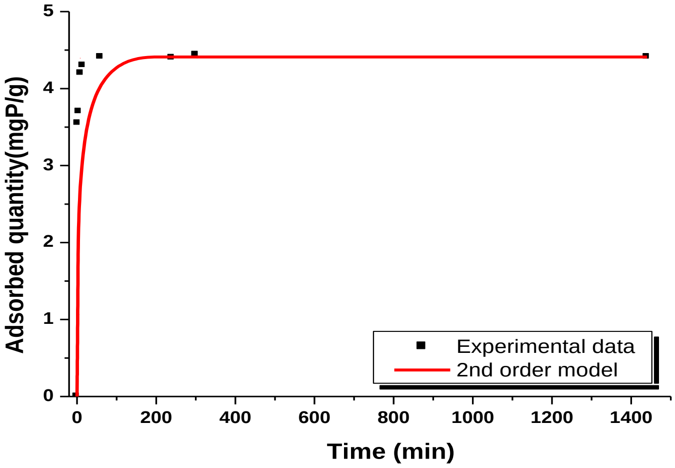

Figure 7: Adsorption kinetics of phosphate on Goethite - Experimental data and Kinetics models

3.2.2. *Effect of solution pH*

pH has a significant effect on the characteristics of surface adsorbent particles. The pH increases the degree of SOH groups protonation [15].In aqueous solution, protonation and deprotonation might take place at the hydroxyl sites on the surface of the metal hydroxides (M-OH). The primary charging behavior of goethite is due to protonation of singly (≡FeOH(H)) and triply coordinated (≡Fe_3O(H)) surface groups [16]. According to the pH_{PZC} value, the surface of goethite is positively charged at pH less than 8.2 favoring the adsorption of phosphate ions. A decrease in phosphate uptake is observed for pH values greater than 6 (Figure 8). This can be attributed to the repulsion of negatively charged phosphate induces by the increase in negative surface sites. The surface charge is also lowered by replacing the less acidic iron hydroxyl groups with the much more acidic phosphate hydroxyl groups [3]. The rapid decrease in phosphate removal at alkaline pH is attributed to the competition effect of hydroxyl ions. The pH evolution during phosphate adsorption is characterized by an increase in the acidic pH range implying ligand exchange reaction accompanied by the release of OH^-. However, a decrease is observed at pH values greater than 7 confirming competition with hydroxyl ions.

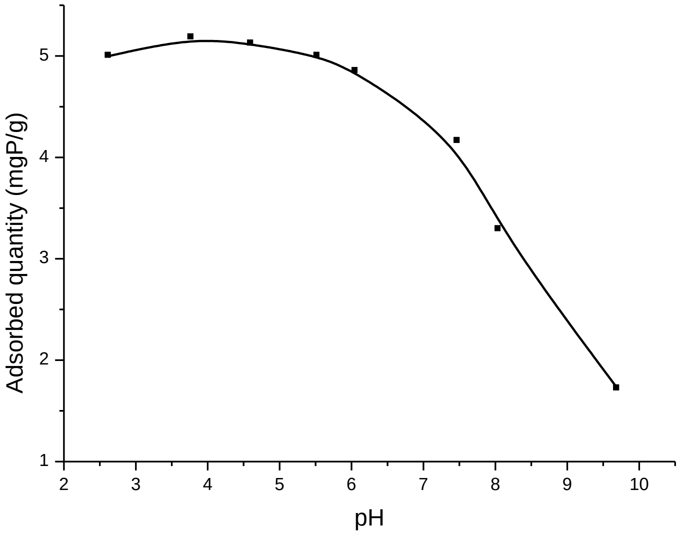

Figure 8: Effect of solution pH on phosphate adsorption on goethite

3.2.3. *Adsorption isotherm*

In the concentrations range studied, no saturation is observed (Figure 9). The experimental isotherm approaches linearity at high phosphate concentrations. It is better described by Freundlich equation than Langmuir and Temkin ones. The calculated value of the Freundlich exponent (1.94) can indicate a favorable adsorption of phosphate onto goethite. However the nonlinear curve shows anomalous for high phosphate concentrations. This can be attributed to precipitation. It has been suggested that the transition from adsorption to precipitation is smooth and no obvious break in the adsorption isotherm can be observed [3].

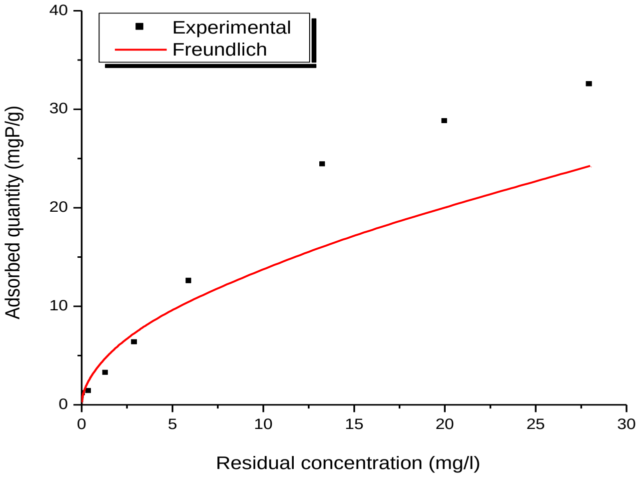

Figure 9: Isotherm of phosphate adsorption onto goethite - Experimental data and Freundlich model (pH 6.7)

3.2.4. *Effect of coexisting ions*

As it can be seen from the results illustrated in Figure 10, the phosphate uptake is reduced in the presence of oxalate ions implying a competitive effect. It has been noted that the adsorption of oxalate ions on iron oxides is rapid [17]. The organic anions such as oxalate were very effective in reducing phosphate adsorption on kaolinite, gibbsite and goethite [18]. In a more recent study, it has been shown that oxalate was coadsorbed with but unable to out compete phosphate from goethite [19]. In the pH range studied, phosphate removal is not influenced by the presence of sulphate (Figure 10). In a previous study undertaken on sulfate adsorption on hydrous iron oxide freshly prepared, we have observed significant effect of phosphate on sulfate adsorption [20]. In the presence of chromate ions, a slight decrease in phosphate uptake by goethite is observed. Similar results have been found for competitive effect of these anions on phosphate sorption on hydrous iron oxide freshly prepared [21].

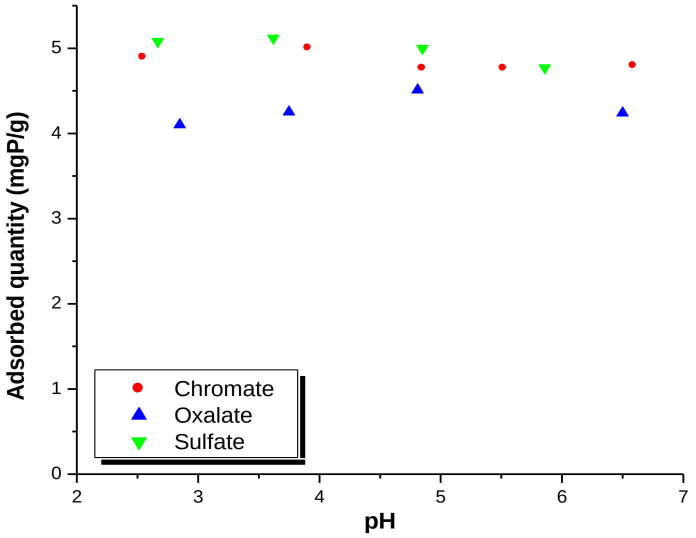

Figure 10: Effect of coexisting anions (1mM) on phosphate adsorption on Goethite

In the case of metallic ions (Figure 11), the effects are also related to the nature of the metal. In the case of copper and cadmium, phosphate uptake is decreased. The two metals can compete with phosphate for the surface complexation with goethite. The effect of cadmium appears to be more important. However, in the case of lead an enhancement in phosphate rate adsorption is observed. Both electrostatic effects and ternary complex formation may cause this enhancement. According to Scheals and coworkers [22], the metal ion and the ligand adsorb on different surface sites and there is no direct interaction between them. In contrast, when coadsorption results in the formation of a ternary surface complex, there is a direct interaction between the metal ion and the ligand. It has been also suggested that ligands having stronger ligand-metal solution complexes also form stronger surface ternary complexes [7].

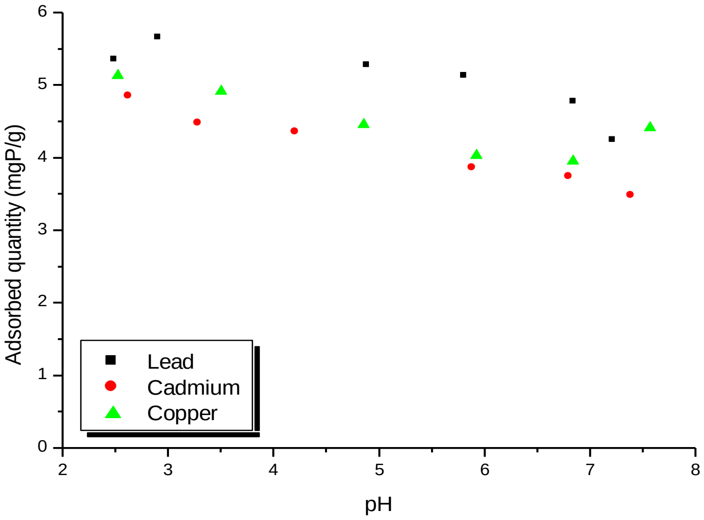

Figure 11: Effect of coexisting metallic ions (0.01mM) on phosphate adsorption on Goethite

3.3. *Phosphate adsorption – spectroscopic analyses*

In IR analyses, the Td symmetry of the PO_4^{3-} ion is characterized by the single strong ν_3 stretching fundamental at around 1006 cm^{-1}. Any degree of protonation results in a lowering of the symmetry. The interpretation of our spectra is based on the number of bands observed in wave number region (900 to 1250 cm^{-1}), which is associated with the vibrational modes of P-O bands [23].

The IR spectra showed in Figure 12, reveal that phosphate interaction with the goethite surface is pH dependent. They indicate that the symmetry of phosphate is lowered. At pH 3.6, the two bands at 994 and 1147cm^{-1} are the results of the formation of outer sphere complex with distortion of the tetragonal symmetry. As pH is increased, a third band as a shoulder appears at about 1046cm^{-1} implying the conversion of the formed complex into an inner sphere one.

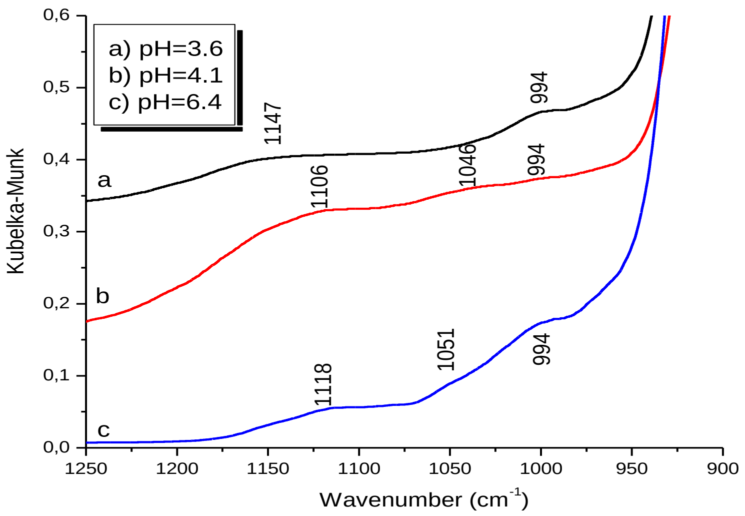

Figure 12: Diffuse reflectance FTIR spectra of phosphate adsorbed on goethite - Effect of pH

At pH around pH 4, only oxalate has an effect on phosphate interaction with goethite (Figure 13). In its presence, phosphate is adsorbed as outer sphere complex. In the presence of chromate and sulfate, the three bands characterizing the inner sphere complex are always present. In the presence of sulfate, the importance of the bands intensity is also attributed to sulfate interaction with goethite. The bands around 975, 1055 and 1135 have been observed in studies on sulfate adsorption on goethite [24, 25].

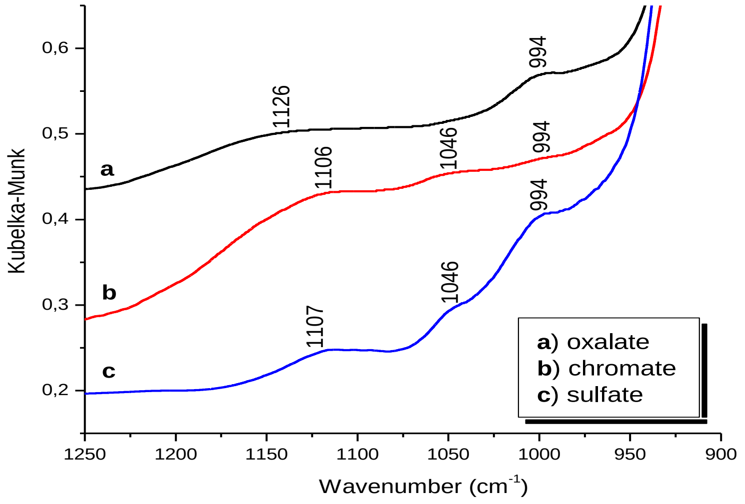

Figure 13: Diffuse reflectance FTIR spectra of phosphate adsorbed on goethite - Effect of anions (pH: 4.2)

In the presence of copper and cadmium, phosphate is adsorbed as outer sphere complex either at pH around 4 or 6 with lower bands intensity at pH about 6 (Figure 14). This is due to the decrease in phosphate uptake observed in macroscopic analyses. In the presence of lead, the observed bands at 983, 1049 and 1124cm^{-1} either at pH 4.4 or 6.3 show the formation of inner sphere complex. The significant bands intensity is in a relation to the phosphate adsorption enhancement observed in the macroscopic analyses.

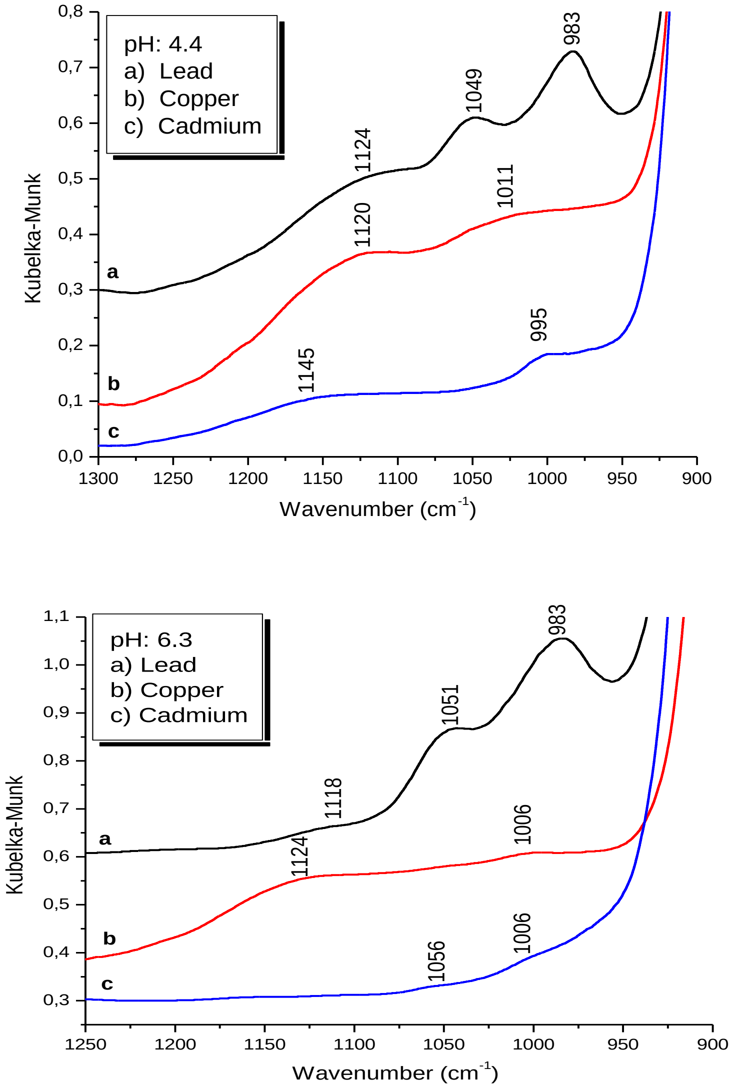

Figure 14: Diffuse reflectance FTIR spectra of phosphate adsorbed on goethite - Effect of metallic ions

Conclusion

Through a combination of macroscopic and spectroscopic results, the present study provides a number of useful results for understanding phosphate adsorption on goethite in different conditions:

1. The phosphate uptake by goethite can be described by both chemical and physical adsorption depending on the solution pH and the nature of the coexisting ions.
2. In the presence of oxalate, cadmium and copper, phosphate sorption by goethite is lowered; the formation of outer sphere complex indicates more mobility of phosphate ions. Chromate and sulfates ions have not a significant effect.
3. Lead presents a particular effect; the phosphate adsorption is enhanced in its presence with the formation of inner sphere complex implying strong interaction with goethite.

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