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Characterization of Phosphate Adsorption on Hematite in Aqueous Solutions.

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ABSTRACT

In the present study, experiments were carried out in order to study the effects of time, phosphate concentration, adsorbent dose, pH and the presence of foreign ions on phosphate adsorption on hematite. The results show that the phosphate uptake is maximum at pH<5. The kinetics is well described by the second order and Elovich models. The Freundlich equation describes the adsorption isotherm. Chromate and sulphate ions compete with phosphate and decrease its removal from the aqueous solutions.

Keywords: phosphate; adsorption; iron oxide; hematite; competitive ions

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INTRODUCTION

Phosphate is of major concern in environmental chemistry. It is often added to soil as a plant nutrient and it is used in many human products. It is not toxic, but it is one of the main species responsible for eutrophication of freshwater [1,2]. Consequently, the fate and the transport of phosphorus in aquatic environments must be well understood to design effective remediation strategies for reducing negative impacts [3]. Iron oxyhydroxides are important in controlling phosphorus in the environment. Adsorption of phosphate onto iron hydroxides has been extensively studied because of the importance of phosphate bioavailability in soil. Much research has been done on the uptake of phosphate by Fe(III)-hydroxide minerals such as goethite and ferrihydrite. The main objective of the present work is the study of phosphate interaction with hematite $\alpha\text{-Fe}_2\text{O}_3$ which is extremely stable and is often the end member of transformations of the other iron oxides.

MATERIAL AND METHODS

Reagents

All chemicals used in this study were of analytical grade reagent and no purification was used. All experimental vessels and storage containers were Pyrex glass. The hematite was prepared from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution. Phosphate solutions were prepared by dissolving KH_2PO_4 . The pH was adjusted by adding NaOH or HCl solution prior to each experiment. pH measurements were calibrated to 0.01 pH units using radiometer analytical buffer solutions. Competitive anions were used as the corresponding sodium salts.

Experimental procedures

Hematite Preparation and characterization

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) was synthesized by the method of Cornell and Schwertmann [4]. A solution of ferric nitrate was titrated to pH 8 with NaOH, and the resulting ferric oxide suspension was heated to 98 °C and aged at this temperature for 4 days, during this time the precipitate transformed into hematite. The precipitate recuperated after filtration was rinsed several times with distilled water and dried at ambient temperature.

The X-ray powder diffraction (XRD) pattern in the 2θ range of 10-70° was recorded using a Thermo Electron ARL'XTRA diffractometer with $\text{CuK}\alpha$ radiation. The IR spectrum was obtained in the 4000 to 400 cm^{-1} range using a Thermo Scientific Nicolet iS10 DRIFT Spectrometer. The granulometry analyses was taken using a Mastersizer S granulometer. The microstructure characterization was carried out using a ZEISS-Ultra+ Scanning Electron Microscope (SEM). The pH of the zero point of charge (pHpzc) was determined by the drift equilibrium method.

Phosphate adsorption experiments

The adsorption experiments were carried out in batch systems to determine adsorption envelopes. The effects of pH, contact time, hematite dose and phosphate concentration were evaluated. In each experiment, one parameter was changed. To examine the effect of foreign ions, additional experiments were performed in the presence of sulfate, oxalate and chromate ions at different pH. Except in the kinetics experiments, the

formed suspensions were agitated for 60min. After centrifugation, residual phosphate concentrations were measured by the molybdenum blue method using UV-1650PC Shimadzu spectrophotometer. The difference between the initial phosphate concentration and the remaining concentration was assumed to be sorbed.

RESULTS AND DISCUSSION

Characterization of hematite

The SEM image (Figure 1a) shows that the prepared hematite surface consisted of highly aggregated nanoparticles. The particle size distribution plot (Figure 1b) is characterized by a maxima centered at 32.9 μm corresponding to the micron-sized particles. The pH_{pzc} of the prepared hematite is estimated to 6,4; similar value of pH_{pzc} for hematite has been reported [5]. The infrared spectrum is shown in Figure 1c; the absorption band at 3124 cm^{-1} can be attributed to structural OH [6]. The bands at 554 and 474 cm^{-1} are attributed to Fe-O, the bands at 801 and 898 cm^{-1} are attributed to the bending vibration of hydroxyl groups of iron oxides (Fe-OH) [7]. The XRD pattern (Figure 1d) shows the main peaks of hematite.

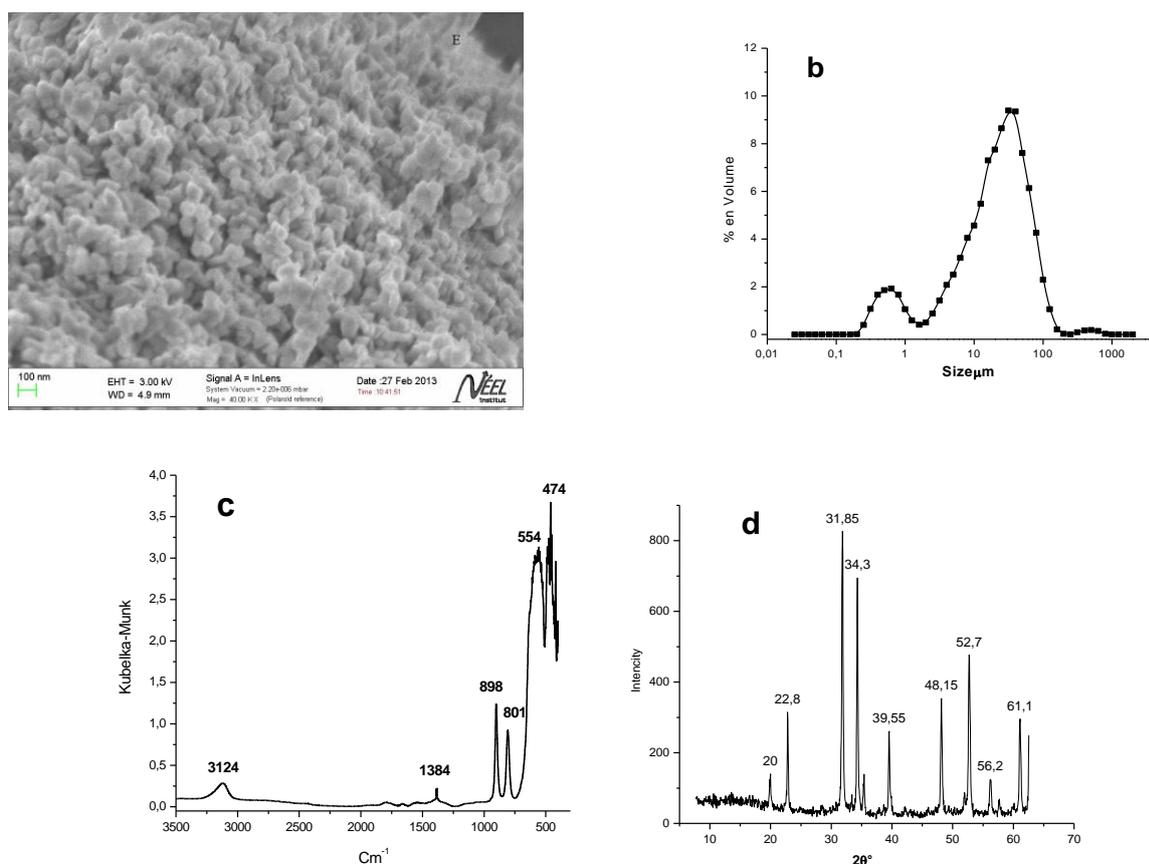


Figure 1: Characterization of the prepared Hematite

Phosphate Adsorption

Effect of adsorbent dose, contact time and phosphate concentration

The experimental results (Figure 2) show that the removal efficiency of phosphate ions increased rapidly with increasing the amount of the adsorbent from low doses to 2g/L; implying the increase of adsorption sites. Then, it increases gradually to attain complete for adsorbent dose of 5g L⁻¹ for 1mM phosphate concentration.

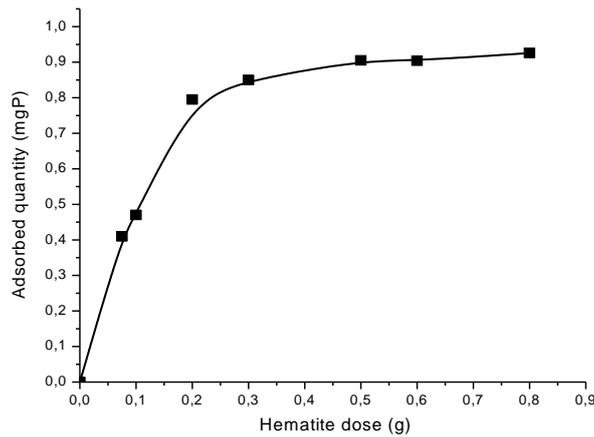


Figure 2: Effect of Hematite dose on phosphates adsorption (pH: 5)

The Figure 3 shows the phosphate adsorption kinetics as measured by batch experiments. The curves show important and fast adsorption in first then a slower adsorption at longer time. Adsorption seems to reach completion at around 240 min. Experimental data have been fitted by several models but the best models describing the kinetics are the second order and Elovich.

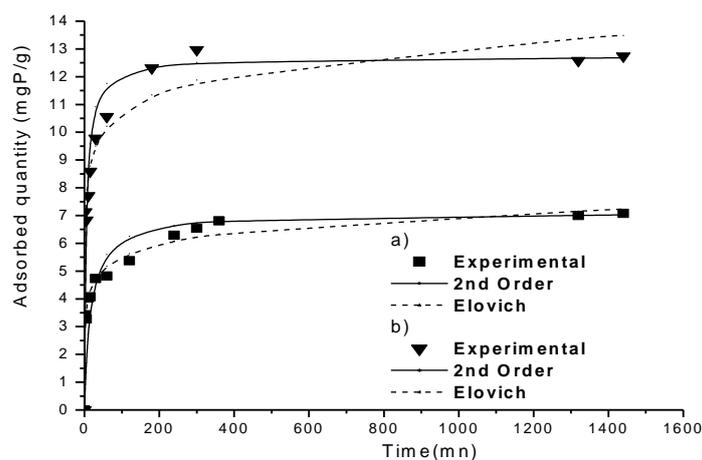


Figure 3: Adsorption kinetics (Hematite dose: 2g/l; phosphate concentration: a) 1mM, b) 2mM; pH: 5)

The adsorption isotherm was evaluated by varying initial phosphate concentrations ranging from 0.05mM to 3mM. The Figure 4, shows the evolution of the adsorption capacity (mg/g) as a function of the equilibrium phosphate concentration. Experimental data have been fitted by several isotherm equations but only the Freundlich model is suitable.

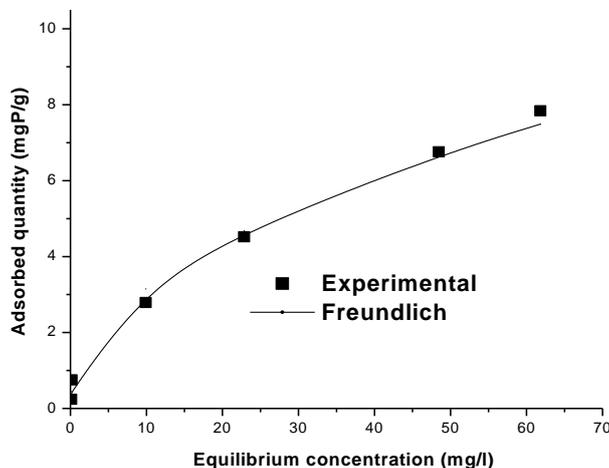


Figure 4: Phosphate adsorption isotherm (Hematite dose: 2g/l; pH: 5)

Effect of pH

The removal of phosphate ion decreases with increasing pH beyond 5 (Figure 5). The pzc of the prepared hematite is about 6, implying that the phosphate interaction with the hematite surface is mainly electrostatic. As the pH increases, the hydroxyl ions competition for the surface sites, contributes to inhibit the phosphate uptake.

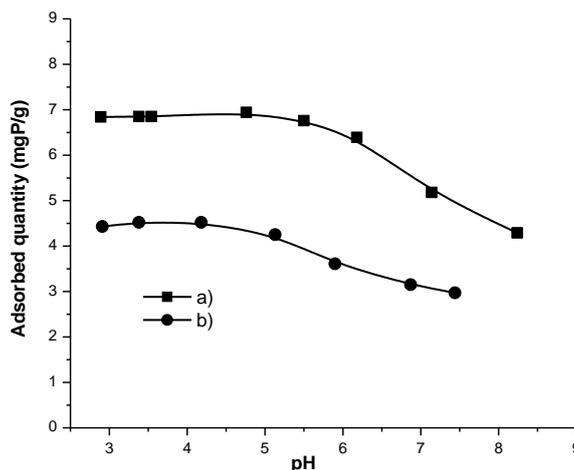
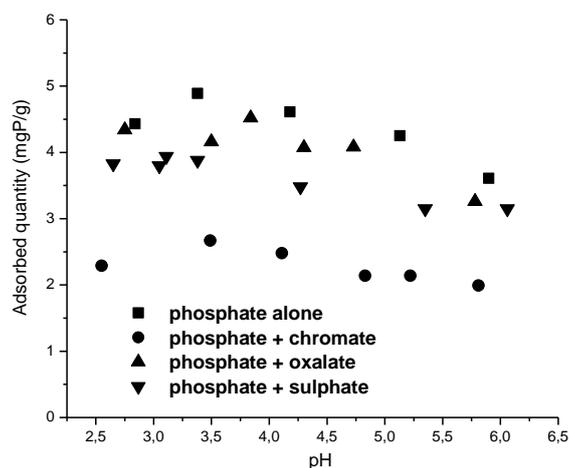


Figure 5: Effect of pH on phosphate adsorption on hematite (Hematite dose: 2g/l; phosphate concentration: a) 2mM, b) 1mM)

Effect of competitive ions

Generally contaminated waters contain several ions which can affect the adsorption of phosphate on iron oxide. In the present study, the effects of sulfate, oxalate and chromate ions on the adsorption of phosphate were evaluated. The obtained results (Figure 6) show that the presence of oxalate ions has no effect on the removal of phosphate by hematite. However in the presence of sulfate and chromate ions, phosphate adsorption is decreased.



**Figure 6: Effect of anions on phosphate adsorption
(Hematite dose: 2g/l; phosphate concentration: 1mM; anion concentration: 1Mm)**

CONCLUSION

Phosphate adsorption on hematite can be described by Freundlich isotherm and second order and Elovich kinetics models. The presence of chromate ions decreases severally the phosphate uptake by the iron oxide. The phosphate interaction with the hematite surface is mainly electrostatic.

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