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Characterization of Phosphate Interaction with α-Al_2O_3 in Aqueous Solution

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ABSTRACT

The objective of the present work is to study phosphate uptake by Alumina (α-Al_2O_3) in aqueous solutions through macroscopic and spectroscopic analysis. The effects of pH, competitive ions, contact time and phosphate concentration are evaluated. The obtained results show that the fixation of phosphate on the aluminum oxide is maximal at around pH 4.5. At pH<7, the effects of competitive anions follow the order: chromate<sulfate<citrate<oxalate. The presence of metallic ions enhances phosphate removal at pH>7. The adsorption kinetics is best described by the pseudo-second order and Elovich models. The experimental isotherm follows the Langmuir model. ATR-FTIR spectra indicate the formation of phosphate inner sphere surface complex.

Keywords: α-Al_2O_3, Phosphate, Adsorption, Competitive ions, ATR-FTIR

INTRODUCTION

Aquatic environments are generally polyphases. They can be correctly described by considering the intervention of various minerals which regulate the bioavailability and the mobility of several ions. Thus, the knowledge of the interaction nature with these surfaces in aqueous solution is of great importance. Among these minerals, aluminum oxides and oxyhydroxides are abundant and can exist under numerous forms, such as Corundum (α-Al_2O_3), Gibbsite (α-$Al(OH)_3$), Boehmite (γ-AlOOH) and Bayerite (β-$Al(OH)_3$) [1]. Phosphorus is commonly found in aquatic environment. It is considered as a nourishing element limiting the growth of plants. However, at excessive concentration in water, it is recognized as a main factor driving to eutrophication phenomenon [2,3]. Several studies can be found about phosphorus interaction with metal oxides [4,5]. However, they focus on the single ion and ignore any effect of other solutes. The main objective of this work is to study the interaction of phosphate ions in the absence and in the presence of other ions with α-Al_2O_3 which has a particular interest in interfacial chemistry because of its well-known structure.

MATERIALS AND METHODS

All chemical reagents used in this study were of analytical quality and all solutions were prepared with distilled water.

Characterization of the used alumina

The aluminum oxide used in the present study is a commercial product (*Sigma*). Its DRX spectrum confirmed that it is α-Al_2O_3 [6]. The purity of the oxide was evaluated by X-analysis using Bruker AXS Microanalysis GmbH. The specific surface area was measured by adsorption of N_2 using the instrument ASAP 2020 Micromeritics.

Phosphate adsorption-macroscopic analyses

Macroscopic analysis

Phosphate adsorption was carried out by batch experiments. The phosphate stock solutions were prepared by dissolving KH_2PO_4. The pH was adjusted by addition of NaOH or HCl solutions. The effects of pH, competitive ions, contact time and initial concentration were evaluated. In all experiments, phosphate analysis was carried out in solutions obtained after centrifugation by the molybdenum method using Schimadzu 1650 PC UV-Visible spectrophotometer. The adsorption efficiency was calculated from the difference between the initial and the final concentrations.

Spectroscopic analysis

ATR-FTIR spectra of aluminum oxide before and after phosphate adsorption were obtained using Thermo Scientific Nicolet iS10 FTIR spectrometer. After phosphate adsorption, the solid samples obtained by filtration were air dried.

RESULTS AND DISCUSSION

Alumina characterization

The EDX spectrum of the used α-Al_2O_3 (Figure 1) shows the absence of any impurity. The measured specific surface area is about 6.4 m^2/g. This value is slightly lower than those obtained by other authors [7-9].

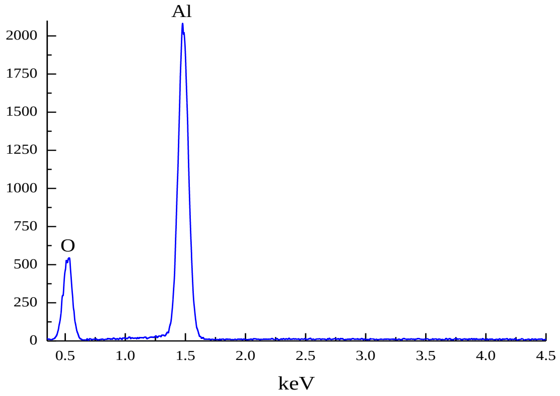

Figure 1: EDX spectrum of the used α-Al_2O_3

Phosphate adsorption-macroscopic analyses

Effect of pH

The phosphate adsorption capacity increases with the increase of the aqueous solution pH to reach a maximum at around pH 4.5; then decreases gradually (Figure 2). This evolution is in agreement with the results obtained for phosphate adsorption on other aluminum oxides [10,11] and those for fluoride [12] and chromate [6] adsorption on α-Al_2O_3. The low uptake of phosphate at very acidic pH may be related to the predominance of low charged phosphate species. According to the pHpzc of the used α-alumina [6], at pH<7.6, the oxide surface has a positive charge favorable for electrostatic attraction with phosphate ions. Consequently, the decrease in phosphate adsorption at pH>4.5 is not due to electrostatic repulsion but can be in a relation to phosphate speciation. At pH >7.6, in addition to electrostatic repulsion induced by the negative surface charge, the competition of hydroxyl ions is also responsible for the decrease of phosphate uptake as a decrease in solution pH was observed during adsorption.

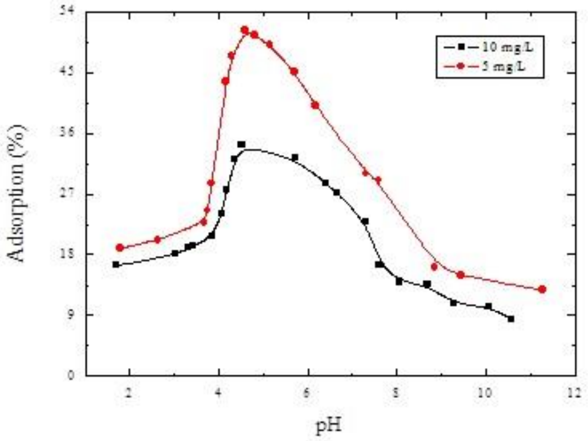

Figure 2: Effect of pH on phosphate adsorption on α-Al_2O_3
(Time: 1 h; α-Al_2O_3 dose: 3 g/l)

Effect of competitive ions

Phosphate adsorption on α-Al_2O_3 decreases in the presence of competitive anions (Figure 3). The significant effect is observed in the presence of citrate and oxalate ions at pH 4.5 which is close to pKa_2 of citric and oxalic acids favoring the adsorption of these ions. Whatever the pH, the effects of the studied competitive anions follow the order: chromate<sulfate<oxalate ≈ citrate. Concerning inorganic anions, their effects seem to have a relation to their affinity to alumina. The uptake rate of sulfate on γ-Al_2O_3 [13] is higher than that of chromate [14]. Generally, for the same charge, the competition for sites and the electrostatic effect will have a negative mutual influence on the interaction of ions with metal oxides [15,16].

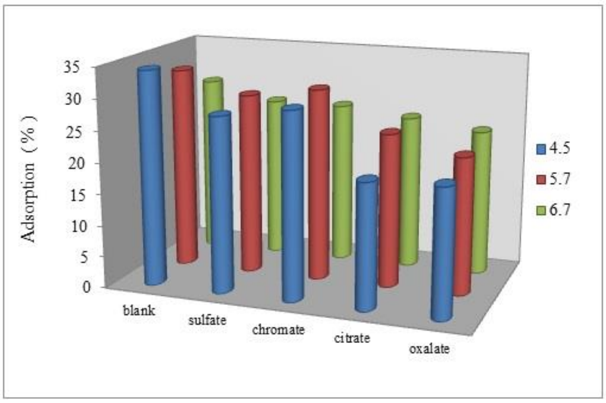

Figure 3: Effect of competitive anions on phosphate adsorption on α-Al_2O_3 (C_0: 10 mg/l; α-Al_2O_3 dose: 3 g/l; time: 1 h)

At pH>7, the presence of metallic ions improves the phosphate uptake by α-alumina (Figure 4). The presence of Zn, Cd and Pb implies the same effect. However, in the presence of Cu, phosphate uptake is more important at height pH. According to Ostergren and coauthors [17], electrostatic effect will have a positive mutual influence on the interaction of ions with opposite charge with metal oxides.

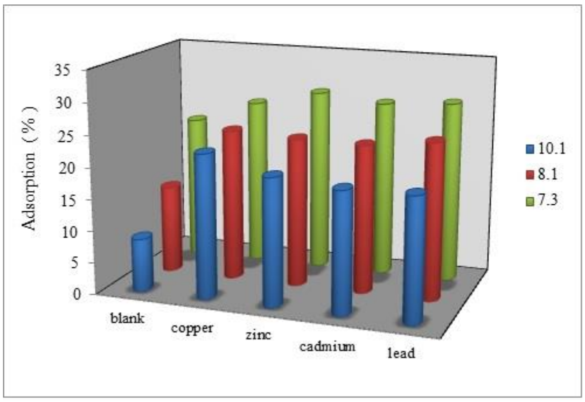

Figure 4: Effect of cations on phosphate adsorption on α-Al_2O_3 (C_0 phosphate: 10 mg/l; C_0 metals (Cr, Cu, Zn, Cd and Pb): 0.01 mM; α-Al_2O_3 dose: 3 g/l)

Kinetic study

The kinetic of phosphate sorption on α-Al_2O_3 (Figure 5) is characterized by a rapid first step followed by a slower continue phosphate uptake, due to diffusion processes [4]. This evolution has been also observed for phosphate adsorption on γ-Fe_2O_3 [18]. The equilibrium time is reached at about 54 h and the sorption capacity at equilibrium increases when the initial phosphate concentration increases; indicating that sorption is not limited by saturation of a limited amount of highly reactive sites on α-Al_2O_3. In regard to characterize the possible phosphate interaction mechanism with α-Al_2O_3, various kinetic models are applied. The calculated parameters are summarized in Table 1. Regarding correlation coefficients and adsorbed quantity at equilibrium, it can be deduced that the kinetics of phosphate adsorption on α-alumina is best described by the pseudo second order model. The rate constant calculated by this model decreases as the initial phosphate concentration increases. In the other hand, the calculated kinetic curves show that the adsorption of phosphate on α-alumina can be described by both the pseudo-second order model and the Elovich model. Consequently, the phosphate uptake is mainly due to chemisorption processes.

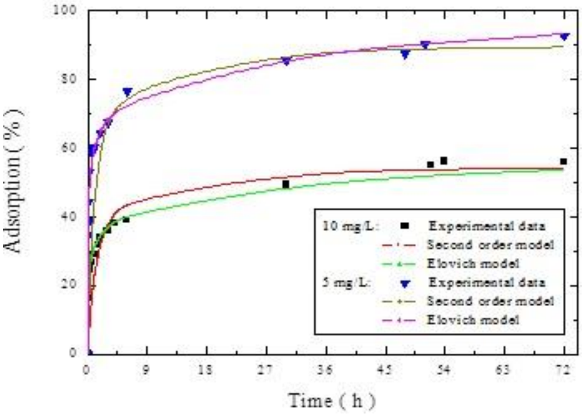

Figure 5: Kinetic of phosphate adsorption on α-Al_2O_3 (α-Al_2O_3 dose: 3 g/l; pH: 5)

Table 1: Parameters of the kinetic models

Model	Equation	Parameters	10 mg/l	5 mg/l
Pseudo first order	$\ln(Q_e - Q_t) = \ln Q_e - Kt$	Q_e (mg.g^{-1})	1.051	0.588
		K (h^{-1})	0.063	0.048
		R	0.992	0.949
Pseudo second order	$\frac{t}{Q_t} = \frac{1}{KQ_e^2} + \frac{1}{Q_e} t$	Q_e (mg.g^{-1})	1.841	1.512
		K (g.mg^{-1}.h^{-1})	0.389	0.656
		R	0.997	0.998
Elovich	$Q_t = \frac{1}{\beta} \ln(\alpha . \beta) + \frac{1}{\beta} \ln t$	α (mg.g^{-1}.h^{-1})	64.199	2.984×10^{-2}
		β (g.mg^{-1})	5.684	7.741
		R	0.990	0.997
Intra-particular diffusion	$Q_t = C + K\sqrt{t}$	C (mg.g^{-1})	0.768	0.813
		K (mg.g^{-1}.h$^{-1/2}$)	0.152	0.101
		R	0.960	0.901
Extern diffusion	$\ln\left(1 - \frac{C_t}{C_0}\right) = k\,t$	K (h^{-1})	0.015	0.012
		R	0.807	0.743

Effect of phosphate initial concentration

The increase of phosphate initial concentration implies an increase in adsorption capacity and a decrease in adsorption rate. In the concentrations range studied, no saturation is observed (Figure 6). The experimental isotherm follows the L type and can be described by the equilibrium models in the order: Langmuir>Freundlich>Temkin (Table 2). According to the calculated curves, the suitability of these models depends on phosphate concentration. At low concentrations, Langmuir equation is more appropriate. However, at high concentrations, Freundlich and Temkin equations are more suitable. Langmuir equation has also been successfully applied to the adsorption of other solutes on α-Al_2O_3 [9,18,19] and to phosphate adsorption on γ-Al_2O_3 [11].

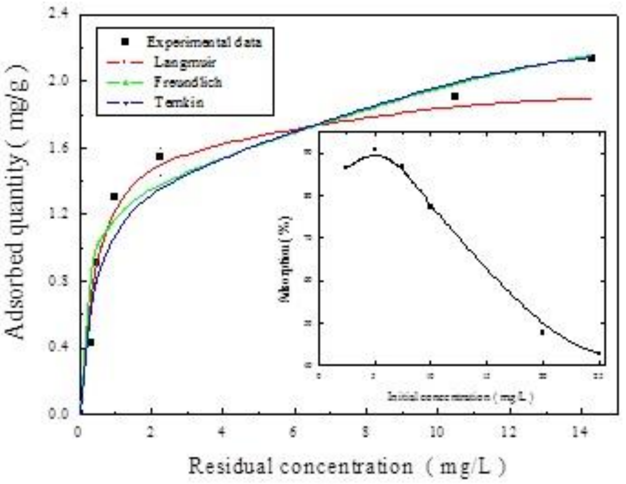

Figure 6: Isotherm of phosphate adsorption on α-Al_2O_3 (α-Al_2O_3 dose: 5 g/l; pH: 6; time: 72 h)

Table 2: Parameters of the isotherm models

Model	Equation	Parameters	
Langmuir	$\frac{1}{q} = \frac{1}{q_{max} K} \times \frac{1}{C_r} + \frac{1}{q_{max}}$	q_{max} (mg.g^{-1})	1.963
		K (L.mg^{-1})	1.904
		R	0.998
Freundlich	$\ln q = \frac{1}{n} \ln C_r + \ln K$	n	4.538
		K (mg.g^{-1})	1.197
		R	0.971
Temkin	$q = q_{max} \cdot \left(\frac{RT}{\Delta Q}\right) \ln K_T + q_{max} \cdot \left(\frac{RT}{\Delta Q}\right) \ln C_r$	ΔQ (J/mol)	5.761×10^3
		K (L.mg^{-1})	18.147
		R	0.964

Phosphate adsorption-spectroscopic analyses

ATR-FTIR spectra of alumina before and after phosphate adsorption at different pH are shown in Figure 7. In the presence of phosphate, two bands and a shoulder appear in the range 950-1200 cm^{-1} at pH: 4 and pH: 6, implying the formation of phosphate inner sphere surface complex with the symmetry C_{2v}. At pH: 8, the disappearance of the shoulder can imply the formation of a complex with a symmetry C_{3v}. The evolution of bands intensity is in agreement with that of the adsorption rate already observed in macroscopic analysis. The formation of a surface precipitate of aluminum phosphate is ruled out due to the absence of its characterized band at about 1130-1137 cm^{-1} [20].

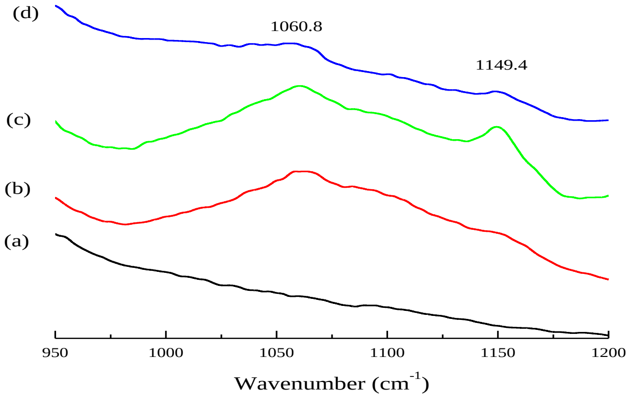

Figure 7: ATR-FTIR spectra of α-Al_2O_3 before and after phosphate adsorption
((a): Before adsorption, (b-d): After phosphate adsorption at pH: 4; pH: 6; and pH: 8 respectively)

CONCLUSION

The results of the present study show that in aqueous solution, phosphate uptake by α-Al_2O_3 is more significant at pH 4.5. It decreases significantly in the presence of organic anions at acidic pH and increases in the presence of metallic ions at pH>7. Kinetic, equilibrium and spectroscopic studies imply the chemical nature of phosphate interaction with α-Al_2O_3.

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