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Characterization of phosphate removal from aqueous solution by manganese oxyhydroxyde

Loubna Bouhouf[a], Chahrazed Boukhalfa[a,*], Laurence Reinert[b], Laurent Duclaux[b]

[a]*Laboratory of Pollution and Water Treatment, Chemistry Department, University Mentouri Constantine, Algeria, emails: chahrazed_boukhalfa@yahoo.com (C. Boukhalfa), loubna_bouhouf@yahoo.fr (L. Bouhouf)*
[b]*Laboratory of Molecular Chemistry and Environment, University Savoie Mont Blanc, F-73000 Chambéry, France, emails: laurence.reinert@univ-savoie.fr (L. Reinert), Laurent.duclaux@univ-savoie.fr (L. Duclaux)*

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ABSTRACT

In the present study, manganese oxyhydroxyde was prepared and used for phosphate adsorption from aqueous solution. Batch experiments were carried out at various experimental conditions. Retention mechanism was evaluated by ATR-FTIR analyses. The obtained results show that phosphate removal by the prepared manganese oxyhydroxyde is maximal at pH around 8.5. Adsorption kinetics is well described by Elovich model. Temkin model is more suitable for describing the experimental isotherm. Phosphate removal decreases in the presence of sulfate, chromate, cadmium and lead, and increases in the presence of citrate, copper and zinc. No effect is observed in the presence of tartrate and oxalate ions. Spectroscopic analyses reveal that phosphate is mainly adsorbed at the surface of the oxyhydroxyde as inner sphere complex.

Keywords: Phosphate; Manganese oxyhydroxyde; Adsorption; Water treatment

1. Introduction

Phosphorus is a major concern in environmental chemistry. It is essential for plants growth in soils and it has been recognized as one of the main nutrients controlling eutrophication of surface waters [1]. Several methods have been adopted for phosphate removal from wastewaters. In the last decades, among these methods, adsorption on low-cost adsorbents has been considered as an alternative method. Iron and aluminium oxides and oxyhydroxydes have been widely used as adsorbents for phosphate ions [2–4]. Their effectiveness has been observed at acidic pH. Thus, it has been found that phosphate adsorption is maximal at pH < 5 for goethite [5,6] and hematite [7], at pH 2 for akaganeite [8], at pH 3 for α-Al_2O_3 [9,10] and at pH 5.5 for γ-Al_2O_3 [11]. Kinetic studies have shown that equilibrium times of phosphate adsorption by these minerals vary from 3 to 30 h. At pH 4.5, the equilibrium time was 360 min for goethite [12], 13 h for ferrihydrite and 31 h for hematite [4]. Few studies have been undertaken on phosphate removal by manganese oxides and no study can be found in the literature on manganese oxyhydroxydes. Mustafa et al. [13,14] have observed that phosphate adsorption on β-MnO_2 decreases with the increase in pH and temperature.

The present work has been undertaken in the objective to evaluate effectiveness of manganese oxyhydroxyde in phosphate removal from aqueous solutions in the absence and in the presence of competitive ions.

2. Materials and methods

2.1. Reagents

All chemicals used were of analytical grade reagent and no purification was used. Manganese oxyhydroxyde was prepared from $MnSO_4$ H_2O solution. Phosphate solutions were prepared by dissolving KH_2PO_4. Competitive inorganic anions were used as the corresponding sodium or potassium

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* Corresponding author.

salts; organic ions were used as the corresponding acids. Metals were used as the corresponding nitrate salts. NaOH and HCl solutions were used for adjusting pH.

2.2. Preparation of the manganese oxyhydroxyde

Manganese oxyhydroxyde was synthesized by precipitation process at pH 8.5. NaOH solution was added to $MnSO_4$ solution dropwise with vigorous stirring at room temperature. The resulting precipitate was aged at 70°C for 60 h, washed thoroughly with distilled water and dried. The pH of zero point of charge (pH_{pzc}) was determined by titration method.

2.3. Adsorption experiments

2.3.1. Macroscopic experiments

All sorption experiments were conducted in batch. Suspensions formed by manganese oxyhydroxyde and phosphate solutions at the adjusted pH were agitated for a desired time, then final pH was measured and suspensions were centrifuged at 2,000 rpm for 15 min. Effects of oxyhydroxyde dose, contact time and phosphate concentration were evaluated. In each experiment, one parameter was changed. To examine the effect of foreign ions, experiments were performed in the presence of sulfate, chromate, oxalate, citrate, tartrate, copper, zinc, lead and cadmium. Residual phosphate concentrations were measured in the recovered supernatants 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.

2.3.2. Spectroscopic analyses

Infrared analysis by attenuated total reflection (ATR-FTIR) was used to characterize the prepared manganese oxyhydroxide before and after phosphate adsorption, using IR Thermo Scientific NICOLET iS10 Smart diffuse reflectance.

3. Results and discussion

3.1. Effect of the oxyhydroxyde dose

Phosphate removal efficiency increases rapidly with the increase of the oxyhydroxyde amount due to the increase of adsorption sites. According to the results shown in Fig. 1, phosphate adsorption approaches saturation for a dose 0.5 g/L.

3.2. Effect of pH

The percentage of phosphate adsorption increases when pH increases to attain a maximum at pH around 8.5, then decreases gradually at higher pH values (Fig. 2). Generally, pH is considered as an important parameter that controls adsorption on oxides and hydroxides. The measured pH_{pzc} of the prepared oxyhydroxyde is estimated to be ~6.4. This value which is within the range reported for MnOOH in the literature [15], implies that the oxyhydroxyde surface is negatively charged at pH higher than 6.4. Consequently, electrostatic interaction is not the predominant adsorption process. Chemical interaction is more probable, as the maximal adsorption occurs at pH > pH_{pzc}. The phosphate species distribution as a function of pH (Fig. 3) shows that the main species involved in the adsorption process is HPO_4^{2-}.

3.3. Adsorption kinetics

Phosphate removal by manganese oxyhydroxyde is fast (Fig. 4). Equilibrium is reached within 60 min. For longer period, adsorption tends to remain constant. To investigate the mechanism of adsorption, four kinetic models, namely pseudo-first-order, pseudo-second-order, Elovich and intra-particular diffusion are used. Their linear equations are, respectively:

$$\ln(q_e - q_t) = \ln q_e - Kt \tag{1}$$

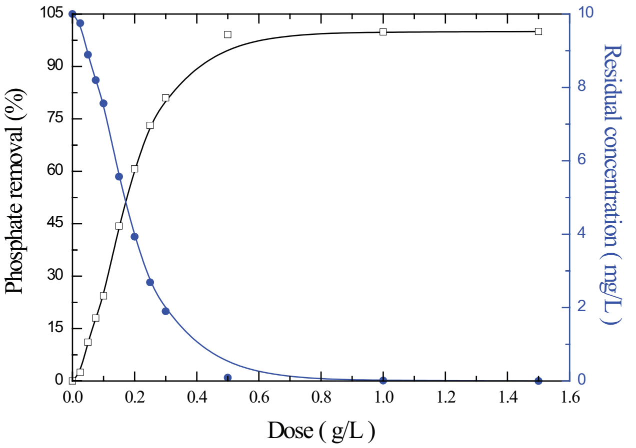

Fig. 1. Effect of manganese oxyhydroxyde dose on phosphate adsorption (C_0: 10 mg/L and t: 60 min).

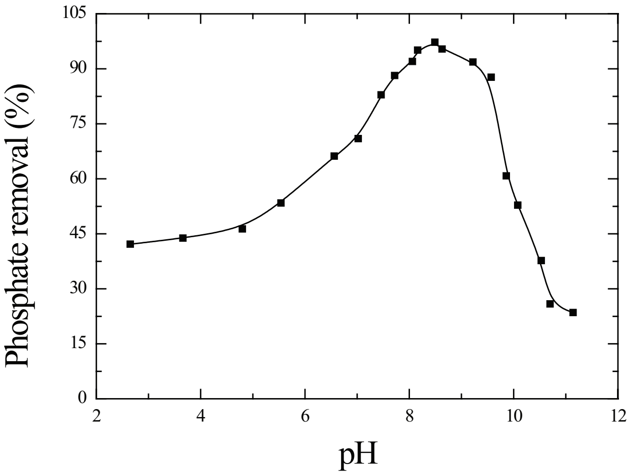

Fig. 2. Effect of pH on phosphate adsorption on manganese oxyhydroxide (C_0: 10 mg/L, t: 60 min and oxyhydroxyde dose: 0.5 g/L).

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{1}{q_e}t \tag{2}$$

$$q_t = \frac{1}{\beta}\ln(\alpha \cdot \beta) + \frac{1}{\beta}\ln t \tag{3}$$

$$q_t = K\sqrt{t} + C \tag{4}$$

The calculated parameters are summarized in Table 1. According to the correlation coefficient values, the kinetic data seem to be better fitted by the pseudo-second-order and Elovich models. The pseudo-first-order model and the diffusion model can be ruled out. The obtained correlation coefficients for the two models are low. In addition, a large difference is found between the experimental equilibrium adsorption capacity and that calculated by the first model. The calculated kinetic curves (figure included in Fig. 4), reveal that Elovich model is more suitable for describing the experimental data, confirming the chemical nature of the adsorption processes. The important initial adsorption rate calculated by this equation (α) implies a significant affinity of phosphate for manganese oxyhydroxyde.

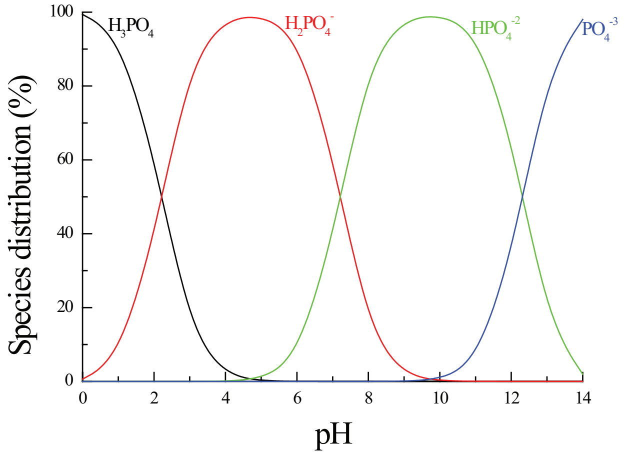

Fig. 3. Distribution of phosphate species.

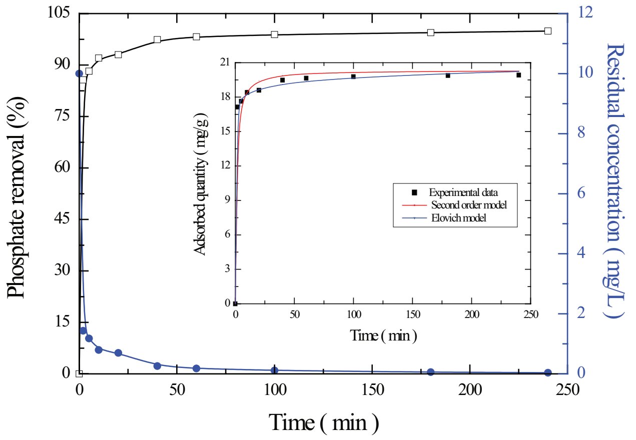

Fig. 4. Kinetics of phosphate adsorption on manganese oxyhydroxide (C_0: 10 mg/L, oxyhydroxyde dose: 0.5 g/L and pH: 8).

3.3.1. Phosphate adsorption isotherm

In the concentration range used, adsorption capacity increases with the increase of initial phosphate concentration (Fig. 5). The evolution of the removal rate shows gradual decrease of available adsorption sites which became fewer at higher concentrations. The experimental isotherm is characterized by no saturation (Fig. 6). Langmuir, Freundlich and Temkin models are applied. Their linear forms are represented by the following equations:

$$\frac{1}{q} = \frac{1}{q_{\max}K_L} \times \frac{1}{C_r} + \frac{1}{q_{\max}} \tag{5}$$

$$\ln q = \frac{1}{n}\ln C_r + \ln K_F \tag{6}$$

$$q = q_{\max} \cdot \left(\frac{RT}{\Delta Q}\right)\ln K_T + q_{\max} \cdot \left(\frac{RT}{\Delta Q}\right)\ln C_r \tag{7}$$

The calculated parameters are listed in Table 2. Highest correlation coefficients are obtained in the case of Langmuir

Table 1
Kinetic parameters

Model	Parameters	
Pseudo-first-order	q_e (mg/g)	2.94
	K (min^{-1})	0.027
	R	0.892
Pseudo-second-order	q_e (mg/g)	19.98
	K (g/mg min)	0.055
	R	0.999
Elovich	α (mg/g min)	3.62×10^{11}
	β (g/mg)	1.610
	R	0. 976
Intraparticular diffusion	K (mg/g.min$^{1/2}$)	0.183
	C	17.637
	R	0.873

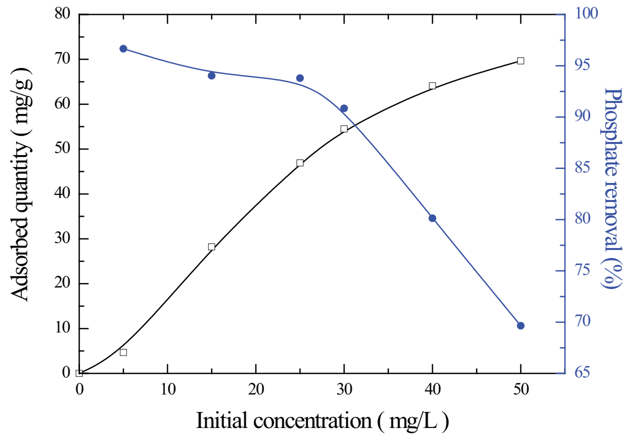

Fig. 5. Effect of initial concentration on phosphate adsorption on manganese oxyhydroxyde (t: 60 min, oxyhydroxyde dose: 0.5 g/L and pH: 7).

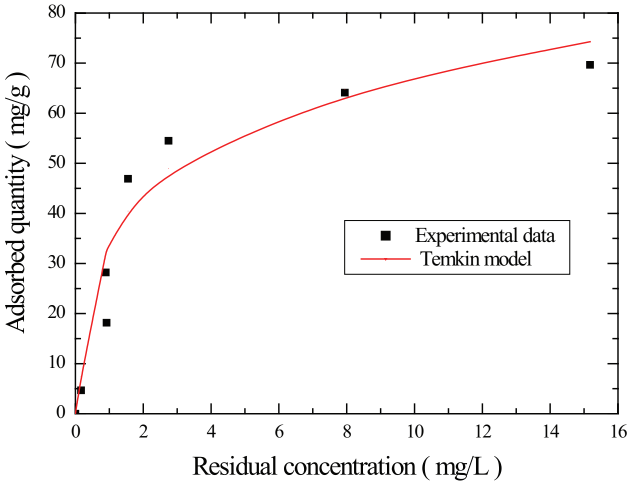

Fig. 6. Isotherm of phosphate adsorption on manganese oxyhydroxyde (*t*: 60 min, oxyhydroxyde dose: 0.5 g/L and pH 7).

Table 2
Isotherm parameters

Model	Parameters	
Langmuir	q_{max} (mg/g)	184.162
	K (L/mg)	0.157
	R	0.997
Freundlich	n	1.735
	K (mg/g)	22.298
	R	0.908
Temkin	ΔQ (J/mol)	2.136×10^4
	K_T (L/mg)	7.508
	R	0.980

and Temkin models. However, according to the calculated curves, the experimental data are best described by Temkin model (Fig. 6). At pH 7, the adsorption capacity calculated by Langmuir equation is about 184 mg/g. This value is higher than that obtained for several iron and aluminum oxyhydroxydes at the same pH [5,7,16].

3.3.2. Effect of foreign ions

Foreign ions have no effect on phosphate removal by manganese oxyhydroxyde at the optimal pH (Fig. 7). At pH 6.6, phosphate removal decreases in the presence of sulfate and chromate due to competition for adsorption sites. It remains unchanged in the presence of tartrate and oxalate and increases slightly in the presence of citrate ions. Generally, adsorption of organic ligands is mainly dominated by electrostatic effects [17]. They are more adsorbed at pH close to their pKa [18]. Consequently, their effects can be explained by the pKa values; the pKa^2 of tartaric and oxalic acids are lower than 6. Therefore, at pH 6.6, the two ions are less adsorbed at the oxyhydroxyde surface. However, the formation of phosphate–citrate surface complex is more probable; as the pKa of the couple ($C_6H_6O_7^{-2}/C_6H_5O_7^{-3}$) is about 6.4. At pH 9.5, phosphate uptake decreases in the presence of cadmium and lead (Fig. 8), implying competition for surface sites and/or formation of soluble phosphate complexes. In the presence of copper and zinc, the observed removal enhancement can be related to the formation of ternary surface complexes.

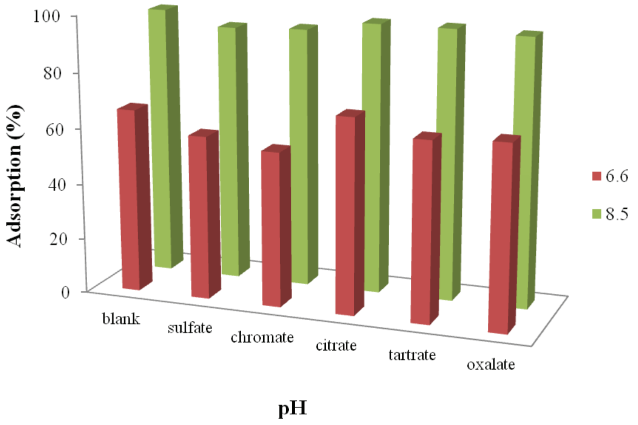

Fig. 7. Effect of foreign anions on phosphate adsorption on manganese oxyhydroxyde (C_0: 10 mg/L, anions 10 mg/L, *t*: 60 min and adsorbent dose: 0.5 g/L).

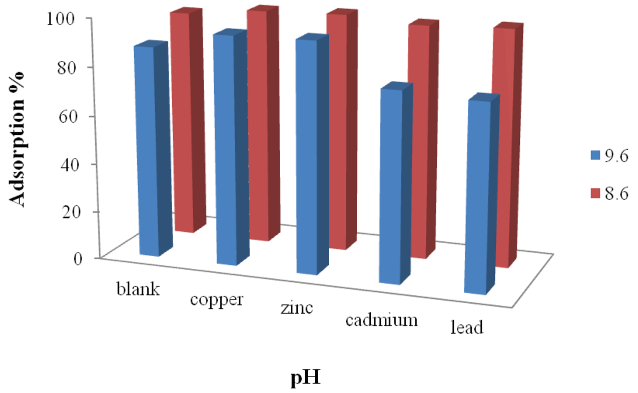

Fig. 8. Effect of foreign cations on phosphate adsorption on manganese oxyhydroxyde (C_0: 10 mg/L, cations: 0.01 mM, *t*: 60 min and adsorbent dose: 0.5 g/L).

3.3.3. Spectroscopic analyses

In the ATR-FTIR spectrum of the prepared manganese oxyhydroxyde (Fig. 9), the bands observed at 1,145.5, 1,112.7 and 1,085.5 cm^{-1}, are associated to functional group Mn–OH [19,20]. After phosphate adsorption, the new bands observed in wave number region (900 to 1,200 cm^{-1}) are associated with the vibrational modes of P–O [21]. Their number suggests the formation of inner sphere monodentate complex with the symmetry C_{3v}. The main interaction of phosphate with the surface of the oxyhydroxyde occurred at pH 8 which is close to the optimal pH for adsorption. At this pH, the band observed at about 1,112 cm^{-1} in the spectrum of the raw oxyhydroxyde disappears, implying that phosphate is fixed by ligand exchange processes where phosphate replaces surface OH. However, in the presence of foreign anions, this

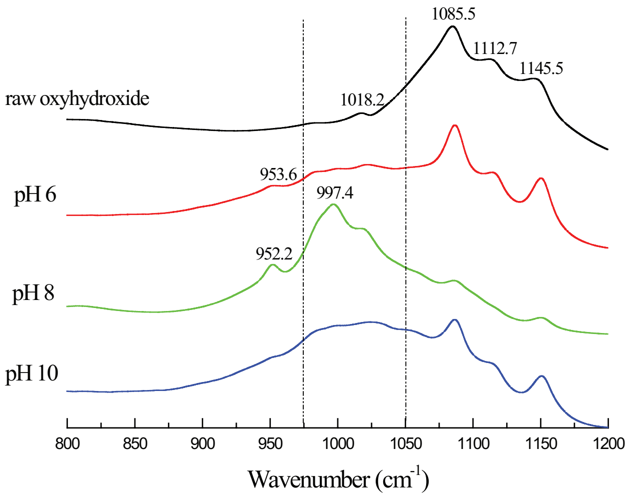

Fig. 9. ATR-FTIR spectra of manganese oxyhydroxyde before and after phosphate adsorption at various pH.

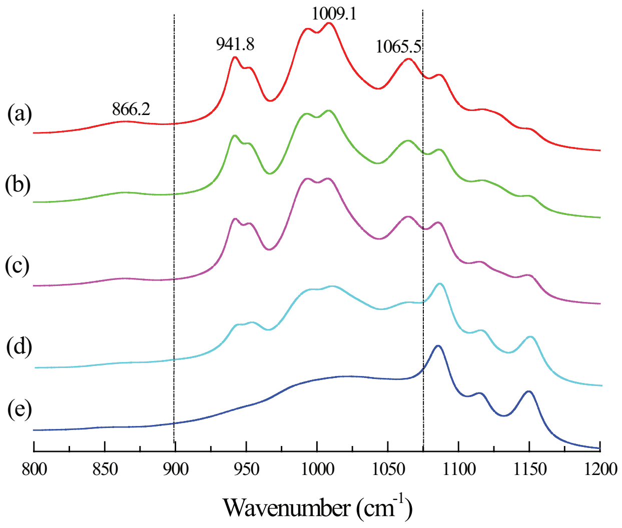

Fig. 10. ATR-FTIR spectra of manganese oxyhydroxyde after phosphate adsorption in the presence of foreign anions at pH: 8 ((a): sulfate, (b): chromate, (c): oxalate, (d): tartrate and (e): citrate).

band is still observed (Fig. 10). Consequently, phosphate is retained by another mechanism. In the presence of citrate, the large band observed at around 1,000 cm^{-1} reveals the formation of phosphate outer sphere complex. The presence of sulfate, chromate, oxalate and tartrate involves the apparition of new bands which can be attributed to the formation of phosphate inner sphere complex with symmetry lower than C_{2V}. The formation of surface foreign anions complexes is not ruled out, but the similarity of the obtained spectra suggests that the observed bands are mainly due to phosphate complexes.

4. Conclusion

Phosphate removal by adsorption on manganese oxyhydroxyde is maximal and selective at pH about 8. The adsorption processes is mainly chemical. With a greater efficiency than several metal oxyhydroxydes and a good selectivity, the prepared manganese oxyhydroxyde may be considered as a good adsorbent for phosphate removal from aqueous solutions.

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