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Characterization of phosphorus interaction with sediments affected by acid mine drainage - the relation with the sediment composition

Lamia Boukemara^a, Chahrazed Boukhalfa^{a*}, Sarah Azzouz^a, Laurence Reinert^b, Laurent Duclaux^b, Abdeltif Amrane^c, Anthony Szymczyk^c

^aLaboratory of Pollution and Water Treatment, Chemistry Department, University Constantine 1, Algeria

^bLaboratory of Molecular Chemistry and Environment, University Savoie Mont Blanc, 73376 Le Bourget du lac, France

^cEcole Nationale Supérieure de Chimie de Rennes, Université Rennes1, CNRS, UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France.

***chahrazed_boukhalfa@yahoo.com**

ABSTRACT

Phosphorus sorption capacity was investigated in surface sediments derived from an abandoned zinc-lead mine area located in northeastern Algeria. The forms and the distribution of phosphorus in the raw sediment were identified using the sequential chemical extractions method. Batch experiments were done to study the adsorption kinetics and isotherms. The pH effect was evaluated by macroscopic and infrared analyses. In raw sediment, speciation results show that phosphorus is dominantly bound to oxyhydroxides. Sorption experiments demonstrate that phosphorus uptake is principally related to sediment composition. The nature of the dominant iron oxyhydroxide has a substantial role in the adsorption capacity and the mechanism interaction. The adsorption kinetics can be described by the second order and Elovich models. The isotherms data are successfully modeled by the Temkin equation. The maximum phosphorus removal is reached under acidic pH. Spectroscopic analyses reveal that the predominance of jarosite implies electrostatic

interaction with sediment particles. However, in the case of schwertmannite predominance, phosphate ions are adsorbed by the ligand exchange mechanism.

Key words: *Phosphorus, Adsorption, Mine sediments, Sorption kinetics, Sorption isotherm.*

1. Introduction

In contaminated environments, iron oxides often are poorly crystalline as a result of their formation at low temperatures. Several iron oxyhydroxides and oxyhydroxy-sulfates can be found in mine areas: ferrihydrite, goethite, lepidocrocite, schwertmannite, and jarosite (Kraal et al., 2009). These compounds result from oxidation of sulfide minerals which develop a phenomenon known as acid mine drainage.

Several studies have been interested in the use of sludge products of acid mine drainage for phosphorus removal from water (Evenson & Nairn, 2000; Penn et al., 2007; Wei et al., 2008). Sibrell et al. (2009), described a method for drying and pelletization of acid mine drainage sludge produced by neutralization with alkaline materials for phosphorus removal from wastewater. Adler and Sibrell (2003) used the solids produced from the neutralization of acid mine water as an addition to the soil and manure to reduce the loss of soluble phosphorus.

The present work contributes to understanding of the phosphorus uptake by sediments in a mining environment. Despite several previous studies undertaken on phosphorus adsorption on sediments (Fang et al., 2013; Huang et al., 2015, 2016; Zhou et al., 2005), no information about phosphorus sorption on sediments in mining zones characterized by high acidity is available in the literature. In addition, much research has been done on phosphate adsorption on iron oxyhydroxydes (Arai & Sparks, 2001; Boukemara et al., 2016; Elzinga & Sparks, 2007) but no study can be found in the literature about iron oxyhydroxy-sulfates which predominate in mining areas.

The propose of this paper is to characterize the phosphorus speciation and adsorption in the sediments of the Sidi Kamber Mine Area. A chemical extraction technique was used to evaluate phosphorus distribution in the sediment fractions. Kinetics and isotherm models are used to fit the experimental adsorption data.

2. Material and methods

2.1 Study site

The Sidi Kamber Mine is an abandoned zinc-lead mine located in northeastern Algeria between Constantine and Skikda (Fig. 1). Generally, the climate of the area is semiarid-Mediterranean type characterized by wet winters and dry summers. The main stream in the area is the River Essouk which is one of the tributaries of the Fessa River on which the Guenitra Reservoir is built. The acid mine drainage produced from the Sidi kamber mine enters into Essouk River. The general characteristics of the Sidi Kamber Mine waters were described in a previous study (Boukhalfa, 2007).

2.2 Sample collection and preparation

Two sediments samples were collected from the surface layer. Sample 1 came from a small channel heavily coated with a yellowish mud. Sample 2 was taken in the neighborhood of a source of groundwater. After storage and transport under cold conditions (4°C), the sampled sediments were dried at 80°C, crushed and passed through a stainless steel sieve (< 0.2 mm) then conserved until use.

2.3 Sediment characterization and phosphorus fractionation

The pH of the sediments was measured in suspensions formed with distilled water. X-ray powder diffraction patterns were recorded from 5 to 60° 2 θ with a scanning speed of 0.05° 2 θ

step size using a Thermo Electron ARL XTRA diffractometer using Cu-K α radiation. Infrared (IR) analyses were done in the range 4000 to 500 cm⁻¹ with an average of 64 scans by IR Thermo Scientific, NICOLET iS10 Smart diffuse reflectance. The surface area was measured by BET-N₂ (nitrogen gas) adsorption-desorption isotherms after degasification under a vacuum (10⁻³ mm Hg) at 77°C for 16 hours using an ASAP 2020 Micromeritics adsorption instrument. The point of zero charge was evaluated by measuring the variation of zeta potential using an Anton Paar zeta-meter. To determine the total phosphorus, sediments were calcined at 550°C and mineralized with hydrochloric acid (HCl) 3.5M. Phosphorus speciation was undertaken using the sequential chemical extractions procedure developed by Hieltjes and Lijklema (1980). In this method, the sedimentary phosphorus is divided into four fractions: exchangeable, associated to oxyhydroxides, bound to calcium, and residual. The three first fractions were extracted by ammonium chloride (NH₄Cl), sodium hydroxide (NaOH) and HCl; residual phosphorus is deduced from the total phosphorus. Each extraction experiment was undertaken in triplicate.

2.4 Phosphorus adsorption experiments

The sorption experiments were done in batch. The effect of sediment dose was studied by adding different sediment amounts (0.01 - 0.8 g) to 100 mL of phosphate solution (0.5 mmol/L). To examine adsorption kinetics, 1g of each sediment was added to 500 mL of phosphate solutions (1mmol/L and 0.5 mmol/L). For adsorption isotherm study, 0.2 g of each sample was added to 100 ml of phosphate solution at various concentrations. To evaluate the pH effect, NaOH or HCl was added to suspensions of 0.2 g of sediment in 100 mL phosphate solutions (1 mmol/L and 0.5 mmol/L).

In all experiments, phosphate analyses were done in solutions obtained after centrifugation using the molybdenum method with a UV-Visible SCHIMADZU 1650 PC spectrophotometer. In this method, orthophosphate ions react with molybdate to form a yellow phosphomolibdic complex which is specifically reduced by ascorbic acid to bleu form.

3 Results and discussion

3.1 Characterization of raw sediment

Sediment suspensions in distilled water are acidic, the measured pH for sample 1 and 2 are 3.14 and 2.47, respectively. These values show the significant development of the acid mine drainage process. The IR and X-ray diffraction (XRD) spectra (Figs. 2 and 3), show that the principal constituents of the studied sediments are jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) and quartz in Sample 1, and goethite (αFeOOH), schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)$), and kaolinite in Sample 2. The following reactions explain, respectively, the presence of jarosite and schwertmannite in such sediments:



Schwertmannite is known as a metastable compound, it transforms to stable crystalline goethite via dissolution and reprecipitation according to the reaction:



Jarosite can be transformed to goethite according to the reaction:



The measured pH at point of zero charge (pH_{PZC}) values are less than 5 (Fig. 4). Sample 1 is characterized by the lower pH_{PZC} ; which is in a relation to the predominance of jarosite and quartz, both characterized by low pH_{PZC} values (Kosmulski, 2006). The observed increase in zeta potential values Sample 2 in the pH range 7-8 can be explained by the probable adsorption of ions. The measured Brunauer-Emmett-Teller (BET) surface area of Sample 1 is very low, that of Sample 2 is about $16.4 \text{ m}^2/\text{g}$. The BET adsorption-desorption curves of Sample 2 show the presence of mesopores (Fig. 5).

3.2 Phosphorus speciation

In raw sediment, phosphorus (P) is mainly bound to oxyhydroxides (Fig. 6). According to Cong et al. (2014), iron (Fe)-bound P is easily desorbed from sediments and released to the overlying water. The fraction bound to calcium (Ca) is low. The importance of this is in relation to the presence of iron pyrite in the Sidi Kamber Mine. In the presence of oxygen, the acid produced from the oxidation reaction of pyrite induces the dissolution of P-bearing Ca-minerals (Chi et al., 2006). Consequently, phosphorus bound to authigenic and detritique apathite is low. Residual fractions account for about 65 % and 60.5 % for the two sediment samples, respectively, implying that the presence of phosphorus is mainly related to the area geochemistry.

3.3 Phosphorus adsorption

3.3.1 Effect of sediment dose

The composition of the sediment appears to have an important role in phosphorus adsorption processes. Sample 1 (S1) has the lowest adsorption capacity, this is in a relation to the presence of crystalline silicates, which present less surface area than other compounds. In addition, the presence of silicates decreases the adsorption capacity of the oxides. In a study

on the removal of phosphorus from wastewater, quartz particles coated with iron and aluminum oxides were evaluated as a filter media to remove phosphorus (Arias et al., 2006). The significant presence of goethite explains the higher adsorption capacity of Sample 2 (S2). The evolution of phosphorus removal as a function of sediment dose is shown in Fig. 7. For the two samples, the residual phosphorus concentration decreases as the sediment dose increases from low doses to 2 g/L. The increase in sediment dose induces an increase in the total available surface area. In the case of Sample 2, the efficiency of phosphorus uptake increases from 22.6% to about 90% for sediment doses of 0.1 g L^{-1} and 2 g L^{-1} , respectively, as the volume of the solution is 0.1 L. Then the adsorption efficiency remained quasi constant and further dose increases do not significantly affect the uptake of phosphorus from the aqueous solution.

3.3.2 Adsorption kinetics

The results shown in Fig. 8 show that the phosphorus adsorption rate is rapid at the beginning of adsorption. Thereafter, a gradual increase occurs. Equilibrium is reached within 4 hours in the case of S1 and 30 minutes in the case of S2. This behavior can be explained by the fact that phosphate ions are first adsorbed at the exterior surfaces then they penetrate into sediment particles. It can be noted that the sediment sample which is characterized by a high sorption capacity has the higher sorption rate. To understand the mechanisms involved, three kinetics models are used: pseudo-first order, pseudo-second order, and Elovich. The first model, which considers reversible adsorption, is ruled out because the theoretical equilibrium quantities do not give acceptable values when compared to the experimental values. The two other models, which assume that the controlling step is a chemical reaction, well describe the kinetics data. The second order model is the best for the two samples. The adsorbed quantities at equilibrium are in agreement with the experimental data.

3.3.3 Adsorption isotherms

The relation between equilibrium phosphorus concentration and adsorption capacity of sediment is shown in Fig. 9. The phosphorus uptake increases with the increase of phosphorus concentration. The increase in the initial concentration implies a higher concentration gradient between the aqueous solution and the solid phase, resulting in more important diffusion rates. According to the Giles classification, the experimental isotherms can be assigned to an L-type isotherm, which suggests progressive saturation (Giles et al., 1974). Experimental data are fitted using Langmuir, Freundlich, and Temkin isotherms. The three models are suitable for describing the phosphorus adsorption onto S1; the corresponding correlation coefficients are, respectively, 0.996, 0.981, and 0.975. In the case of S2, the Langmuir model which assumes a monolayer adsorption with constant adsorption energy at all adsorption sites cannot describe the experimental data; the linear equation gives a low correlation coefficient (0.778). The application of the Temkin and the Freundlich models is better, the obtained correlation coefficients are, respectively, 0.975 and 0.907. In the Temkin model, the adsorption affinity decreases linearly with the increase of adsorption at the adsorbent surface. The Freundlich model describes a nonuniform distribution of adsorption over the surface without saturation at the adsorption sites. The coefficient (n) is proportional to the adsorption energy; and it has a relation with the affinity of the adsorbate to the adsorbent. In the present study, calculated Freundlich coefficients are greater than 1, confirming the chemical nature of the adsorption. The three models used in this study have also been successfully applied to phosphate adsorption on sediments from other rivers (Azzouz & Boukhalfa, 2013).

3.3.4 Effect of solution pH

The effect of pH on phosphorus adsorption by the sampled sediment was examined in the pH range 2 - 9 (Fig. 10). It appears that the adsorbed amount increases slightly at acidic pH

values. A near stable value is observed in the pH range 3-5 for S1 and 3-7 for S2, where dihydrogen phosphate (H_2PO_4^-) is the prevalent species. This behavior has been observed in other studies of phosphate adsorption on sediments (Huang et al., 2016; Wang et al., 2005). In aqueous solutions, protonation and deprotonation might take place at hydroxyl sites on the hydroxide surfaces, resulting in a change of surface charge. At acidic pH values, the adsorption increase can be the result of attraction between the anionic phosphate ions and the particle surfaces positively charged ($> \text{SOH}_2^+$). According to the measured pH_{PZC} value of Sample 2, the adsorption evolution implies chemical interaction. In the case of Sample 1, it can be observed that the phosphorus uptake decreases at pH greater than pH_{PZC} implying electrostatic interaction. The observed decrease in phosphate uptake at $\text{pH} > 7$, results on one hand from electrostatic repulsion between the negatively charged phosphate ions and the negatively charged sites ($> \text{SO}^-$) and on the other hand from the competition of hydroxyls ions for adsorption sites. It can be noted that the precipitation with calcium should not be responsible for phosphate removal because the chemical precipitation of calcium phosphate is favored at alkaline pH values. Consequently, the main mechanism of phosphorus uptake by these sediments is the adsorption on iron oxyhydroxides. This finding is in agreement with the results obtained from phosphorus speciation.

Generally, the sorption mechanism cannot be conclusively determined only from macroscopic experiments. A spectroscopic method is used to verify the conclusions drawn from batch experiments. The IR spectra recorded before and after phosphate adsorption at various pH values are illustrated in Figs. 11 and 12. In the case of Sample 1, a slight shoulder is observed at about 1020 cm^{-1} and no band appears at wavenumber lower than 1000 cm^{-1} . Consequently, the formation of phosphate precipitate is more probable. In the case of Sample 2, the decrease in the intensity of the band observed in the raw sediment spectrum at around 1188 cm^{-1} and

assigned to sulfate in schwertmannite (Bigham et al., 1990) implies a ligand exchange mechanism. The increase of pH has no effect on the phosphate adsorption mechanism.

4. Conclusions

The results of the present work demonstrate that the Sidi Kamber Mine sediments can be considered as naturally adsorbent for phosphorus removal from aqueous solutions at acidic pH levels. The phosphorus uptake is mainly related to the sediment composition. The significant presence of silicate decreases the adsorption rate. The predominance of schwertmannite implies the removal of phosphorus from water by the chemisorption process.

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Figure 1. Location of the Sidi Kamber Mine (S1 and S2 refer to Samples 1 and 2, respectively)

Figure 2. Diffuse reflectance Fourier Transform Infrared (FTIR) spectra of raw sediment
(Gt: goethite, Jt: jarosite, Kt: kaolinite, Qz: quartz)

Figure 3. X-ray diffraction spectra of raw sediment (Jt: jarosite, Qz: quartz, Sh: shwertmannite)

Figure 4. Evolution of Zeta potential

Figure 5. N₂ adsorption-desorption isotherms (Sample 2)

Figure 6. Distribution of phosphorus in raw sediment

Figure 7. Effect of sediment dose on phosphorus adsorption on sediment (C₀: 0.5 mmol/L, t: 60 min)

Figure 8. Phosphorus adsorption kinetics - Experimental data and kinetics models
(sediment dose: 2 g/L)

Figure 9. Phosphorus adsorption isotherms (sediment dose: 2g/L, t: 60 min)

Figure 10. Effect of solution pH on phosphorus adsorption on sediment (sediment dose: 2g/L, t: 60 min)

Figure 11. Diffuse reflectance FTIR spectra of Sample 1 in the absence (a) and in the presence of phosphate (b - pH: 3.2; c - pH: 5.2; d - pH: 6.7; e - pH: 7.3)

Figure 12. Diffuse reflectance FTIR spectra of Sample 2 in the absence (a) and in the presence of phosphate (b - pH: 4.1; c - pH: 5.7; d - pH: 6.3; e - pH: 7.1)











