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Phosphate Adsorption on Sediments from Rhumel and Boumerzoug Rivers in the Northeast of Algeria

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ABSTRACT

The present work aims to study the adsorption of phosphate ions on the sediments of Rhumel and Boumerzoug rivers located in the Northeast of Algeria. Sediments samples were collected in April 2012. They were characterized by physicochemical analysis, X-ray fluorescence and infrared analyses. The phosphorus uptake was evaluated under different conditions. The adsorption kinetics and isotherms were modeled using various equations. The obtained results show that the studied sediments are characterized by high organic matter contents. The main inorganic components of the sediments are calcium, iron, silicon and aluminum. The evolution of phosphate uptake with time indicates two steps; a first rapid and a second slow. The adsorption kinetics are best described by the second-order and Elovich models for the two sediments. The adsorption isotherms are best described by Temkin model. In the case of Boumerzoug River, the adsorption can be also described by Langmuir and Freundlich models.

Keywords: phosphorus; sediment; adsorption; Rhumel River; Boumerzoug River

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INTRODUCTION

Phosphorus is the primary cause of water eutrophication. It leads to an increase in algal biomass, which causes deoxygenation by chemical decomposition involving deterioration in water quality of rivers and lakes [1]. As a consequence of organic matter degradation and chemical adsorption, phosphorus in aquatic systems is largely incorporated in the sediments [2]; which play an important role in its dynamics [3]. They are considered as a sink. However, changes in physicochemical conditions can cause a release of a portion of the sedimentary phosphorus in the water column [4]. Generally, a sediment in contact with water exchanges phosphorus with it until a dynamic equilibrium is reached; adsorption-desorption and precipitation-dissolution processes may be involved. Understanding the process of phosphorus fixation onto aquatic sediments is important for controlling water quality. Several studies are cited in literature [5, 6, 7]. However, the diversity in sediments structures requires more work in a relation with the nature and the characteristics of the sediments.

MATERIAL AND METHODS

Samples collection and pretreatment

Rhumel River is located in the north east of Algeria. Its main tributary is Boumerzoug River. The two rivers traverse industrial and urban zones in Constantine city.
The studied sediments were collected in April 2012. In Rhumel River, sediments were sampled downstream Constantine city. In Boumerzoug river, they were sampled upstream the confluence with Rhumel River and downstream El-khroub city. The samples were placed in plastic bags and transported to the laboratory where they were first air dried then at 40°C, ground and sieved using a 0.215 mm sieve and stored in polyethylene bottles until use.

Physicochemical characterization

Measurements of pH and electrical conductivity were performed in suspensions formed with distilled water. Organic matter content was determined by loss on ignition at 550 ° C. The total phosphorus was extracted with HCl (3.5M) after calcination at 550 ° C; phosphorus was measured in extracts by UV-visible spectrophotometry using the method of Murphy and Riley [8]. In this method, orthophosphate ions react with molybdate to form a yellow phosphomolybdic complex which is specifically reduced by ascorbic acid to give a blue form. The absorbance was measured with a spectrophotometer Shimadzu UV-1650PC. X-ray fluorescence and infrared analysis were performed using a fluorescent X mini pairs PAL2 and Hyper IR Shimatzu E spectrophotometer respectively.

Phosphate adsorption on sediments

Adsorption experiments were conducted in batch by varying sediment dose, initial phosphorus concentration and agitation time. In summary, samples of dried sediments were put in contact with 100ml phosphate solutions. The suspensions formed were stirred and

then centrifuged. Residual phosphorus concentrations were determined in the supernatant by the described method.

RESULTS AND DISCUSSION

Sediment characterization

The results of the physicochemical analyses are summarized in Table 1. The sediments samples have neutral to alkaline pH, which can be related to the presence of carbonates. The electrical conductivity values indicate significant mineralization. The studied sediments have low water content, reflecting a relatively low fluidity. They are characterized by high contents of organic matter; which are related to the discharge of domestic wastewaters. The sediment of Rhumel River contains more phosphorus and organic matter.

Table 1: Physicochemical analysis of Rhumel (SR) and Boumerzoug (SB) the sediments

Sediment	SR	SB
pH	7.90	7.91
Electrical conductivity (μs/cm)	860	865
Residual moisture (%)	0.40	2.01
Organic matter (%)	8.50	5.26
Total phosphorus (mg/kg)	1368	1066

The X-ray fluorescence results (Table 2) show that the main constituents of the elemental composition of sampled sediments are calcium, iron, aluminum and silicon in the two rivers.

Table 2: Elemental contents of Rhumel (SR) and Boumerzoug (SB) sediments (%)

Element	SR	SB
Ca	42.5	39.6
Al	21	14
Si	18	26
Fe	13.8	15.6
K	1.6	1.7
P	0.9	1
Ti	0.82	0.83
Ag	1	1.2
Mn	0.13	0.1
Cr	0.06	0.02

The infrared spectra of the two samples show the presence of the characteristic bands of aluminosilicates (1033.8cm^{-1}; 1018.3cm^{-1}) and iron oxyhydroxides (875.6cm^{-1}; 790.8cm^{-1}) in addition to organic matter (Table 3). IR Bands occurred at about 1400cm^{-1} reflect the presence of carbonates. Only some differences in the nature of the organic matter are observed between the two sediments.

Table 3: IR bands of Rhumel (SR) and Boumerzoug (SB) sediments (cm^{-1})

SR	SB
3452	3622.1; 3413.8; 3344.3
2927.7	2989.5
2866.0	2877.6
2500	2515.0
1998.1	1994.3; 1874.7
1797.5	1797.5
1639.4	1635.5
1438.8	1434.9
1033.8	1018.3
921.9	921.9
875.6	875.6
790.8	790.8
702.8; 702.0	698.2
528.5	524.6
466.7	470.6

Adsorption of phosphate ions Effect of sediment dose

The effect of sediment dose has been studied with a phosphate concentration 0.1mM and a stirring time of 60 minutes. The obtained results are presented in Figure 1. For the two sediments, the increase in sediment dose induces an increase in phosphate uptake due to the increase of the number of adsorption sites. At sediment concentration lower than 1g/l, the two sediments show the same adsorption capacity. However, at higher sediment concentration, adsorption efficiency remains quasi constant for Rhumel sediment and slightly increases in the case of Boumerzoug sediment. This can be attributed to the intervention of other parameters such as the particles nature and size distribution.

Figure 1: Evolution of phosphate adsorption on Rhumel (SR) and Boumerzoug (SB) sediments - Effect of sediment dose
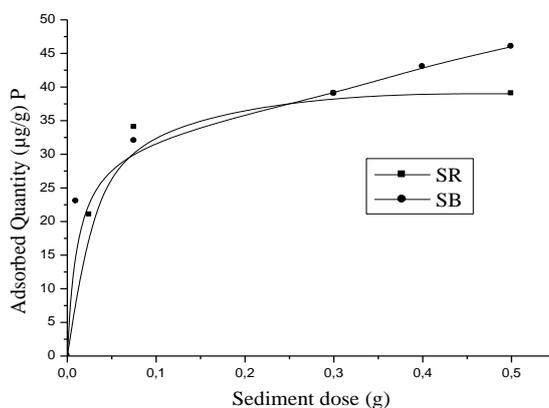
Effect of contact time - Adsorption kinetics

The adsorption of phosphorus onto the two sediments is characterized by two steps (Figure 2). The first one is rapid, it takes about 15minutes. The equilibrium time is reached within 5 hours for the two samples. These results are in agreement with the results of several studies. Wang and coworkers [9], have observed a rapid adsorption step of 6 hours in a study on the adsorption of phosphate on sediments from the three Gorges Reservoir on the Yangtze River (China). In their study on phosphate adsorption on sediments of Lake Taihu in China, Zhou and coworkers [10] have found a first adsorption quick step completed in about five hours, followed by a second slower step.

The kinetic adsorption of a solute through a solid in an aqueous solution is often complex. The adsorption rate is strongly influenced by several parameters related to the solid; which is generally characterized by heterogeneous surface and is sensitive to the physicochemical conditions. Mathematical models are often used to facilitate the discussion of the experimental data. Various kinetic models have been elaborated; the table 4 summarizes the equations of the more used models.

Table 4: Equations of kinetics adsorption models

Model	Nonlinear equation	Linear equation	Parameters
Pseudo-first order	$Ln(Qe/(Qe-Qt))=k.t$	$Ln(Q_e-Q_t)=LnQ_e-k.t$	K: adsorption rate constant
Pseudo-second order	$1/(Qe-Qt)=(1/Qe)+k.t$	$t/Q_t= 1/kQ_e^2 +(1/Q_e).t$	K: adsorption rate constant
Elovich	$Q = (1/b).Ln(ab)+(1/b)\,lnt$	$Q = A + B\,lnt$	A: initial adsorption rate B: a constant related to the activation energy and the heat of adsorption

(Qe: adsorption capacity at equilibrium; qt: adsorption capacity at time t)

The parameters of the kinetics models applied to the adsorption of phosphate ions on the sediments of Rhumel and Boumerzoug Rivers are summarized in Table 5.

**Table5: Kinetics models parameters of phosphate adsorption on Rhumel (SR) and Boumerzoug (SB) sediments**

Model	Sediments	
	SR	SB
Pseudo-first order	K=0.0049 Q_e=1.18 (mg/g) R=0.986	K=0.0072 Q_e=1.81 (mg/g) R= 0.999
Pseudo-second order	K=0.0172 Q_e= 2.28 (mg/g) R=0.999	K= 0.0175 Q_e= 3.24mg/g R=0.999
Elovich	a=0.3286 b=0.2804 R=0.965	a=0.59428 b=0.38803 R=0.946

(R: correlation coefficient)

According to the calculated correlation coefficients, the three kinetic models can describe the experimental data. However, the theoretical nonlinear curve of the first model did not give acceptable values when compared to the experimental ones (data not shown). The two other models are more suitable, with small differences between theoretical and experimental values (Figure 2). In a study on phosphate adsorption on sediments rich in organic matter, it has been shown that the pseudo second order model describes the kinetics adsorption [11]. This model admits a chemisorption mechanism where the adsorption takes place on localized sites with no interaction between the adsorbed molecules. It also assumes that the adsorption capacity is proportional to the number of active sites occupied by the adsorbate. The maximum adsorption is the formation of a monolayer on the surface of the adsorbent [12]. The Elovich model is one of the most used to describe activated chemisorption.

The adsorption of phosphate on Rhumel and Boumerzoug are characterized by almost the same calculated second order rate constants showing the identical behavior of the two sediments for phosphate adsorption. However, the amount of phosphate adsorbed at equilibrium (Qe) on Boumerzoug sediments is higher. Generally, the adsorption capacity depends upon porosity as well as chemical reactivity of functional groups at the surface. As the two sediments have the same chemical functions observed in the IR spectra (Table 3), the difference could be probably related to the importance of the iron oxyhydroxides in the sample of Boumerzoug in comparison to the one of Rhumel where aluminum oxides are more important (Table 2). Elovich model is more appropriate in the first six hours, after this time the kinetic is best described by the second order model in the case of boumerzoug. However, in the case of Rhumel, the equilibrium phosphate adsorption capacities calculated by the two models are slightly different from the experimental data.

Figure 2: Adsorption kinetics of phosphate adsorption on Rhumel (SR) and Boumerzoug (SB) sediments
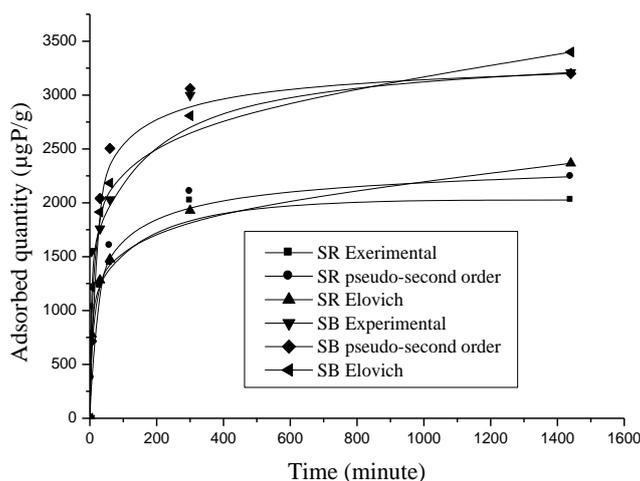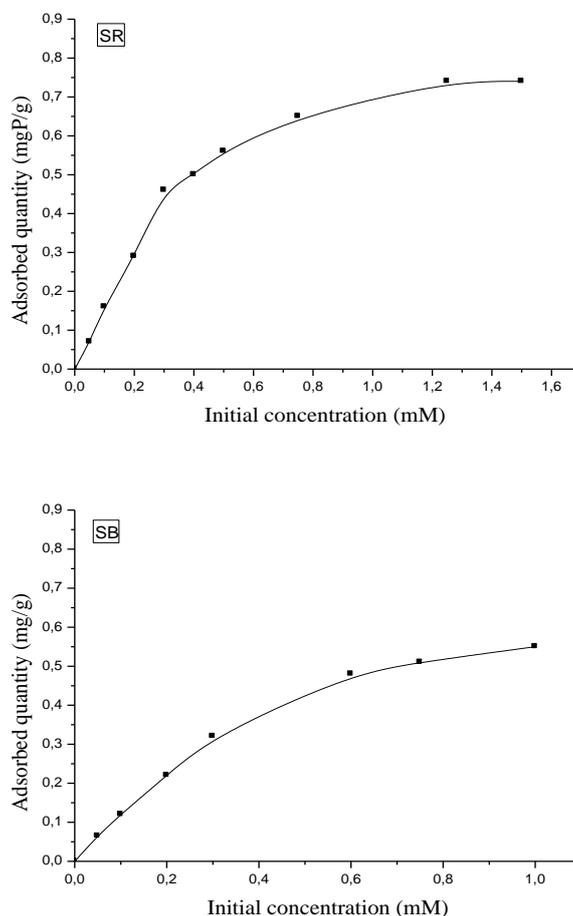

Effect of concentration-Adsorption isotherm

The removal of phosphate ions by sediment increases with the increase of initial phosphate concentration (Figure 3). The rate of adsorption decreases for high phosphate

concentrations. The decrease in adsorption efficiency when solute concentration increases is probably due to less available active sites [13].

Figure 3: Effect of initial phosphate concentration on the adsorption of phosphate on Rhumel river (SR) and Boumerzoug river (SB)

Adsorption is often described by isotherms that reflect the relationship between the amount adsorbed per unit mass of solid (Q) and the concentration of the solution under equilibrium conditions (Ce) at constant temperature. Several models have been developed to describe this relationship. The more used equations with their parameters are summarized in table 6.

Table 6: Equations of isotherms adsorption models

Model	Nonlinear equation	Linear equation	Parameters
Langmuir	$Qe = Qmax.K.Ce/(1+KCe)$	$1/Qe=(1/Qmax)+1/(Qmax.K).1/Ce$	Qmax: maximum adsorption capacity K: Langmuir constant
Freundlich	$Qe = KCe^{1/n}$	$Ln\ Qe = Ln\ K + (1/n)Ln\ Ce$	K and n are Freundlich constants.
Temkin	$Qe = (RT/b)\ Ln\ (K.Ce)$	$Qe = A + B\ ln\ Ce$	A and B are Temkin isotherm constants

(Qe: adsorbed amount per gram of adsorbent; Ce: Concentration in solution at equilibrium)

The experimental isotherms obtained for the two sediments (Figure 4) show an increase in the adsorption efficiency with the concentration of the adsorbate to reach an equilibrium value for Rhumel sediment. The same evolution has been observed for siliceous sediments characterized by high total phosphorus concentrations [13]. The application of the various equations to our results gives the parameters presented in table 7. The correlation coefficients values are higher than 0.9 indicating that the three models can be used for describing the experimental data.

Table 7: Isotherms parameters of phosphate adsorption on Rhumel (SR) and Boumerzoug (SB) sediments
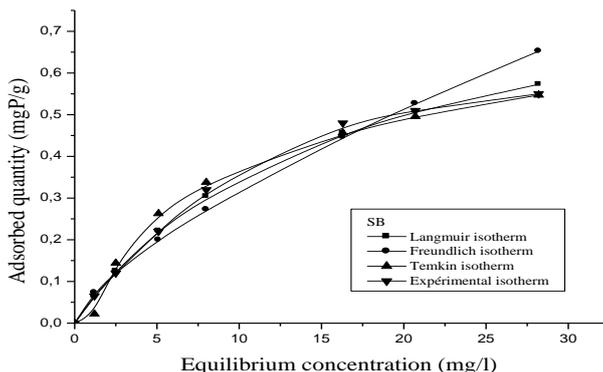
Model	Sediments	
	SR	SB
Langmuir	Q_{max}=2.14(mg/g)	Q_{max} =0.88(mg/g)
	K= 0.03	K = 0.066
	R=0.991	R=0.999
Freundlich	K=0.094	K=0.064
	n=1.58	n= 1.44
	R= 0.947	R=0.989
Temkin	a=0.021	a=0.008
	b=0.20	b=0.17
	R=0.991	R=0.988

(R: correlation coefficient)

In the objective to determine the more appropriate model, we have plotted the nonlinear isotherms for each model. The obtained curves show that Temkin model is the more suitable to describe the experimental isotherm in the case of Rhumel river. This model considers a non- uniform surface and a preferential occupation of the most adsorbent sites. It takes into account the fact that the heat of adsorption of molecules of the entire covering layer decreases linearly with the recovery due to the decrease of adsorbent - adsorbate interactions. The adsorption is characterized by a uniform distribution of the binding energy on the surface [14]. The three tested models can describe the phosphate adsorption on Boumerzoug sediment in the order Temkin, Langmuir and Freundlich.

Figure 4: Adsorption isotherms of phosphate adsorption on Rhumel (SR) and Boumerzoug (SB) sediments
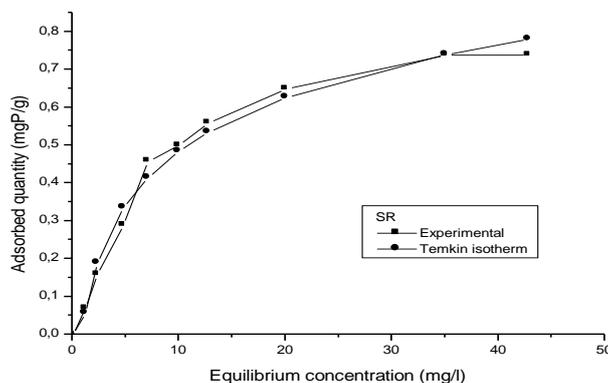
CONCLUSION

Phosphate adsorption on Rhumel and Boumerzoug sediments is mainly chemical. The adsorption capacity depends on their composition. Boumerzoug sediments retain more phosphate than Rhumel sediments.

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