Research Article

Study of the Phosphorus Adsorption on the Sediments

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The objective of this work is to determine the reflection elements, allowing the understanding of the phosphorus fixation mechanisms. The samples were taken from Oued Boufekrane in the Meknes region (Northwest of Morocco). In fact, the sediment characterization was examined by the Brunauer–Emmett–Teller (BET) specific surface area and Fourier-transform infrared (FTIR) spectroscopy measurements. A series of experiments were then carried out to study the impact of some parameters on the adsorption capacity. Indeed, the effect of contact time, sediment mass, pH, initial concentration of potassium dihydrogen phosphate KH₂PO₄, and the temperature has been studied. The characterization of sediment by FTIR spectroscopy shows the existence of carbonates, iron hydroxides, and organic matter. The results obtained showed that the retention of phosphorus on the sediments studied is maximal at pH = 12 and increases with the temperature and the mass of sediments. Phosphorus adsorption kinetics of phosphorus on sediments studied follows the pseudo-second-order model, and the activation energy value (48.51 kJ/mol) indicates the predominance of chemical nature of adsorption (>40 kJ/mol). The experimental data of the adsorption isotherms are well interpreted by the Freundlich model. The values of the thermodynamic parameters ΔG°, ΔH°, and ΔS° indicate that the adsorption reaction is endothermic and occurs spontaneously on the surface of the sediments studied.

1. Introduction

Phosphorus is one of the essential elements of life, and it plays a major role in the trophic status of watercourses by regulating ecological processes such as primary production or decomposition.

Sediments are considered as phosphorus storage tanks [1]. This accumulation in sediments due to domestic, agricultural, and industrial discharges is not definitive, under the influence of certain physicochemical and meteorological conditions, a significant amount of this phosphorus can again be released into the water phase, which sometimes poses serious problems in the water of watercourses.

Several researchers have studied the adsorption of phosphorus with different solids [2–4]. The objective of this study is to determine the adsorptive capacity of surface sediments of Oued Boufekrane toward phosphorus. We also aim to analyze the influence of certain parameters, namely, pH, the sediment mass, and the temperature on phosphorus fixation on sediments studied. As a result, we have studied the pseudo-first-order and pseudo-second-order kinetic models. We then studied the adsorption isotherms using the Langmuir and Freundlich models and thus determined the thermodynamic parameters (ΔH°, ΔS°, and ΔG°) of the phosphorus adsorption on the Oued Boufekrane sediments.

2. Materials and Methods

2.1. Sampling Station. The Oued Boufekrane is a permanent watercourse of the Middle Atlas; its source is West of El Hajeb, in the Causse Middle Atlasic at 750 m altitude [5]. It takes first the name of Ain Maârouf, then that of Boufekrane at 10 km from the source. The upstream part of the network crosses limestone, dolomitic, and sandy terrains, and its downstream part flows into open valleys delimited by marl hills. At its middle course, it receives domestic and industrial discharges from the city of Meknes [6].

Sampling of this study was carried out using the Eckman grape to pick 5 cm of upper sediments downstream from Oued Boufekrane (Figure 1).
2.2. Sediment Characterization

2.2.1. Fourier-Transform Infrared (FTIR) Spectroscopy. The principle of this measurement is based on the sample irradiation by an infrared beam whose wave number varies between 400 and 4000 cm$^{-1}$.

The analysis of the sample studied was carried out using a JASCO 4100 type apparatus equipped with a TriGlycine sulfate detector (TGS) and a ceramic source separated by an optical system using a Michelson interferometer.

2.2.2. BET. The specific surface of the solid estimated by the BET (Brunauer, Emett, and Teller) method $[7]$ is based on the theory of multilayer gas adsorption on a solid. It allows the measurement of the specific surface from the hysteresis curves of adsorption and desorption of a gas (typically nitrogen) at low temperature ($T = -196°C$).

The textural parameters of the analyzed powders were measured using Micrometrics ASAP 2010. The powders undergo, before each measurement, a degassing at a temperature $T$ during a given time. After degassing, the cell containing the sample is immersed in a Dewar filled with liquid nitrogen ($T = -196°C$). The volumes of N$_2$ adsorbed and desorbed are determined at each equilibrium pressure between the adsorbate and the adsorbent, allowing to trace the hysteresis curves.

2.3. Experimental Procedure. The adsorption experiments were carried out in batch by stirring 0.5 g of dry sediment in 25 ml of the KH$_2$PO$_4$ solution at 5 mg of phosphorus per liter. After separation of the liquid phase and the adsorbent using the 0.45 µm Millipore filter, the absorbance of the supernatant was measured using a UV/visible spectrometer at the wavelength of 700 nm.

The calculation of the retention capacity ($Q_t$) was carried out using the following equation:

$$Q_t = \frac{(C_0 - C_e) \times V}{m},$$

where $C_0$ and $C_e$ are, respectively, the initial and equilibrium phosphorus concentration, $V$ is the volume of solution, and $m$ is the mass of sediment.

The pH effect on phosphorus adsorption was studied over the range from 2 to 12. The pH was adjusted by NaOH and HCl solutions. The effect of sediments mass is also studied by varying the mass from 0.5 to 3 g.

The kinetic study was carried out by stirring 0.5 g of sediment into the aqueous KH$_2$PO$_4$ solution at 5 mg P/L. The adsorption kinetics was evaluated by pseudo-first-order and pseudo-second-order models. The Langmuir and Freundlich isotherms were studied, and the characteristic parameters of each isotherm were determined. Also, in order to evaluate the effect of temperature on the adsorption phenomenon, the thermodynamic parameters were determined as a function of temperature from 24°C to 45°C.

3. Results and Discussion

3.1. FTIR Spectroscopy. For further investigation to identify surface functions of the studied sediments, their structures were observed by infrared spectroscopy.
The infrared spectroscopy characterization (Figure 2) shows that the band at about 3430 cm\(^{-1}\) would be assigned to the valence vibration of the hydroxyl groups, OH [8]. The 2924 cm\(^{-1}\) band typically characterizes C-H stretching vibration [9]; Igisu and its collaborators assigned the 1797 cm\(^{-1}\) band to the Si-O bonds of quartz and its harmonics [10]. In addition, the band having the 1036 cm\(^{-1}\) wave number probably corresponds to the organic matter, including C-O bonds (esters, alcohols, and ethers). The band at 874 cm\(^{-1}\) could be related to the presence of goethite (FeOOH) [11]. It may also be noted that the band located at 796 cm\(^{-1}\) due to aromatic or to the presence of quartz and the band at 1426 cm\(^{-1}\) indicates the presence of carbonates [9].

3.2. BET. Figure 3 shows the adsorption-desorption isotherms of N\(_2\) obtained at \(-196^\circ\)C, and it shows that these isotherms are of type II according to the IUPAC classification (International Union of Pure and Applied Chemistry) [12]. This type of isotherm characterizes materials containing aggregates of flat particles forming pores in the slits form. An \(H_3\)-type hysteresis loop occurs at higher relative pressures (\(P/P_0 \geq 0.4\)). It is observed for aggregates generating pores in nonuniform size slits. The BET results for specific surface, energy constant, and adsorbed volume on the monolayer are summarized in Table 1.

3.3. Effect of Mass. In order to examine the effect of the sediment mass on the amount adsorbed, experiments were conducted using 25 ml of KH\(_2\)PO\(_4\) at 5 mg P/L, with a stirring time of 6 hours at a temperature of 24 °C, varying the mass from 0.5 to 3 g.

Figure 4 shows the evolution of the adsorbed amount as a function of the mass, and it appears that the increase in the sediments mass leads to an increase in the amount of adsorbed phosphorus; this may be due to the increase of the number of active sites.

3.4. Effect of pH. The initial pH of the solution is an important parameter that must be considered [13, 14]. The effect of this factor on the evolution of adsorption capacity was studied at pH from 2 to 12. The experiments were carried out by adding 0.5 g of sediments to 25 ml of the KH\(_2\)PO\(_4\) solution (5 mg P/L). The results illustrated in Figure 5 show that the adsorption capacity is influenced by the pH variations, where low quantities are adsorbed at acidic pH; however, significant fixation capacities are recorded at the basic pH levels.

The increase in the adsorption capacity of phosphorus with the increase in pH can be explained by the richness of the sediments studied in carbonates which have the ability to fix the phosphorus at basic pH [15, 16]. However, the decrease of the phosphorus retention capacity at the iron oxides is due to the competition between hydroxide (OH\(^-\)) and phosphorus ions [17, 18].

3.5. Adsorption Kinetics. The study of phosphorus adsorption on the sediments studied implies the monitoring of the amount adsorbed over time, in order to determine the contact time corresponding to the equilibrium.

The results obtained are shown in Figure 6, where the evolution of the adsorbed amount over time shows that the adsorption process takes place in a rapid step in one hour, followed by another slower step which tends to equilibrate after 6 hours at 24 °C, and 4 hours at 35 °C, 40 °C, and 45 °C.

The rapidity of adsorption kinetics during the first few minutes can be interpreted by the availability of a significant number of active sites on the surface at the beginning of adsorption, compared to that remaining after a certain time [19, 20]. Kinetics provides information on the adsorption
mechanism and the mode of solute transfer from the liquid phase to solid phase [21].

The kinetics of solute adsorption on a solid in an aqueous solution is often a complex process. Mathematical models are often used to facilitate the discussion of experimental data.

The kinetic modeling of phosphorus adsorption on sediments studied was carried out according to two models: pseudo-first-order and pseudo-second-order.

3.5.1. Pseudo-First-Order Model. It was assumed that in this model, the rate of adsorption at time $t$ is proportional to the difference between the equilibrium amount adsorbed $Q_e$ and the amount adsorbed at this instant $Q_t$, and that the adsorption is reversible [22]. The constant rate is given by Lagergren [23]:

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1t,$$  \hspace{1cm} (2)

where $Q_t$ is the amount of phosphorus adsorbed at the instant ($t$) (mg/g), $Q_e$ is the amount of phosphorus adsorbed at equilibrium (mg/g), and $k_1$ is the pseudo-first-order rate constant of adsorption (min$^{-1}$).

The constants of the pseudo-first-order model were determined by using equation (2) by plotting the $\ln(Q_e - Q_t)$ as a function of time ($t$) (Figure 7), the adsorbed amount values $Q_e$ and the pseudo-first-order constants $k_1$; the determination coefficients $R^2$ are given in Table 2.

3.5.2. Pseudo-Second-Order Model. The pseudo-second-order model characterizes the adsorption kinetics, by taking into account both the case of rapid solutes fixation on the most reactive sites and that of a slow fixation on the low energy sites. This model suggests the existence of a chemisorption [24, 25].

The expression of the pseudo-second-order reaction model was obtained by the equation proposed by Ho and Coll [26]:

$$\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{1}{Q_e}t,$$  \hspace{1cm} (3)

where $k_2$ is the pseudo-second-order rate constant of adsorption (g/mg·min).

From (3), the adsorbed quantity at equilibrium $Q_e$ and the pseudo-second-order constant $k_2$ can be determined experimentally from the slope and the ordinate at the origin of $t/Q_t$, as a function of $t$. The results are shown in Figure 8 and Table 2.

The results summarized in Table 2 show that the determination coefficient values ($R^2$) of the pseudo-second-order kinetic model are very close to 1 and that the amounts adsorbed at equilibrium ($Q_e$) determined experimentally by this model are closer to those calculated and increase with temperature. These results show that the kinetics of phosphorus retention by the sediments studied are better described by the pseudo-second-order model than that of pseudo-first-order. This model assumes that the adsorption capacity is proportional to the number of active sites occupied by phosphorus. The maximum adsorption is the formation of a monolayer on the sediments surface [27].

3.6. Adsorption Isotherm. The study of the adsorption isotherms consists in representing at constant temperature, the equilibrium relation between the adsorbed amounts ($Q_e$), the amount of phosphorus adsorbed at equilibrium (mg/g), and the temperature ($T$). The adsorption isotherms are shown in Figure 9. The equilibrium concentration was calculated using the following equation:

$$Q_e = \frac{C}{1 + \frac{C}{K}}$$

where $Q_e$ is the amount of phosphorus adsorbed at equilibrium (mg/g), $C$ is the equilibrium concentration of phosphorus in the solution (mg/L), and $K$ is the equilibrium constant (L/mg).

The adsorption isotherms were studied at five temperatures: 24°C, 35°C, and 45°C, with five concentrations of phosphorus in the solution: 5, 10, 15, 20, and 25 mg/L. The isotherms were studied according to the following models: Langmuir [28], the Freundlich [29], and the Dubinin-Radushkevich [30]. The constants of these models were obtained using the following equations:

- **Langmuir** model:
  $$\frac{Q_e}{K} = \frac{1}{KQ_m} + \frac{1}{Q_m}C$$

- **Freundlich** model:
  $$Q_e = K_C C^{1/n}$$

- **Dubinin-Radushkevich** model:
  $$Q_e = \frac{Q_m}{1 + |\psi|}$$

where $Q_e$ is the amount of phosphorus adsorbed at equilibrium (mg/g), $Q_m$ is the monolayer capacity (mg/g), $K$ is the equilibrium constant (L/mg), $C$ is the equilibrium concentration of phosphorus in the solution (mg/L), $K_C$ is the Freundlich constant (mg/L$^{1/n}$), and $n$ is the Freundlich exponent ($0<n<1$).

The results showed that the Langmuir model was the best-fitting model for the adsorption of phosphorus on Oued Boufekrane sediments. This model was obtained by the equation proposed by Ho and Coll [26]:

$$t = \frac{k_2Q_e^2}{Q_t} + \frac{1}{Q_e}t,$$  \hspace{1cm} (3)

where $k_2$ is the pseudo-second-order rate constant of adsorption (g/mg·min).
and the residual concentration in the liquid phase after equilibrium \((C_e)\). In order to determine the isotherm which better represents the phosphorus adsorption on the sediments studied, we varied the initial concentration from 3 to 14 mgP/L. The results obtained are treated by the application of the Langmuir model and that of Freundlich. These two models have been used by several researchers for the study of phosphorus adsorption isotherms on aquatic sediments [28–30].

### 3.6.1. Langmuir Adsorption Isotherm.

The model of the isotherm proposed by Langmuir in 1918 [31] is valid for the adsorption of monolayer molecules.

This model is described as follows:

\[
\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m},
\]

where \(Q_m\) is the maximum adsorption capacity (mg/g) and \(K_L\) is the Langmuir adsorption constant (l/mg).
The linear representations of $C_e/Q_e$ versus $C_e$ (Figure 9) allow us to calculate $Q_m$ and $K_L$ from the slope and the ordinate at the origin.

### 3.6.2. Freundlich Adsorption Isotherm

The Freundlich adsorption model is generally applies when the adsorbed amounts are very low. This model, which is empirical, considers the possible interactions between the adsorbed molecules of surface heterogeneity [32].

The equation of this model can be linearized in the following form:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e,$$

where $K_F$ is the Freundlich adsorption constant (mg/g) (L/mg)$^{1/n}$ and $n$ is the intensity factor.

The graphical representation of $\ln(Q_e)$ as a function of $\ln(C_e)$ for the adsorption of phosphorus on the sediments studied is a straight line whose slope and ordinate at the origin are $1/n$ and $\ln(K_F)$, respectively (Figure 9). The value $1/n$ gives information on the validity of the adsorbate adsorption on the adsorbent [33]. If this value is between 0 and 1, the adsorption capacity increases and new adsorption sites appear, confirming that the adsorption is favorable.

The different equilibrium parameters and the determined Langmuir and Freundlich constants values are presented in Table 3.

According to these results, the determination coefficients ($R^2$) of the Freundlich model are more important than those of Langmuir, which confirms that the adsorption of phosphorus by the sediments studied is better described by the Freundlich model than the Langmuir model and this for the three temperatures studied. This confirms that the phosphorus adsorption on sediments is multilayer with the possibility of interaction between the adsorbed molecules and that this adsorption is done on heterogeneous surfaces. This heterogeneity confirms that the phosphorus is adsorbed on different sites, which is in agreement with the studies.
carried out on the chemical fractionation of phosphorus on the same sediments, which show that phosphorus exists in different forms within the sediments [16]. Numerical values of $1/n$ at different temperatures indicate that the adsorption of phosphorus on the sediments studied is favorable throughout the Oued Boufekrane.

3.7. Activation Energy ($E_a$). From the pseudo-second-order model results, the constant adsorption $k_2$ can be used at each temperature to calculate the activation energy using the Arrhenius equation:

$$\ln k_2 = \ln A - \frac{E_a}{R} \frac{1}{T}$$ (6)

Figure 9: Linearization of the Langmuir (a, c, e) and Freundlich (b, d, f) equations for the phosphorus adsorption on Oued Boufekrane sediments.
where $k_2$ is the pseudo-second-rate constant of adsorption (g/mg-min), $A$ is the preexponential factor (min$^{-1}$); $E_a$ is the activation energy (J/mol), and $T$ is the solution temperature (K).

The value of the activation energy ($E_a$) makes possible the determination of the adsorption nature (chemical or physical). The physisorption process is characterized by low activation energy (5–40kJ/mol), where the energies greater than 40kJ/mol suggest chemisorption [34].

Figure 10 presents the Arrhenius line obtained by plotting $\ln(k_2)$ as a function of $1/T$; the activation energy deduced from the slope is equal to 48.51kJ/mol, which confirms the predominance of the chemisorption, which is characterized by the covalent bonds formation between adsorbate-adsorbent.

### 3.8. Thermodynamic Parameters

The thermodynamic parameters of the equilibrium adsorption reaction, standard free enthalpy $\Delta G^o$, standard enthalpy $\Delta H^o$, and standard entropy $\Delta S^o$, were determined from the following equations [35–37]:

\[
\begin{align*}
K_e &= \frac{C_0 - C_e}{C_e}, \\
\ln K_e &= \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}, \\
\Delta G^o &= -RT \ln K_e,
\end{align*}
\]

where $K_e$ is the equilibrium constant; the linear plot of the variation of $\ln(K_e)$ as a function of $1/T$ is a straight line (Figure 11), where ($-\Delta H^o/R$) and $\Delta S^o/R$ are, respectively, the slope and the ordinate at the origin.

The thermodynamic parameters were determined from the experimental results at the various temperatures, which are grouped in Table 4.

The results obtained show that the adsorption reactions of phosphorus on the sediments studied are spontaneous ($\Delta G^o < 0$) and endothermic ($\Delta H^o > 0$), which confirms the increase of the adsorption capacity by increasing the temperature from 24 to 45°C. The positive value of entropy ($\Delta S^o$) indicates the increase of the disorder at the solid-solution interface during the fixation of the phosphorus on the sediments studied.

### 4. Conclusion

This work has highlighted that pH and temperature are among the essential elements that can contribute to the understanding of phosphorus adsorption on sediments at the scale of the studied watercourse. The adsorbed amount of phosphorus on the studied sediments increases with pH, and this is interpreted by the fixation of phosphorus on calcium carbonates which is characterized by FTIR spectroscopy. The kinetic study showed that the equilibrium was established after 6 hours at 24°C, and 4 hours at 35, 40, and 45°C. The kinetic modeling of phosphorus adsorption showed that the pseudo-second-order model is better suited to describe kinetics adsorption of phosphorus. The adsorption isotherms seem better described by the Freundlich model, which represents the adsorption phosphorus on the sediments studied. The heterogeneity of surfaces found by this model confirms the existence of phosphorus in different forms within sediments. This adsorption is characterized by the predominance of the chemical type ($E_a > 40$ kJ/mol). The values of $\Delta H^o$ which is in the order of 28.87 kJ·mol$^{-1}$ indicated that the adsorption process is endothermic. Negative values of $\Delta G^o$ (-1.44 at 24°C, -2.41 at 35°C, -2.96 at 40°C,

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**Table 3: Langmuir and Freundlich model parameters.**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$K_L$ (L/mg)</th>
<th>$Q_m$ (mg/g)</th>
<th>$R^2$</th>
<th>$K_F$ (mg/g)·(L/mg)$^{1/n}$</th>
<th>$1/n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>0.27</td>
<td>0.509</td>
<td>0.849</td>
<td>0.12</td>
<td>0.54</td>
<td>0.976</td>
</tr>
<tr>
<td>35</td>
<td>0.35</td>
<td>0.507</td>
<td>0.825</td>
<td>0.14</td>
<td>0.51</td>
<td>0.961</td>
</tr>
<tr>
<td>45</td>
<td>0.69</td>
<td>0.453</td>
<td>0.886</td>
<td>0.18</td>
<td>0.40</td>
<td>0.960</td>
</tr>
</tbody>
</table>

**Table 4: Thermodynamic parameters of phosphorus adsorption on the Oued Boufekrane sediments as a function of temperature.**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\Delta H^o$ (kJ·mol$^{-1}$)</th>
<th>$\Delta S^o$ (J·mol$^{-1}$·K$^{-1}$)</th>
<th>$\Delta G^o$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>-1.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>-2.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>-2.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>-3.67</td>
<td></td>
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</tr>
</tbody>
</table>
and −3.67 at 45°C (kJ·mol\(^{-1}\)) showed that the adsorption reactions are spontaneous, and the positive value of \(\Delta S\) (101.67 J mol\(^{-1}\)·K\(^{-1}\)) confirms the increase of the disorder at the sediment interface during the retention of phosphorus on sediments studied.

### Data Availability

The data used to support the findings of this study are available from the corresponding author upon reasonable request.

### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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