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## ORIGINAL ARTICLE

# A kinetic modeling study of phosphate adsorption onto *Phoenix dactylifera* L. date palm fibers in batch mode



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**Abstract** The removal of phosphates from aqueous solutions by adsorption onto date palm fibers (DPF) has been studied in batch mode. The aim of this study was to understand the mechanisms that govern phosphate sorption and find an appropriate model for the kinetics of removal. In order to investigate the mechanism of sorption and potential rate controlling steps, pseudo first-order, pseudo second-order, intra-particle diffusion and the Elovich equations have been used to test experimental data. Kinetic analysis of the four models has been carried out for initial phosphate concentration in the range of 30–110 mg/L. The rate constants for the four models have been determined and the correlation coefficients have been calculated in order to assess which model provides the best fit predicted data with experimental results. Seven statistical functions were used to estimate the error deviations between experimental and theoretically predicted kinetic adsorption values, including the average relative error deviation (ARED), Marquardt's percent standard error deviation (MPSED), the hybrid fractional error function (HYBRID), the sum of the squares of the errors (SSE) and three alternative statistical functions, including the Chi-square test, the *F*-test and Student's *T*-test. The results showed that, both Elovich equation and pseudo second-order equation provide the best fit to experimental data for different initial phosphate concentrations.

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## 1. Introduction

The date palm *Phoenix dactylifera* L. is the most important fruit tree found in arid, tropical, and sub-tropical regions of the world specifically those stretching from North Africa to the Middle East [1]. This type of palm tree produces a large quantity of agricultural waste. Each date tree produces about 20 kg of dry leaves yearly. Other wastes such as date pits which account for about 15% by weight of the date fruits represent another huge solid waste of little or no economic value except in limited scales for cattle's food, and in fact present a disposal

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problem. Also, after annually trimming operations of date palm trees, enormous quantities of palm fiber wastes are thrown away, except in smaller scales for artisan products [2]. Although these agriculture wastes consist of cellulose, hemicelluloses, lignin and other compounds which could be used in many biological processes, they were burned in farms causing serious threat to environment [3].

Large quantities of phosphates present in wastewater are one of the main causes of eutrophication that negatively affects many natural water bodies. Before discharging wastewater into water bodies, removing phosphate is usually obligatory, even though in many cases it is not performed, and leads to major contamination on a worldwide level [4]. Removal of these nutrients, especially phosphorus by advanced treatment is necessary in areas where the regulations on effluent standards are strict [5,6]. Phosphorus is usually difficult to remove by way of conventional water or wastewater treatment plants. There are some methods, such as reverse osmosis or electro-dialysis, now available and running, but at a high capital cost. The broad categories of phosphate effluent treatment include chemical [7], biological [8] and electrochemical methods [9]. Electrochemical depolluting methods are mainly electro dialysis, electrocoagulation, electroflotation, anodic processes, cathodic processes and electrochemical advanced oxidation processes that have been successfully used. Also, flotation has been used to remove phosphates from aqueous solutions [10]. Chemical removal techniques are the most effective and well established methods up to date, including phosphate precipitation with calcium, aluminum and iron salt [11,12]. Recycling of phosphorus is converting an acute disposable problem into a raw material that will benefit industry and society, as phosphorus has a significant contribution, as fertilizer, to the well being of human societies. What is needed is a process of phosphorus removal that separates it from other waste components, so that it can be recycled as a fertilizer or an ingredient in other valuable phosphorus products.

The main aim of this research was to find an appropriate model for the kinetics of orthophosphate species removal onto *P. dactylifera* L. date palm fibers in a batch reactor. In order to investigate the mechanism of sorption and potential rate controlling steps, pseudo first and second-order equations, intra-particle diffusion equation and the Elovich equation have been used to test experimental data. We also try to investigate the applicability of some statistical functions. Hence, several error calculation functions have been widely used to estimate the error deviations between experimental and theoretically predicted kinetic adsorption values. In this study, seven statistical functions four commonly used error functions, including the average relative error deviation (ARED), Marquardt's percent standard error deviation (MPSED), the hybrid fractional error function (HYBRID), the sum of the squares of the errors (SSE) and three alternative statistical functions, including the Chi-square test, the *F*-test and Student's *T*-test, are analyzed to investigate their applicability as suitable tools to evaluate kinetic model fitness.

## 2. Materials and methods

### 2.1. Material preparation and characterization

The natural fibers used in this study are from the surface of *P. dactylifera* L. date palm tree obtained from Kébili (southern of

Tunisia). One type of date palm fibers (DPF), corresponding to the principal palms: Deglette-Nour (local name), was selected for the investigated study. The date palm fibers are naturally weaved, and are pulled out from trunk in the form of nearly rectangular mesh formed with tree superposing layers. The layers are easily separated when immersed in water as individual fibers of diameter 0.2–0.8 mm. Date palm fibers were then washed with distilled water and dried at 105 °C for 24 h. Only the particles with diameter inferior to 175 µm were used. This fraction was chosen in order to have a good mixing between date palm fibers and the aqueous phase when the reactor is stirred with the magnetic stirrer and consequently to ensure a good contact between aqueous phosphate species and the adsorbent.

The  $pH_{zpc}$  of date palm fibers was determined using the batch equilibrium technique with 1 g of date palm fibers in 50 mL of  $KNO_3$  solution 0.01 M. The initial pH value of the  $KNO_3$  solution was adjusted ranging from 2 to 9 by adding 0.1 (M) HCl or NaOH. The solutions were allowed to equilibrate for 24 h in a magnetic stirrer at  $25 \pm 2$  °C. The suspensions were filtered through filter paper, and the pH values were measured again using an ion pH meter. The BET specific area and pore diameter were determined using a Quantachrom Autosorb sorptiometer. The percentage of Neutral Detergent Fiber (NDF) and Acid Detergent Fiber (ADF) was also determined using ANKOM 200 apparatus. The elemental composition of date palm fibers was achieved by energy dispersive spectroscopy (EDS) using a Quanta-200-Fei apparatus. The main physical, biochemical and elemental characteristics of raw date palm fibers are given in Table 1.

### 2.2. Adsorption kinetic measurements

Phosphate adsorption kinetic study was carried out with different initial concentrations of phosphate and a fixed dose of the adsorbent at constant temperature in a shaker bath ( $18 \text{ °C} \pm 02$ ). Before the start of each kinetic experiment, the phosphate species stock solution containing 1000 mg P/L was

**Table 1** Main physical, biochemical and elemental characteristics of the raw date palm fibers.

<i>Physical characteristics</i>	
$pH_{PZC}$	7.11
Specific surface ( $m^2/g$ )	1.46
Pore diameter (Å)	848
<i>Biochemical characteristics (%)</i>	
NDF	55.8
ADF	11.4
<i>Elemental composition (wt.%)</i>	
Carbon	75.86
Oxygen	20.45
Hydrogen	2.20
Cobalt	0.62
Calcium	0.20
Magnesium	0.15
Sulfur	0.12
Siliceous	0.12
Iron	0.09
Aluminum	0.07
Nitrogen	0.07
Phosphorus	0.05

prepared by dissolving potassium dihydrogenophosphate ( $\text{KH}_2\text{PO}_4$ ) powders (analytical reagent grade) in distilled water. Six levels of initial phosphate concentrations (30, 50, 70, 90 and 110 mg P/L) were used. The pH of the solution was maintained at a defined value by manually adding 0.1 M  $\text{H}_2\text{SO}_4$  and/or NaOH solutions. The flask was capped and stirred magnetically at 200 rpm for 240 min to ensure approximate equilibrium. At the end of the adsorption period, the solution was filtered through a 0.45  $\mu\text{m}$  membrane filter and then analyzed for orthophosphate species.

The analysis of orthophosphate anions was done spectrophotometrically at 880 nm, following the ascorbic acid method [13]: dilute solutions of orthophosphate react with ammonium molybdate and potassium antimonyl tartrate in an acid medium forming a heteropolyacid–phosphomolybdic acid that is reduced to the intensely colored molybdenum blue by ascorbic acid. The triplicate experiments demonstrated the high repeatability of this adsorption method and the experimental error could be controlled within 5%. The capacity of adsorbed phosphate (mg/g) was calculated from the decrease of the phosphate concentration in solution with respect to  $V$ , the volume of the solution in L and  $M$  the mass of sorbent in g from mass balance equation as follows:

$$q_e = \frac{C_i - C_e}{M} V \quad (1)$$

### 2.3. Kinetic models

The study of adsorption kinetics is very useful for understanding the involved mechanisms and also for the design of future large scale adsorption facilities. Many models are used to fit the kinetic adsorption experiments. The most used ones are the pseudo-first order, pseudo-second order, intra-particle diffusion and Elovich models [14,15]. In order to examine the mechanism of adsorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the rate data. Most models used in the literature have been extensively applied in batch reactors in this study to describe the transport of adsorbates inside the adsorbent particles. All constants were calculated from the intercept and slope of the line obtained from linearized form of models. The equations corresponding to each model and their linearized forms, plots, slopes and intercepts are presented in Table 2.

#### 2.3.1. Pseudo first-order equation

The pseudo first-order equation is generally expressed as follows:

$$\frac{dq_e}{dt} = k_I(q_e - q_t) \quad (2)$$

After integration and applying the boundary conditions, for  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ , the integrated form of Eq. (2) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_I}{2.303} t \quad (3)$$

where  $q_e$  and  $q_t$  are the amounts of phosphates sorbed at equilibrium and at time  $t$  (mg/g), respectively, and  $k_I$  is the rate constant of pseudo first-order sorption (l/min).

#### 2.3.2. Pseudo second-order equation

If the rate of sorption is a second-order mechanism, the pseudo second-order chemisorption kinetic rate equation after integration is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_{II}q_e^2} + \frac{1}{q_e} t \quad (4)$$

where  $k_{II}$  is the rate constant of pseudo second-order sorption (g/(mg min)) and  $q_e$  is the amount of phosphates sorbed at equilibrium (mg/g).

#### 2.3.3. Intra-particle diffusion equation

The fractional approach to equilibrium changes according to a function of  $(D/r^2)^{1/2}$ , where  $r$  is the particle radius and  $D$  the diffusivity of solute within the particle. The initial rate of the intra-particle diffusion is the following:

$$q_t = k_d t^{1/2} \quad (5)$$

where  $k_d$  is the intra-particle diffusion rate constant (mg/g min<sup>1/2</sup>).

In order to identify the main steps governing the overall removal rate of the sorption process, the particle and film diffusion models were applied according to the methodology presented by Karthikeyan et al. [16]. The two diffusion coefficients through the boundary layer and intra-particle  $D_f$  and  $D_p$  (m<sup>2</sup>/s) were calculated by employing Eqs. (6) and (7).

$$\frac{q_t}{q_e} = 6 \left( \frac{D_f}{\pi r^2} \right)^{1/2} t^{1/2} \quad (6)$$

$$\text{Ln} \left( 1 - \frac{q_t}{q_e} \right) = \text{Ln} \left( \frac{6}{\pi^2} \right) - \left( \frac{D_p \pi^2}{r^2} \right) t \quad (7)$$

where  $D_f$  is the diffusion coefficient with the unit m<sup>2</sup>/s;  $t^{1/2}$  is the time (s) for half-adsorption of phosphate and  $r$  is the average radius of the adsorbent particle.

#### 2.3.4. The Elovich equation

The Elovich equation is given as follows:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \quad (8)$$

The integration of the rate equation with the same boundary conditions as the pseudo first- and second-order equations becomes the Elovich equation.

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (9)$$

where  $\alpha$  is the initial sorption rate (mg/g min), and the parameter  $\beta$  is related to the extent of surface coverage and activation energy for chemisorption (g/mg).

### 2.4. Commonly used error functions

#### 2.4.1. Average relative error deviation (ARED)

The main advantage of this error function is the minimization of the fractional error distribution across the entire studied concentration range.

$$\text{ARED} = \frac{1}{N} \sum \left( \frac{q_c - q_e}{q_e} \right) 100 \quad (10)$$

**Table 2** Linearized form, plots, slopes and intercepts of the used kinetic models.

Kinetic model	Linearized form	Plots	Slopes	Intercepts
Pseudo-first order	$\log(q_e - q_t) = \log(q_e) - \frac{k_t}{2.303} t$	$\log(q_e - q_t)$ vs $t$	$-\frac{k_t}{2.303}$	$\log(q_e)$
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_d q_e^2} + \frac{1}{q_e} t$	$\frac{t}{q_t}$ vs $t$	$\frac{1}{q_e}$	$\frac{1}{k_d q_e^2}$
Intra-particle diffusion	$q_t = k_d t^{1/2} + C$	$q_t$ vs $t^{1/2}$	$k_d$	$C$
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	$q_t$ vs $\ln(t)$	$\frac{1}{\beta}$	$\frac{1}{\beta} \ln(\alpha\beta)$

where  $N$  is the number of experimental data points,  $q_c$  (mg/g) is the theoretically calculated adsorption capacity at equilibrium and  $q_e$  (mg/g) is the experimental adsorption capacity at equilibrium.

#### 2.4.2. The sum of the squares of the errors (SSE)

Despite its wide use, this function has a major drawback. Indeed, the calculated isotherm parameters derived from such error function will provide a better fit at the higher end of the liquid-phase concentration range. This is because the magnitude of the errors and hence the square of the errors will increase as concentration increases.

$$SSE = \sum (q_c - q_e)^2 \quad (11)$$

#### 2.4.3. Marquardt's percent standard deviation (MPSED)

This error estimation tool was previously used by many researches in different research fields. It is similar to a geometric mean error distribution which was modified to allow for the number of degrees of freedom of the system.

$$MPSED = \sqrt{\frac{\sum \left[ \frac{(q_e - q_c)}{q_e} \right]^2}{N - P}} \cdot 100 \quad (12)$$

where  $P$  is the number of parameters in each isotherm model.

#### 2.4.4. The hybrid fractional error function (HYBRID)

This error function was developed in order to improve the fit of the SSE method at low concentration values. In this approach, each SSE value was divided by the experimental solid-phase concentration  $q_e$  value. Furthermore, a divisor was included as a term for the number of degrees of freedom for the system.

$$HYBRID = \frac{1}{N - P} \sum \left[ \frac{q_e - q_c}{q_e} \right] 100 \quad (13)$$

#### 2.4.5. Alternative statistical functions

In addition to the previously mentioned error equations, three other alternative statistical tests, namely Chi-square test,  $F$ -test and Student's  $T$ -test, are examined for their suitability to be appropriate functions to predict the best-fitting kinetic model.

### 3. Results and discussion

#### 3.1. Kinetic study

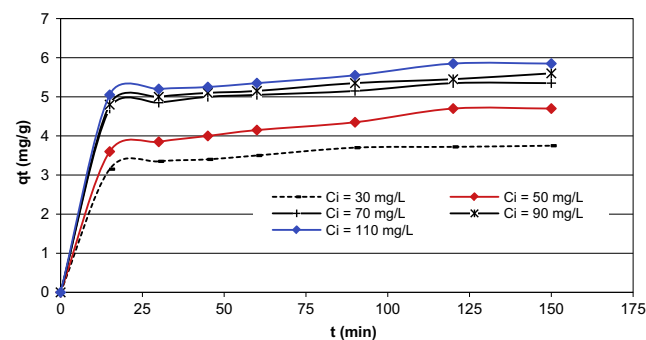
Experiments were undertaken to study the effect of varying initial concentrations (30–110 mg/L) on orthophosphate species removal onto date palm fibers. The experiments were

carried out at  $18 \text{ }^\circ\text{C} \pm 02$ , an adsorbent dose at 6 g/L, an agitation speed at 200 rpm and for a contact period of 240 min at  $\text{pH} = 5$ . The results show that adsorption process is clearly time dependent. It was observed that most of the orthophosphate species uptake occurs within a time of 30 min at 88.9% of the total sorption for an initial phosphate concentration of 110 mg/L (Fig. 1). For periods greater than 30 min, the uptake is further increased but with a much slower rate. Equilibrium began establishing itself after approximately a contact period of 120 min. This outcome is generally in line with previous similar studies such as the adsorption of orthophosphates onto some natural and low cost adsorbent, where the equilibrium time was evaluated to be about 1–2 h [17,18].

The orthophosphate species uptake increased with increasing initial phosphate concentration from 3.75 mg/g for 30 mg/L initial phosphate concentration to 5.85 mg/g for 110 mg/L initial phosphate concentration. This may be due to the fact that at a fixed adsorbent dose, the number of active adsorption sites to accommodate the adsorbate ion remains unchanged while with higher adsorbate concentrations, the adsorbate ions to be accommodated increase. Corresponding cumulative removal (mg/g) is higher at higher initial concentrations. This is attributable to an increase in contact between orthophosphate species and adsorbent at higher adsorbate concentrations [18,19].

#### 3.2. Adsorption kinetic modeling

Adsorption kinetic modeling is very useful for better understanding of phosphate adsorption mechanisms onto date palm fibers such as the importance of the chemical reactions and the intra-particle diffusion processes. To fit the obtained phosphate adsorption experimental data, we used the most well-known of them, namely the pseudo first-order, the pseudo



**Figure 1** Phosphate biosorption onto date palm fibers as a function of initial concentration (temperature at  $18 \text{ }^\circ\text{C} \pm 02$ , adsorbent dose at 6 g/L, agitation speed at 200 rpm and  $\text{pH}$  at 5).

second-order, the intra-particle diffusion model and the Elovich kinetic model. The experimental data were correlated with the linear forms of the four models, respectively. The derived rate constants together with the correlation coefficient  $R^2$  for the different initial concentrations of phosphates have been listed in Table 3. Fig. 2 displays the best-fitting results, also shown in the figures are the experimental data.

For the pseudo-first-order model, the correlation coefficients are relatively low lying between 0.68 and 0.89. In addition, the difference between experimental and theoretical adsorbed masses at equilibrium is very high. The experimental values are two to three times higher than the theoretical one. These results state a bad fit between the model and the experimental data. As a consequence, adsorption of phosphates onto date palm fibers is not an ideal pseudo-first-order reaction. For the pseudo-second-order model, the correlation coefficients for all initial phosphate concentrations are higher than 0.99. In addition, the difference between the experimental and theoretical adsorbed masses at equilibrium is very small (less than 1%). The equilibrium adsorption capacity,  $q_e$ , increases as the initial phosphate concentration,  $C_i$ , increased from 30 to 110 mg/L. For example, the values of  $q_e$  increased from 3.8 mg/g for 30 mg/L to 5.9 mg/g for 110 mg/L. Further, it was found that the variations of the rate constant,  $K_{II}$ , seem to have a decreasing trend with increasing initial phosphate concentration. These results show a good concordance between the experimental data and the pseudo-second-order kinetic model. The analysis of the adsorption of phosphorus onto date palm fibers with film and intra-particle diffusion models showed that the depicted two-phase plot suggests that the adsorption process proceeds by surface adsorption at the earlier stages and by intra-particle diffusion at later stages, especially, for the high aqueous concentrations. The correlation coefficients ( $R^2$ ) for the intra-particle diffusion model are between 0.63 and 0.75. It was observed that intra-particle rate constant values  $K_d$  increased with initial phosphate con-

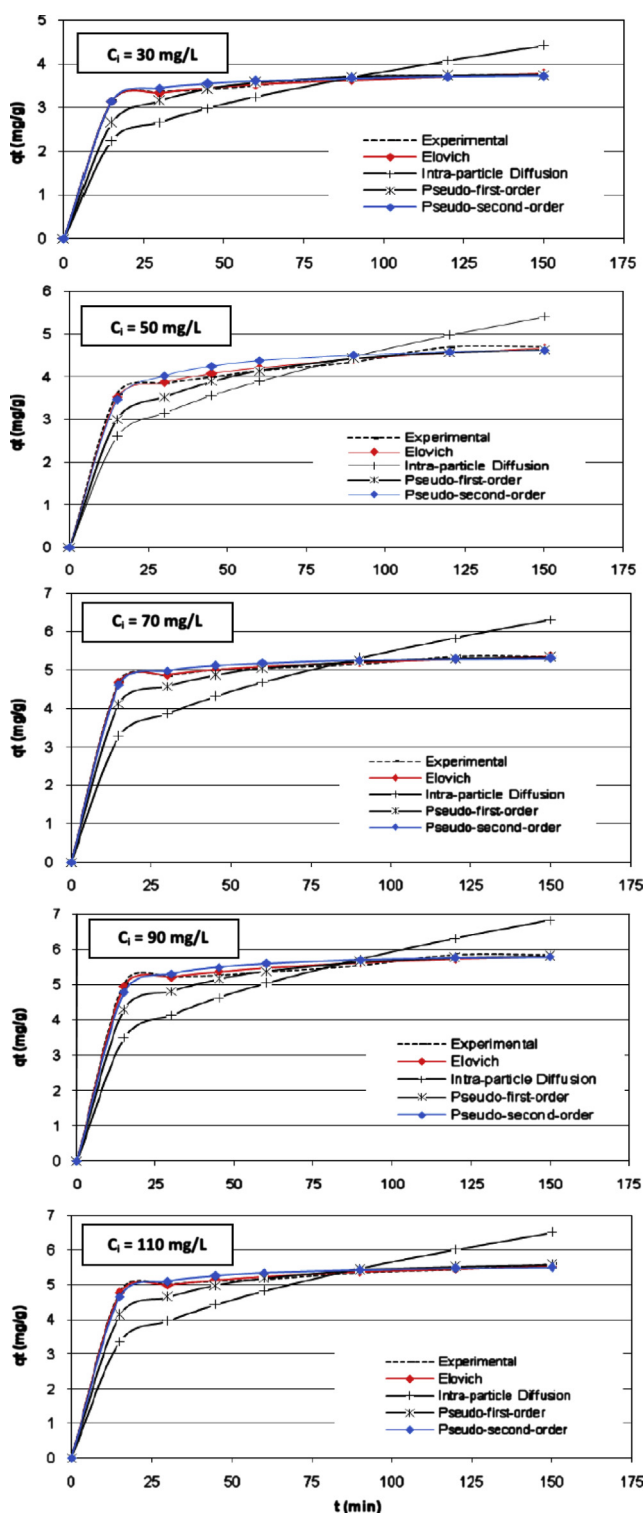
centration. The observed increase in  $K_d$  values with increasing initial phosphate concentration can be explained by the growing effect of driving force resulted in reducing the diffusion of orthophosphate species in the boundary layer and enhancing the diffusion in the solid. The average values of diffusion coefficients, for the studied phosphate aqueous concentrations,  $D_f$  and  $D_p$  are evaluated to be 0.0135 and  $0.0837E-11 \text{ m}^2 \text{ s}^{-1}$ , respectively. The values of diffusion coefficients indicate that for all the initial aqueous concentrations, the intra-particle diffusion coefficients are greater than those of the film diffusion through the boundary layer. This finding confirms that in case of date palm fibers, the film diffusion process controls significantly the rate of adsorption of phosphorus ions. This result is consistent with other phosphorus adsorption studies using phosphate mine wastes and *Posidonia oceanica* (L.) fiber adsorbents [18,20]. Table 3 lists also the kinetic constants obtained from the Elovich equation. It will be seen that the value of  $\alpha$  and  $\beta$  varied as a function of the initial phosphate concentration. Thus, on increasing the initial phosphate concentration from 30 to 110 mg/L, the values of  $\alpha$  and  $\beta$  have no significant variation. For the Elovich model, the correlation coefficients ( $R^2$ ) are relatively high lying between 0.9 and 0.97. It indicates that the Elovich model can also be suitable for describing the adsorption kinetic of phosphate onto date palm fibers.

A comparison of calculated and measured results for all initial phosphate concentrations is shown (Fig. 2). The pseudo first-order and intra-particle equations do not give a good fit to the experimental data for the phosphate adsorption onto date palm fibers. The Elovich equation provides the best correlation for all of the sorption process, whereas the pseudo second-order equation also fits the experimental data well. This suggests that the sorption systems studied belong to both the Elovich equation and the pseudo second-order kinetic model with experimental data and may be explained as below. The agreement of the pseudo second-order kinetic model with experimental data may be explained, based on the assumption

**Table 3** Kinetic parameters for the adsorption of phosphates onto date palm fibers.

	Initial phosphate concentrations (mg/L)				
	30	50	70	90	110
Experimental $q_e$ (mg/g)	3.75	4.7	5.35	5.6	5.85
<i>Pseudo first-order model</i>					
$K_I$ ( $\text{min}^{-1}$ )	0.040	0.034	0.030	0.028	0.026
$q_e$ (mg/g)	2.027	2.445	1.935	2.238	2.296
$R^2$	0.893	0.796	0.710	0.719	0.682
<i>Pseudo second-order model</i>					
$K_{II}$ (g/(mg.min))	0.083	0.075	0.072	0.057	0.047
$q_e$ (mg/g)	3.805	4.807	5.402	5.614	5.920
$R^2$	0.998	0.995	0.999	0.998	0.997
<i>Intra-particle diffusion model</i>					
$K_d$ ( $\text{mg}/(\text{g min}^{0.5})$ )	0.258	0.333	0.360	0.375	0.396
$D_f$ ( $\text{m}^2/\text{s}$ ) ( $\times 10^{-11}$ )	0.0136	0.0146	0.0132	0.0129	0.0132
$D_p$ ( $\text{m}^2/\text{s}$ ) ( $\times 10^{-11}$ )	0.1043	0.0745	0.0925	0.0708	0.0767
$R^2$	0.671	0.752	0.634	0.648	0.658
<i>Elovich model</i>					
$\alpha$ (mg/g min)	1726.6	35.6	144979.9	32426.8	15043.7
$\beta$ (g/mg)	3.644	1.980	3.386	2.981	2.692
$R^2$	0.974	0.961	0.974	0.971	0.904





**Figure 2** Comparison between the measured and modeled time profiles for phosphate adsorption.

that the rate limiting step, as chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate [21,22]. The agreement of the Elovich equation with experimental data may be explained as below. The previous successful application of the Elovich equation to heterogeneous catalyst surfaces helps

to explain its success in predicting the adsorption of phosphates onto date palm fibers. The general explanation for this form of kinetic law involves a variation of the energetics of chemisorption with the active sites that are heterogeneous date palm fibers (DPF) and therefore, exhibit different activation energies for chemisorption [23] because the cell walls of DPF mainly consist of cellulose and lignin, and many hydroxyl groups, such as tannins or other phenolic compounds [15]. Elovich model gives a good correlation for adsorption on highly heterogeneous surfaces and also it shows that along with surface adsorption chemisorption is also a dominant phenomenon taking place. But, in a highly heterogeneous system along with surface adsorption, chemisorptions, ion exchange, precipitation and intra-particle diffusion are occurring concurrently. It was not possible to find which process was dominant. In the case of using the Elovich equation, the correlation coefficients are lower than those of the pseudo second-order equation. The Elovich equation does not predict any definite mechanism, but it is useful in describing adsorption on highly heterogeneous adsorbents. The adsorption system obeys the pseudo second-order kinetic model for the entire adsorption period and thus supports the assumption behind the model that the adsorption is due to chemisorption. These results imply that chemisorption mechanism may play an important role for the adsorption of phosphate onto raw date palm fibers. The adsorption of phosphates onto date palm fibers takes place probably via surface exchange reactions until the surface functional sites are fully occupied; thereafter phosphate molecules diffuse into date palm fiber pores confirmed by TEM analysis for further interactions and/or reactions such as ion-exchange, complexation interactions [19,23,15]. Thus, the adsorption of phosphates onto date palm fibers is very well described by the pseudo-second-order model. This result is consistent with other studies related to phosphate removal by adsorption [20,24] and electrocoagulation process [25,26].

### 3.3. Applicability of some statistical tools to predict optimum phosphate adsorption kinetic

Adsorption kinetic data are the basic requirements for the design of adsorption systems. In order to optimize the design of a specific sorbate/sorbent system to remove phosphates from aqueous solution, it is important to establish the most appropriate correlation for the experimental kinetic data. Applicability of some statistical tools to predict optimum adsorption kinetic of phosphates onto date palm fibers after linear regression analysis showed that ARED, SSE, MSPED, HYBRID,  $F$ -test,  $\chi^2$ -test and Student's  $T$ -tests could be suitable and meaningful tools to predict best-fitting equation models. This suggests that the sorption systems studied belong to both the Elovich equation followed by pseudo second-order kinetic model.

#### 3.3.1. Error estimation using commonly used functions

Among the four studied kinetic models, the best fitting one is determined based on the use of four well known functions to calculate the error deviation between experimental and predicted equilibrium adsorption kinetic data, after linear analysis. Hence, according to Table 4, it seems that the Elovich model and pseudo-second order model were the most suitable models to satisfactorily describe the studied

**Table 4** Kinetic error deviation data related to the biosorption of phosphates onto date palm fibers using commonly used functions.

Initial phosphates concentration	Error functions			
	$C_i = 30 \text{ mg/L}$			
Kinetic models	ARED	SSE	MSPED	HYBRID
Pseudo first-order	2.8435861	0.294983	7.636315866	5.03415486
Pseudo second-order	1.782665114	0.047567	2.847572651	2.49573116
Intra- particle diffusion	13.74819794	2.102228	19.28117865	19.24747712
Elovich	<b>0.759938214</b>	<b>0.007833</b>	<b>1.102283992</b>	<b>1.0639135</b>
	$C_i = 50 \text{ mg/L}$			
Pseudo first-order	4.872852214	0.500579	8.554164483	6.8219931
Pseudo second-order	4.017358686	0.21319	5.089321173	5.62430216
Intra-particle diffusion	12.42534464	2.340572	17.50713712	17.3954825
Elovich	<b>1.582400371</b>	<b>0.03997</b>	<b>2.107749985</b>	<b>2.21536052</b>
	$C_i = 70 \text{ mg/L}$			
Pseudo first-order	3.407183043	0.438776	6.240260411	4.77005626
Pseudo second-order	1.873163514	0.068653	2.350174462	2.62242892
Intra-particle diffusion	14.54877369	4.788973	19.93528279	20.36828316
Elovich	<b>0.578820542</b>	<b>0.009208</b>	<b>0.832033653</b>	<b>0.81034876</b>
	$C_i = 90 \text{ mg/L}$			
Pseudo first-order	3.965258429	0.608462	7.177336553	5.5513618
Pseudo second-order	2.170246957	0.105188	2.842945655	3.03834574
Intra-particle diffusion	14.19880813	4.884312	19.63331582	19.87833138
Elovich	<b>0.6444186</b>	<b>0.012845</b>	<b>0.965971014</b>	<b>0.90218604</b>
	$C_i = 110 \text{ mg/L}$			
Pseudo first-order	4.111129986	0.744777	7.571087769	5.75558198
Pseudo second-order	3.074063957	0.227388	4.046961823	4.30368954
Intra-particle diffusion	13.79954669	5.215169	19.42851152	19.31936536
Elovich	<b>1.529880657</b>	<b>0.057375</b>	<b>1.971796136</b>	<b>2.07721752</b>

The lowest ARED, SSE, MSPED and HYBRID values are in bold.

adsorption phenomenon. Indeed, the lowest ARED, SSE, MSPED and HYBRID values were found when modeling the kinetic data using the Elovich and pseudo-second order models. Such trend was previously proven by other researchers for the equilibrium studies of isotherm curves [27,28]. Therefore, based on these mentioned results, the best useful error estimation statistical tools should point out the Elovich followed by pseudo-second order as the best-fitting models. In that context, it has to be mentioned that ARED, SSE, MSPED and HYBRID are the most suitable and meaningful tools to predict best-fitting equation when investigated models do not contain the same number of inner parameters [28].

### 3.3.2. Error estimation using alternative statistical tools

The results, given by Table 5, showed that  $F$ -test,  $\chi^2$ -test and Student's  $T$ -tests are suitable to adequately determine the best-fitting kinetic model. Indeed, among the three investigated tools, only those statistical tests were able to point out the Elovich model as the most appropriate one to satisfactorily fit the studied adsorption kinetic of phosphates onto date palm fibers. Except for the initial phosphate concentration of 50 mg/L and 70 mg/L, both  $\chi^2$  and Student's  $T$ -tests were suitable to determine the most appropriate fitting-model for all initial phosphate concentrations, which is also the Elovich. On the other hand, the results showed that the  $F$ -test seems to be adequate to point out the best-fitting kinetic model, which is the pseudo-second order kinetic model.

### 3.4. Adsorption mechanism

Previous results from orthophosphate adsorption kinetic experiments agreeing with the pseudo-second-order equation suggested a chemisorption process [18,29]. The attachment of orthophosphates must occur at the active sites on the surface of the date palm fibers. Therefore, the adsorption of orthophosphate species can be reasonably speculated to occur in two steps: (i) transfer of orthophosphate from the aqueous solution to the sites on the adsorbent; (ii) chemical complexation/ion exchange at the active sites and precipitation on the adsorbent surface.

To highlight the mechanism of ion exchange in the case of the adsorption of orthophosphates onto date palm fibers (DPF), EDS analyses were carried out before and after the adsorption process [19]. This finding indicates that the process of ion exchange between the surface of fibers and orthophosphate ions present in aqueous solution may be one of the main processes involved for the adsorption of orthophosphate onto date palm fibers.

The ligand exchange between orthophosphate species and sulfide groups of hemicelluloses [18,30], can be realized according to the following reaction:



On the other hand, the ionized O-H group of "free" hydroxyl groups and bonded O-H bands of carboxylic acids in the inter- and intra-molecular hydrogen bonding of polymeric

**Table 5** Kinetic error deviation estimation related to the biosorption of phosphates onto date palm fibers using alternative statistical tools.

Error functions			
Initial phosphates concentration	$C_i = 30 \text{ mg/L}$		
Kinetic models	$F$ -test	$\chi^2$ test	Student's $T$ -test
Pseudo first-order	0.185120056	0.999974545	0.316821579
Pseudo second-order	0.822085563	0.99999995	0.191831713
Intra-particle diffusion	0.008323812	0.993267598	0.431678883
Elovich	<b>0.97557353</b>	<b>1</b>	<b>0.959975476</b>
$C_i = 50 \text{ mg/L}$			
Pseudo first-order	0.400231077	0.999923508	0.099387163
Pseudo second-order	0.973482113	0.999997358	0.324692833
Intra-particle diffusion	0.051394711	0.993957049	0.431252355
Elovich	<b>0.963817063</b>	<b>0.999999982</b>	<b>0.992910575</b>
$C_i = 70 \text{ mg/L}$			
Pseudo first-order	0.168431528	0.99997785	0.13772911
Pseudo second-order	0.980047211	0.999999949	0.311608021
Intra-particle diffusion	0.002033311	0.976857619	0.430289742
Elovich	<b>0.97534179</b>	<b>1</b>	<b>0.970463589</b>
$C_i = 90 \text{ mg/L}$			
Pseudo first-order	0.140402278	0.999943072	0.216282204
Pseudo second-order	0.863704993	0.999999826	0.399304647
Intra-particle diffusion	0.003312697	0.976847814	0.430727769
Elovich	<b>0.972930725</b>	<b>1</b>	<b>0.981242391</b>
$C_i = 110 \text{ mg/L}$			
Pseudo first-order	0.201920245	0.999907509	0.148730461
Pseudo second-order	0.820179418	0.999998396	0.565387414
Intra-particle diffusion	0.005229494	0.97463145	0.431843179
Elovich	<b>0.907221882</b>	<b>0.999999976</b>	<b>0.991124238</b>

The highest  $F$ -test,  $\chi^2$  test and Student's  $T$ -test values are in bold.

**Table 6** Comparison of phosphorus adsorption onto DPF with other natural adsorbents.

Material	$C_i$ (mg P/L)	Adsorption capacity (mg P/g)	Refs.
Posidonia fibers	15–100	7.45	[18]
Graphene	100	89.37	[24]
Apatite	0–500	4.76	[35]
Calcite	–	1.9	[36]
Dolomite	0–100	0.168	[37]
Sand	0–100	0.417	[38]
Wood fibers	0–100	4.3	[39]
Bauxite	0–100	2.95	[40]
Zeolite	500–10.000	2.15	[41]
Date palm fibers	30–110	5.85	This study

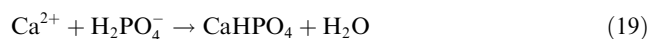
compounds, such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin [18,30], can also be involved in the ligand exchange process, according to the following reactions:



Furthermore, the presence of the Al–OH and Fe–OH functional groups could contribute to the adsorption of orthophosphate as described by [18,31]:



Also, the removal of orthophosphate is accompanied by a decrease in the  $\text{Ca}^{2+}$  ion concentration [18,32] which may lead to the precipitation of calcium orthophosphate, according to the following reaction:



In addition to ion exchange, the formation of complexes between orthophosphate ion species in solution and functional



groups of date palm fibers, confirmed by FTIR analysis [19], could also play a role in biosorption. Since plant fibers consist mainly of cellulose, hemicelluloses, lignin, pectin and extractives, ions sorb mainly to carboxylic (primarily present in hemicelluloses, pectin and lignin), to some extent hydroxylic (cellulose, hemicelluloses, lignin, extractives and pectin) and carbonyl groups (lignin, pectin) [33,34].

### 3.5. Comparison with other adsorbents

The application of low-cost and easily available materials in wastewater treatment has been widely investigated during recent years. Particularly, the phosphate adsorption on different materials has been widely studied during recent years. In order to situate our natural adsorbent among those used to remove orthophosphate from aqueous solutions, a comparison based on adsorption capacity (mg/g) was made. The results, illustrated in Table 6, had shown that the date palm fibers (DPF) could be considered as a promising material to remove orthophosphate when compared with the common natural mineral and lingo-cellulosic materials. The adsorption capacity of date palm fibers is higher than mineral materials such as apatite [35], calcite [36], dolomite [37] and sand [38] and lower than grapheme [24]. In comparison with other lingo-cellulosic fibers the adsorption capacity of date palm fibers is higher than wood fiber [39]. Thus, raw date palm fibers could be considered among the most efficient natural material for the removal of orthophosphate species.

### 3.6. Prospect of using date palm fiber adsorbents

The results reported herein indicate that date palm fibers could be successfully used to remove orthophosphates from aqueous solution by sorption process. The regeneration of the saturated date palm fibers with orthophosphates does not required while the agronomic reuse is possible. Thus, desorption and recovery processes could be avoided and the related costs reduced. Consequently, for environmental, economic and operational considerations, the use of date palm fibers for the removal of orthophosphates and other nutrients appears to be more interesting. In addition, orthophosphates in wastewater represents a considerable renewable resource ready for technological exploitation comparable with the requirements of the orthophosphate industry and there is no environmental or technical reason which impedes recycling of orthophosphates. Certainly, there are many potential environmental benefits such as reducing reliance on phosphate rock and its associated impurities. Currently, phosphate resources are limited and there have been some alarming reports that deposits of high grade phosphate ores are likely to be depleted in the next few decades. Thus, it is very important to develop a recovery process of orthophosphates from wastewater as alternative resources to compensate for such global exhaustion of high grade phosphate ores. Consequently, the removal of orthophosphates from wastewater by date palm fibers can be an effective method for its recovery and control of eutrophication in lakes and similar confined water bodies and reduce application of chemical fertilizer [18].

Date palm fibers are one of ligno-cellulosic waste materials that are available in abundance, renewable and low-cost. The

low cost and the simplicity of the current treatment system and the abundance of date palm fibers in arid or semi-arid regions like southern of Tunisia allow the application of this technique for the removal of phosphates from industrial wastewater and for the treatment of gray wastewater from hotels for example which could be reused for flushing toilets as useful strategy for saving water and for watering the green and the garden area.

## 4. Conclusion

The adsorption kinetic of phosphates onto date palm fibers was studied by using pseudo first-order and pseudo second-order equations, intra-particle diffusion equation and the Elovich equation. The sorption kinetic of phosphates was studied as a function of initial phosphate concentration. For all initial phosphate concentration values, Elovich equation model provided the best correlation of the experimental data. This supports the heterogeneous sorption mechanism likely to be responsible for phosphate uptake. The sorption of phosphates onto date palm fibers can also be successfully interpreted by the pseudo second-order equation. This kinetic model is based on the sorption capacity on the solid-phase and is in agreement with a chemisorption mechanism being the rate controlling step. All findings presented in this study suggest that phosphates/date palm fiber systems cannot be described by a first-order reaction and intra-particle diffusion model. Two kinetic models have been used extensively to describe the sorption of phosphates onto date palm fibers. The examination of all these error estimation methods showed that both the Elovich and the pseudo-second order model provide the best fit for the experimental equilibrium data. Finally, the low cost, availability and high adsorption capability of the date palm fibers make them promising and potentially attractive biosorbents for orthophosphate species and may be a friendly material to the environment because of its potential application to acid soil fertilization in arid climate such as southern Tunisia. Further tests should be carried out on the modeling of phosphate removal in CSTR and dynamic mode.

## References

- [1] W.H. Barreveld, Date palm products, FAO Agricultural Services Bulletin No. 101, Food and Agriculture Organization of the United Nations, Rome, 1993.
- [2] K. Riahi, A.B. Mammou, B.B. Thayer, Date-palm fibers media filters as a potential technology for tertiary domestic wastewater treatment, *J. Hazard. Mater.* 161 (2009) 608–613.
- [3] M. Khiyami, I. Masmali, M. Abu-khuraiba, Composting a mixture of date palm wastes, date palm pits, shrimp, and crab shell wastes in vessel system, *Saudi J. Biol. Sci.* 15 (2008) 199–205.
- [4] L.E. Bashan, Y. Bashan, Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003), *Water Res.* 38 (2004) 4222–4246.
- [5] O. Oenema, L. Van Liereb, O. Schoumansa, Effects of lowering nitrogen and phosphorus surpluses in agriculture on the quality of groundwater and surface water in the Netherlands, *J. Hydrol.* 4 (2005) 289–301.
- [6] A. Kontas, F. Kucuksezgin, O. Altay, E. Uluturhan, Monitoring of eutrophication and nutrient limitation in the Izmir Bay (Turkey) before and after wastewater treatment plant, *Environ. Int.* 29 (2004) 1057–1062.

- [7] L. Ruixia, G. Jinlong, T.J. Hongxiao, Adsorption of fluoride, phosphate, and arsenate ions on a new type of ion exchange fiber, *J. Colloid Interface Sci.* 248 (2002) 268–274.
- [8] H.D. Stensel, Principles of biological phosphorus removal, in: R.I. Sedlak (Ed.), *Phosphorus and Nitrogen Removal from Municipal Wastewater—Principles and Practice*, second ed., H.K. Lewis, London, 1991, p. 141.
- [9] S. Vasudevan, M.A. Oturan, Electrochemistry: as cause and cure in water pollution – an overview, *Environ. Chem. Lett.* (2013), <http://dx.doi.org/10.1007/s10311-013-0434-2>.
- [10] G.N. Anastassakis, K.K. Karageorgiou, M. Paschalis, Removal of phosphate species from solution by flotation, in: I. Gaballah, B. Mishra, R. Solozabal, M. Tanaka (Eds.), *REWAS'04-Global Symposium on Recycling, Waste Treatment, Clean Technology, TMS-INASMET*, 2004, pp. 1147–1154.
- [11] J.P. Boisvert, T.C. To, A. Berrak, C. Jolicoeur, Phosphate adsorption in flocculation processes of aluminium sulphate and polyaluminium-silicate-sulphate, *Water Res.* 31 (1997) 1939–1946.
- [12] A.I. Omoike, G.W. Vanloon, Removal of phosphorus and organic matter removal by alum during wastewater treatment, *Water Res.* 33 (1999) 3617–3627.
- [13] *Standard Methods for the Examination of Water and Wastewater*, 19th ed., APHA, AWWA, WPCF, Washington, DC, 1995.
- [14] M. Ozacar, I.A. Sengil, Application of kinetic models to the sorption of disperse dyes onto alunite, *Colloids Surf. A* 242 (2004) 105–113.
- [15] A. Ornek, M. Ozacar, I.A. Sengil, Adsorption of lead onto formaldehyde or sulphuric acid treated acorn waste: equilibrium and kinetic studies, *Biochem. Eng. J.* 37 (2007) 192–200.
- [16] T. Karthikeyan, S. Rajgopal, L.R. Miranda, Chromium (VI) adsorption from aqueous solution by *Hevea brasiliensis* sawdust activated carbon, *J. Hazard. Mater.* B124 (2005) 192–199.
- [17] B.K. Biswas, K. Inoue, K.N. Ghimire, S. Ohta, H. Harada, K. Ohto, H. Kawakita, The adsorption of phosphate from an aquatic environment using metal-loaded orange waste, *J. Colloid Interface Sci.* 312 (2007) 214–223.
- [18] M.A. Wahab, R. Ben Hassine, S. Jellali, *Posidonia oceanica* (L.) fibers as a potential low-cost adsorbent for the removal and recovery of orthophosphate, *J. Hazard. Mater.* 191 (2011) 333–341.
- [19] K. Riahi, B.B. Thayer, A.B. Mammou, A.B. Ammar, M.H. Jaafoura, Biosorption characteristics of phosphates from aqueous solution onto *Phoenix dactylifera* L. date palm fibers, *J. Hazard. Mater.* 170 (2009) 511–519.
- [20] S. Jellali, M.A. Wahab, R. Ben Hassine, A.H. Hamzaoui, L. Bousselmi, Adsorption characteristics of phosphorus from aqueous solutions onto phosphate mine wastes, *Chem. Eng. J.* 169 (2011) 157–165.
- [21] M.C. Ncibi, B. Mahjoubi, M. Seffen, Investigation of the sorption mechanisms of metal-complexed dye onto *Posidonia oceanica* (L.) fibres through kinetic modelling analysis, *Bioresour. Technol.* 99 (2008) 5582–5589.
- [22] S. Jellali, M.A. Wahab, M. Anane, K. Riahi, N. Jedidi, Biosorption characteristics of ammonium from aqueous solutions onto *Posidonia oceanica* (L.) fibers, *Desalination* 270 (2011) 40–49.
- [23] M. Özacar, I.A. Sengil, A kinetic study of metal complex dye sorption onto pine sawdust, *Process Biochem.* 40 (2005) 565–572.
- [24] S. Vasudevan, J. Lakshmi, The adsorption of phosphate by graphene from aqueous solution, *RSC Adv.* 2 (2012) 5234–5242.
- [25] S. Vasudevan, G. Sozhan, S. Ravichandran, J. Jayaraj, J. Lakshmi, S.M. Sheela, Studies on the removal of phosphate from drinking water by electrocoagulation process, *Ind. Eng. Chem. Res.* 47 (2008) 2018–2023.
- [26] S. Vasudevan, J. Lakshmi, G. Sozhan, Optimization of the process parameters for the removal of phosphate from drinking water by electrocoagulation, *Desalination Water Treat.* 12 (1–3) (2009) 407–414.
- [27] J.C.Y. Ng, W.H. Cheung, G. McKay, Equilibrium studies for the sorption of lead from effluents using chitosan, *Chemosphere* 52 (2003) 1021–1030.
- [28] M.C. Ncibi, Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis, *J. Hazard. Mater.* 153 (2008) 207–212.
- [29] L.G. Yan, Y.Y. Xu, H.Q. Yu, X.D. Xin, Q. Wei, B. Du, Adsorption of phosphorus from aqueous solution by hydroxy-aluminum, hydroxy-iron and hydroxy-iron–aluminum pillared bentonites, *J. Hazard. Mater.* 179 (2010) 244–250.
- [30] K. Adam, T. Krogstad, L. Vrale, A.K. Sovik, P.D. Jenssen, Phosphorus retention in the filter materials shellsand and Filtralite P (R)–batch and column experiment with synthetic P solution and secondary wastewater, *Ecol. Eng.* 29 (2007) 200–208.
- [31] Y. Xue, H. Hou, S. Zhu, Characteristics and mechanisms of phosphorus adsorption onto basic oxygen furnace slag, *J. Hazard. Mater.* 162 (2009) 973–980.
- [32] S.G. Lu, S.Q. Bai, L. Zhu, H.D. Shan, Removal mechanism of phosphorus from aqueous solution by fly ash, *J. Hazard. Mater.* 161 (2009) 95–101.
- [33] G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, *Prog. Polym. Sci.* 30 (2005) 38–70.
- [34] M.A. Wahab, S. Jellali, N. Jedidi, Ammonium biosorption onto sawdust: FTIR analysis, kinetics and adsorption isotherms modelling, *Bioresour. Technol.* 101 (2010) 5070–5075.
- [35] P. Molle, A. Lienard, A. Grasmick, A. Iwema, A. Kabbabi, Apatite as an interesting seed to remove phosphorus from wastewater in constructed wetlands, *Water Sci. Technol.* 51 (9) (2005) 193–203.
- [36] K. Karageorgiou, M. Paschalis, G.N. Anastassakis, Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent, *J. Hazard. Mater.* A 139 (2007) 447–452.
- [37] C.A. Prochaska, A.I. Zouboulis, Removal of phosphate by pilot vertical-flow constructed wetlands using a mixture of sand and dolomite as substrate, *Ecol. Eng.* 26 (2006) 293–303.
- [38] M. Del Bubba, C.A. Arias, H. Brix, Phosphorus adsorption maximum of sands for use as media in subsurface flow constructed reed beds as measured by the Langmuir isotherm, *Water Res.* 37 (2003) 3390–3400.
- [39] T.L. Eberhardt, S.H. Min, J.S. Han, Phosphate removal by refined aspen wood fiber treated with carboxymethyl cellulose and ferrous chloride, *Bioresour. Technol.* 97 (2006) 2371–2376.
- [40] H.S. Altundogan, F. Tümen, Removal of phosphorus from aqueous solutions by using bauxite. 1. Effect of pH on the adsorption of various phosphates, *J. Chem. Technol. Biotechnol.* 77 (2002) 77–85.
- [41] K. Sakadevan, H.J. Bavor, Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems, *Water Res.* 32 (1998) 393–399.