



Posidonia oceanica (L.) fibers as a potential low-cost adsorbent for the removal and recovery of orthophosphate

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ABSTRACT

Adsorption efficiency of orthophosphate from aqueous solution onto *Posidonia oceanica* fibers (POF) as a raw, natural and abundant material was investigated and compared with other common natural materials. A series of batch tests were undertaken to assess the effect of the system variables, i.e. initial aqueous orthophosphate concentration, contact time, adsorbent dosage, pH and temperature. Results indicate that orthophosphate uptake increased with increasing initial orthophosphate concentration, temperature and adsorbent dosage and decreased with increasing pH values. The maximum adsorption capacity (Q_m) determined from the Langmuir isotherm was calculated to be 7.45 mg g^{-1} for the studied orthophosphates concentration range of $15\text{--}100 \text{ mg L}^{-1}$, pH 7; adsorbent dosage of 2 g L^{-1} and temperature of $20 \pm 2^\circ\text{C}$. The adsorption data were very well described by the pseudo-second order model predicting a chemisorption process. The energy dispersive spectroscopy (EDS) and FTIR analysis before and after adsorption of orthophosphate onto POF showed that the main involved mechanisms are ligand exchange between orthophosphate and Cl^- , SO_4^{2-} and OH^- and precipitation with calcium. In comparison with other natural adsorbents, raw POF could be considered as one of the most efficient natural materials for the removal of orthophosphate with the possibility of agronomic reuse.

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1. Introduction

Phosphorus is an essential nutrient for all forms of life and cannot be replaced by any other element. However, the wide use of phosphorus inevitably results in large amounts of orthophosphate-bearing wastes, which are usually discharged into municipal and industrial water effluent streams [1]. Therefore, the release of orthophosphate from anthropogenic sources such as municipal wastewater, runoff from agricultural areas and landfill leachate to lakes, rivers, and coastal areas constitutes the main risk for reduced water quality deterioration and eutrophication [2]. In the same time, phosphate deposits with high-grade ores are likely to be depleted in the next few decades. Thus, in order to reduce the negative effects of overloading the ecosystems with orthophosphate as well as reducing the high costs that accompany the mining and processing of phosphate and to find alternative resources of phosphate, it is necessary to investigate various techniques and materials that could contribute to the removal as well as recycling of orthophosphate.

Various physical, chemical and biological treatment processes have been developed to remove orthophosphate from water. Physical processes such as reverse osmosis, electro dialysis and contact filtration have the drawback of high costs [2–4]. Since biological processes require highly skilled operation techniques regarding microbial adaptation, and strict anaerobic and aerobic conditions, it is very difficult to operate the process stably in the actual orthophosphate removal treatment plants [5]. The precipitation, which is the most widely used chemical process for orthophosphate removal, using lime, alum or iron salts requires a large amount of chemicals and produces a great quantity of waste sludge [4]. Therefore, adsorption technique using solid adsorbents, could find a wide application in orthophosphate removal due to its high efficiency, relatively inexpensive operation and potential for saving and recycling orthophosphate resources. In recent years, considerable attention has been paid to the development of effective and low-cost adsorbents from natural materials such as apatite [6,7], bauxite [8], dolomite [9], gravels [10], Limestone [11], Shellsand [12] and zeolite [13]. However, chemicals and thermal procedure are needed for the desorption of orthophosphate from these mineral materials which lead to the increase of the operational adsorption costs. Thus, the use of biodegradable materials such as plant residues seems to be more advantageous to ensure both the removal of orthophosphate from wastewater and the possibility of recycling the resulting complex biodegradable

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material-orthophosphate in agriculture as organic fertilizer which may also reduce the use of chemical fertilizer and their environmental risks. Wahab et al. [14] showed that the use of these abundant, renewable and eco-friendly materials as inexpensively alternative adsorbents for the removal of nutrients would be beneficial to the environment and have attractive agricultural value. Indeed, the biodegradability of these materials would allow utilization of these saturated adsorbents with nutrients as compost and fertilizer. Thus desorption and recovery processes could be avoided and the related costs be reduced [14,15].

In fact, plant materials are the most abundant and renewable wastes in the world. These wastes can be found in great amount and may cause many environmental and socio-economic problems for many countries. *Posidonia oceanica* fibers (POF) is one of these most abundant plant wastes found in all coastal zones of Mediterranean Basin [16]. Starting from September–October, leaves and part of rhizomes detach off the marine plant (*Posidonia oceanica*) and reach the beaches. Onshore residues represent a great environmental, economical, social and hygienic problem in all coastal zones of Mediterranean Basin because of the great disturb to the bathers and population, and the high costs for their removal and disposal to landfill. Indeed, the uncontrolled decomposition of *posidonia* organic residues causes, beside unpleasant and anaesthetic aspects, the release of hydrogen sulphide and the development of beach flies, thus reducing the potential utilization of coast and beaches for recreational and touristy purposes [17]. As consequence, huge quantities of POF are either transported in landfills, or possibly buried, which result in the loss of enormous mass of organic material [16]. In order to manage all these environmental and socio-economic problems in coastal zones of Mediterranean Basin, we have developed a promising strategy which proposes alternative solutions to the landfill and to reutilize these plant wastes in agricultural applications (as organic fertilizer to substitute chemical fertilizer), and at the same time ensure the removal and the recovery of orthophosphate from wastewater.

Our purpose is to make out of these dead POF, which pose a problem in all Mediterranean countries, a useful tool to preserve the environment as a novel non-conventional adsorbent for the removal of orthophosphate.

The main focus of this study was to evaluate the adsorption aptitude of this low cost and renewable biomass for the removal of orthophosphate in batch mode by investigating the effect of the key process parameters such as initial aqueous orthophosphate concentration, contact time, adsorbent dosage, pH, temperature and the competing effect of other anions. Moreover, kinetic and equilibrium models were used to fit experimental data. Physicochemical properties of POF before and after adsorption were also studied to determine the adsorption mechanisms involved in the removal of orthophosphate and to characterize the complex POF–orthophosphate.

2. Materials and methods

2.1. Adsorbent and orthophosphate solution preparation

POF were collected from Borj Cedria beach (North Eastern coast of Tunisia). The fibers were manually separated, washed with distilled water to remove the surface-adhered particles and then dried in an oven at 40 °C for 48 h, to a constant weight. The dried fibers were converted into fine powder by grinding with a mechanical grinder. The powder was sieved and the size fraction lower than 150 μm was used in this study.

Wahab et al. [16] have investigated the physicochemical characteristics of POF and have indicated that POF as a vegetal biomaterial, constituted principally by lignin and cellulose as major con-

stituents, can be viewed as natural ion-exchange materials that primarily contain weak acidic and basic groups on the surface. The pH of POF was estimated at about 7.6. The raw POF conductivity and DCO are about 12.2 dS m⁻¹ and 23.3 mg L⁻¹, respectively. The POF was washed many times to remove both soluble organic compounds and salts contained in POF. Ash and moisture content of dry POF are about 1.8% and 16%, respectively. The retention and absorption capacities of water by POF are 12.6 g g⁻¹ and 4.56 g g⁻¹, respectively.

The orthophosphate stock solution containing 1000 mg L⁻¹ was prepared by (KH₂PO₄). Orthophosphate working solutions in different concentrations were prepared by diluting the orthophosphate stock solution with distilled water. The initial pH was adjusted to the desired value using 0.1 N HCl or NaOH.

2.2. Batch adsorption experiments

Batch adsorption tests were carried out to determine the effect of initial aqueous orthophosphate concentration, contact time, adsorbent dosage, pH of solutions, and temperature on orthophosphate adsorption by POF. The adsorption experiments were conducted by agitating 0.2 g of POF powder with 100 mL of synthetic orthophosphate solution at the desired concentration and pH. The flasks were capped and agitated with a magnetic stirrer at 400 rpm for 90 min to ensure equilibrium between orthophosphate and biomass. Solutions of different initial concentrations 15; 30; 50; 80 and 100 mg L⁻¹ were used to investigate the effect of concentration on orthophosphate removal by shaking 0.2 g of adsorbent in 100 mL of solution for 90 min. Various masses (0.2, 0.5, 0.8, 1, 1.5 and 2 g) of adsorbent were shaken continuously with 100 mL of 15 mg L⁻¹ at pH 7.0 for 90 min in order to investigate the effect of the adsorbent dosage on orthophosphate removal. To determine the initial aqueous solution pH effect on orthophosphate adsorption, 0.2 g of adsorbent were shaken continuously with 100 mL of 15 mg L⁻¹ for 90 min at initial pH values of 3, 5, 7, 9 and 11. The effect of temperature was investigated at 20, 30, 40, 50 and 60 °C in a constant temperature shaker bath by agitating 0.2 g of adsorbent in 100 mL of 15 mg L⁻¹ at pH 7.0 for 90 min. In order to assess the competing effect of other anions on orthophosphate removal by POF, batch adsorption tests of orthophosphate (15 mg L⁻¹) were also carried out by addition of other anions such as chloride (303; 910 and 1517 mg L⁻¹) and sulphate (150; 750; 1100 and 1500 mg L⁻¹) at pH 7.0 for 90 min.

At each contact time, the suspension was filtered through 45 μm filter paper and the filtrate was analyzed by spectrophotometric measurement at 880 nm, following the ascorbic acid method [18], in order to determine dissolved orthophosphate concentration. Triplicate tests showed that the standard deviation of the results was ±3%. The initial aqueous concentration C_0 (mg L⁻¹) and leftover orthophosphate concentration at different time intervals, C_t (mg L⁻¹), were measured and the orthophosphate uptake Q_t (mg g⁻¹) was calculated from mass balance equation as follows:

$$Q_t = \frac{(C_0 - C_t)V}{M} \quad (1)$$

where V is the volume of the aqueous solution (L) and M is the dry weight of the used adsorbent (g).

The adsorption efficiency in percentage is calculated from the following relation:

$$\text{Adsorption removal efficiency (\%)} = \frac{(C_0 - C_t) \times 100}{C_0} \quad (2)$$

2.3. Physicochemical properties of POF

The elemental composition of the POF was achieved by energy dispersive spectroscopy (EDS) using a Quanta-200-Fei apparatus.

Table 1
The most popular kinetic model and their linear forms.

Model	Equation	Linear form
Pseudo-first-order	$\frac{dQ_t}{dt} = k_1(Q_e - Q_t)$ (3)	$\ln(Q_e - Q_t) = \ln Q_{e1} - k_1 t$ (4)
Pseudo-second-order	$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2$ (5)	$\frac{t}{Q_t} = \frac{1}{k_2 Q_{e1}^2} + \frac{1}{Q_{e1}} t$ (6)
Film diffusion		$\frac{Q_t}{Q_e} = 6 \left(\frac{D_f}{\pi a^2} \right)^{1/2} \sqrt{t}$ (7)
Intraparticle diffusion		$\ln \left(1 - \frac{Q_t}{Q_e} \right) = \ln \left(\frac{6}{\pi^2} \right) - \left(\frac{D_{ip} \pi^2}{a^2} \right) t$ (8)

Table 2
Isotherms and their linear forms.

Isotherm	Linear form	Plot	
Langmuir	$Q_e = \frac{Q_m k_1 C_e}{1 + k_1 C_e}$ (9)	$\frac{C_e}{Q_e} = \frac{1}{k_1 Q_m} + \frac{1}{Q_m} C_e$ (10)	$\frac{C_e}{Q_e}$ vs. C_e
Freundlich	$Q_e = K_F C_e^{1/n}$ (11)	$\ln Q_e = \ln K_F + 1/n \ln C_e$ (12)	$\ln(Q_e)$ vs. $\ln(C_e)$
Temkin	$Q_e = \frac{RT}{b} \ln(A C_e)$ (13)	$Q_e = \frac{RT}{b} \ln(A) + \frac{RT}{b} \ln(C_e)$ (14)	Q_e vs. $\ln(C_e)$
DR	$Q_e = Q_m \exp \left[- \left(\frac{\varepsilon}{E} \right)^2 \right]$ (15)	$\ln Q_e = \ln Q_m - k \varepsilon^2$ (16)	$\ln Q_e$ vs. ε^2

To give a qualitative and preliminary analysis of the main chemical groups present on the cell wall of biomass, this plant material was analyzed through Fourier transform infrared spectroscopy (FTIR). For the FTIR study, 0.1 g of finely sized particle of the biomass was encapsulated in 1 g of KBr keeping the ratio 1:10, in order to prepare the translucent sample disks. Infrared spectra were obtained with the help of a Magna-IR 560, Nicolet spectrometer.

2.4. Modeling studies

2.4.1. Kinetic models

Adsorption of a given solute on a solid is a fairly complex mechanism. Indeed, the speed of adsorption is strongly influenced by several parameters such as the status of the solid matrix that has generally heterogeneous reactive sites and the physicochemical conditions under which the adsorption takes place. 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 sorption experiments. The most used ones are the pseudo-first order [19], pseudo-second order [20], intraparticle and film diffusion models [21]. The kinetic model and their linear forms are given in Table 1.

2.4.2. Isotherms models

The adsorption equilibrium defines the distribution of the solute between the liquid and solid phases after the adsorption reaction reaches equilibrium. The amount of adsorbed solute versus the amount of solute in solution at equilibrium is called adsorption isotherm. In this study, Langmuir [22], Freundlich [23], Temkin [24] and Dubinin–Radushkevich (DR) [25] isotherms are investigated to fit the experimental adsorption isotherms. Isotherms and their linear forms are given in Table 2.

3. Results and discussions

3.1. Influence of initial orthophosphate concentration and contact time

The relationship between contact time and orthophosphate adsorption onto POF at different initial orthophosphate concentrations (15–100 mg L⁻¹) is presented in Fig. 1. From this figure, it is observed that all curves have almost the same shape. Furthermore, the adsorption process is clearly time dependent. Indeed,

the amount of adsorbed orthophosphate increased with agitation time and reach 88.6% of the totally adsorbed orthophosphate within a time of 20 min, for an initial orthophosphate concentration of 100 mg L⁻¹. For periods greater than 20 min, the uptake is further increased but with a much slower rate and the equilibrium states were reached at about 40 min. At the beginning, the orthophosphate ions were adsorbed by the exterior surface of POF, the adsorption rate was fast. When the adsorption of the exterior surface reached saturation, the orthophosphate ions entered into the POF particle by the pore within the particle and were adsorbed by the interior surface of the particle. This outcome is generally in line with previous similar studies such as the adsorption of orthophosphate onto some natural and low cost adsorbent, where the equilibrium time was evaluated to be about 1–2 h [1,26].

The orthophosphate uptake increased with increasing initial orthophosphate concentration from 1.83 mg g⁻¹ to 5.48 mg g⁻¹ for initial orthophosphate concentration of 15 and 100 mg L⁻¹, respectively. 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⁻¹) is higher at higher initial concentrations. This is attributable to the orthophosphate

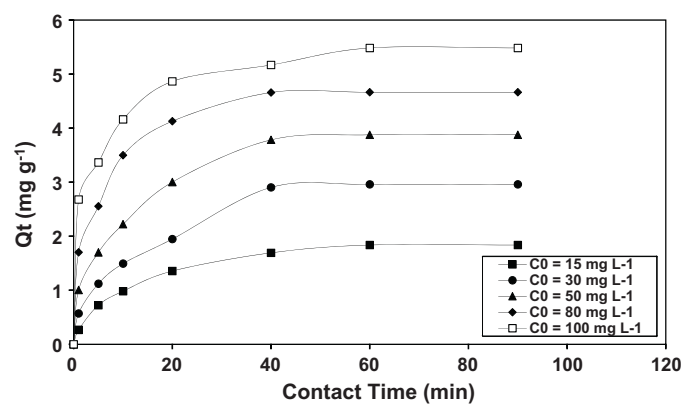


Fig. 1. Effect of contact time on adsorption capacity at different initial orthophosphate concentration (biomass concentration = 2 g L⁻¹, initial solution pH 6, temperature = 20 ± 2 °C).

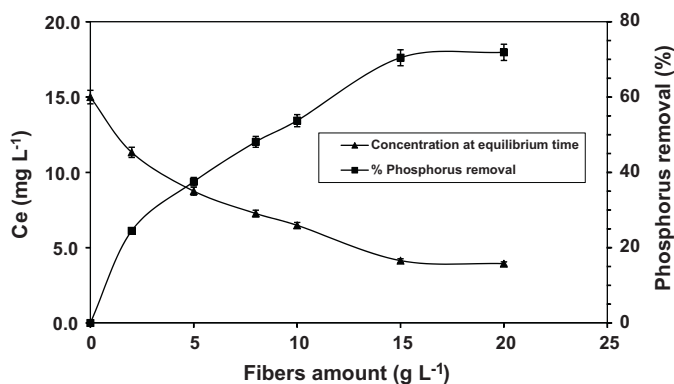


Fig. 2. Effect of adsorbent dosage on the removal of orthophosphate (initial orthophosphate concentration = 15 mg L⁻¹, initial solution pH 7, temperature = 20 ± 2 °C).

concentration gradient between aqueous solutions and the adsorbent.

3.2. Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of orthophosphate ions was investigated at dosages range of 2–20 g L⁻¹ of POF. The result displayed in Fig. 2, shows that an increase in the biomass dosage induces a decrease in the residual orthophosphate concentration at equilibrium and consequently an increase in the adsorption removal efficiency. Indeed, the adsorption removal efficiency values increased from 25% to 75%, as the biomass dose was increased from 1 to 20 g L⁻¹. Such a trend is mainly attributed to an increase in the sorptive surface area and the availability of more adsorption sites. Quite similar tendency was reported for orthophosphate adsorption onto dolomite [3].

3.3. Influence of pH

The pH of the aqueous solution is an important variable that influences the adsorption of ions at the solid–liquid interfaces. The pH value of the orthophosphate solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The effect of pH on the removal of orthophosphate species, through adsorption onto POF show that the adsorption of orthophosphate onto POF tends to decrease with the increase of pH from 2.73 mg g⁻¹ at pH 3–1.32 mg g⁻¹ at pH 11 (Fig. 3). This can be attributed to the fact that at lower pH, the biopolymers, mainly lignin and cellulose chains, may become positively

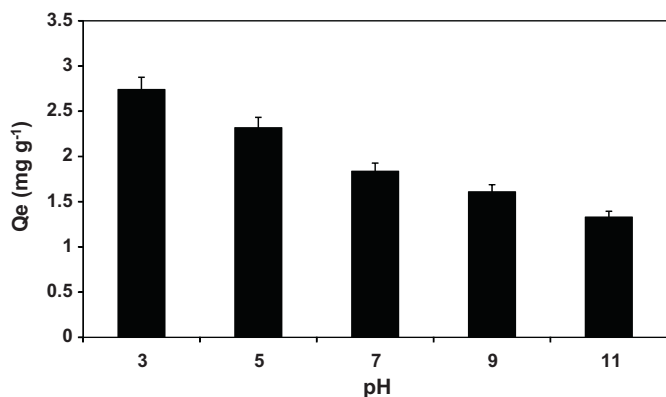


Fig. 3. Effect of pH on the adsorption capacity of orthophosphate onto POF (biomass concentration = 2 g L⁻¹, orthophosphate concentration = 15 mg L⁻¹, temperature = 20 ± 2 °C).

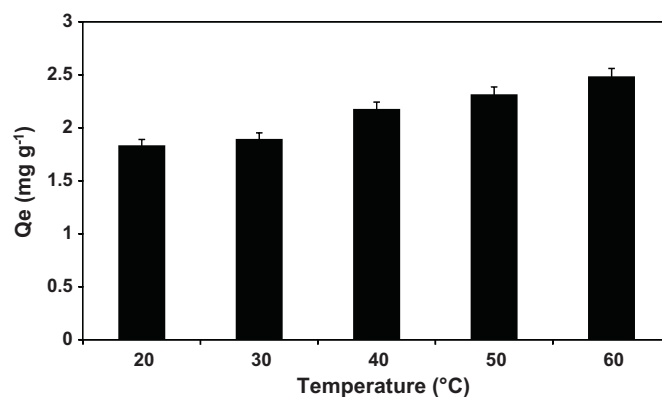


Fig. 4. Effect of temperature on the adsorption capacity of orthophosphate onto POF (biomass concentration = 2 g L⁻¹, orthophosphate concentration = 15 mg L⁻¹, initial solution pH 7).

charged, which enhances the electrostatic and chemical interactions between orthophosphate ions in solution and cationic groups on the fibers surface. However, the low orthophosphate uptake in alkaline pH range can be attributed to the competition of hydroxide ions with orthophosphate ions for adsorption sites. Furthermore, the negatively charged orthophosphate ions adsorption decrease at high pH can also be attributed to electrostatic repulsion with the negatively charged sites.

3.4. Effect of temperature

The orthophosphate uptake capacity onto POF increased with increasing temperature up to 60 °C (Fig. 4), indicating that the adsorption of orthophosphate ions was favoured at higher temperatures. The adsorption of orthophosphate is endothermic, thus the extent of adsorption increases with increasing temperature. The adsorption of orthophosphate onto POF may involve not only physical but also chemical sorption processes. First, the increasing of adsorption capacity with temperature is because of the rise in the kinetic energy of adsorbent particles. Thus, the collision frequency between adsorbent and adsorbate increases; which results in the enhanced adsorption onto the surface of the adsorbent. Second, at high temperature due to bond rupture of functional groups on adsorbent surface (especially pectin molecules) there may be an increase in number of active adsorption sites, which may also lead to enhanced adsorption [27]. Third, it may be due to the dimensions of the fibers pores which increase at high temperatures. Greater is the size of the particle pore, smaller is the contribution of intraparticle diffusion resistance [28]. So, the increase of pores dimensions with the temperature seems to decrease the impact of the boundary-layer effect, and that can increase the amount of orthophosphate ions which could be adsorbed by intraparticle diffusion. In addition, increasing the temperature may produce a swelling effect within the internal structure of fibers [15] enable orthophosphate ions to penetrate further. In previous studies, orthophosphate removal using coal fly ash and scallop shells was proved to be an endothermic process and higher temperature was preferred for the removal of orthophosphate [2,29].

3.5. Competing effect of chloride and sulphate anions

Municipal and industrial wastewaters always contain relatively high contents of chloride and sulphate anions which may compete with the target orthophosphate for the adsorption sites and hence the efficiency of the fibers may be reduced. The competing effect of chloride and sulphate on orthophosphate removal onto POF was investigated and the results are depicted in Fig. 5. As shown in

Table 3
Kinetic rate constants related to the adsorption of phosphorus onto POF.

Kinetic models	Initial phosphate concentration (mg L^{-1})				
	15	30	50	80	100
Experimental Q_e	1.835	2.959	3.876	4.664	5.483
Irreversible first-order model					
k_1 (min^{-1})	0.0617	0.0935	0.0882	0.1644	0.0647
Calculated Q_{e1} (mg g^{-1})	1.647	3.299	3.724	5.266	3.224
R^2	0.995	0.936	0.981	0.955	0.898
Pseudo-second-order model					
k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.0560	0.0328	0.0379	0.0646	0.0620
Calculated Q_{eII} (mg g^{-1})	1.857	3.009	3.919	4.702	5.485
R^2	0.997	0.992	0.995	0.998	0.999

Fig. 5a, chloride anions cause low interference with the adsorption of orthophosphate onto POF. This observation can be attributed to the fact that the affinity between fibers and tested competing anion is weaker than that between fibers and orthophosphate. A similar trend was also observed for sulphate anions until an aqueous concentration of 150 mg L^{-1} (Fig. 5b). However, further increase in sulphate concentration, from 150 to even 1500 mg L^{-1} , results in a significant drop of orthophosphate adsorption. This can be reasonably interpreted by the fact that sulphate anions are divalent and expected to offer greater competition and can be effectively exchanged onto POF through electrostatic interaction or formation of outer-sphere complexes.

3.6. Adsorption kinetic modeling

In order to predict the main mechanisms involved during the present adsorption process and the potential rate controlling steps

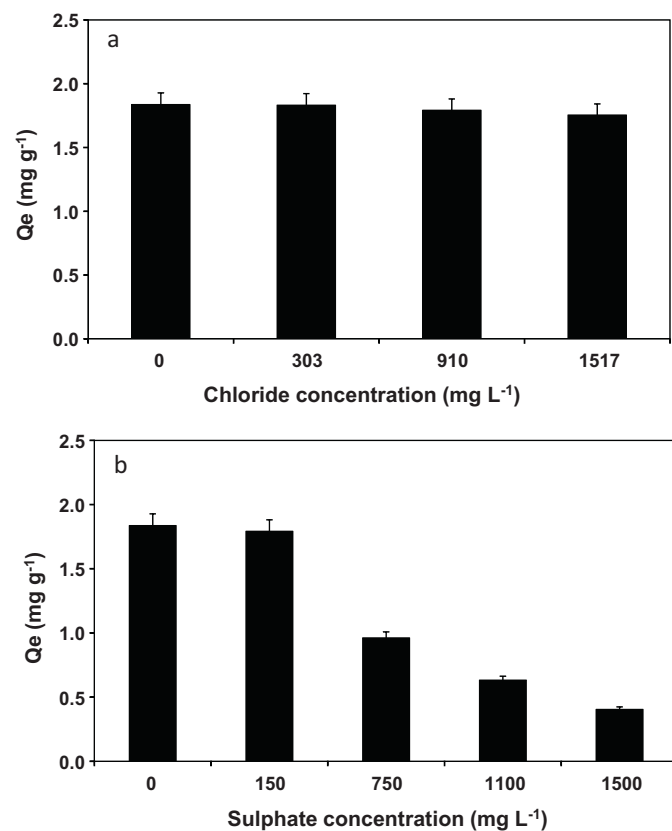


Fig. 5. Effect of chloride (a) and sulphate (b) anions on the adsorption capacity of orthophosphate onto POF (biomass concentration = 2 g L^{-1} , orthophosphate concentration = 15 mg L^{-1} , temperature = $20 \pm 2^\circ \text{C}$).

such as mass transport, pore diffusion and chemical reaction processes, irreversible first-order, pseudo-second-order, intraparticle and film diffusion models were used to fit the experimental data. The best-fit model was selected based on both linear regression correlation coefficient (R^2) and the calculated Q_e values.

According to the kinetic modeling results, shown in Table 3, the correlation coefficients for Lagergren irreversible first-order model obtained at all studied initial orthophosphate concentrations were low and the theoretical adsorbed masses at equilibrium, Q_{e1} , determined from the plots intercepts of $\ln(Q_e - Q_t)$ versus t , did not give acceptable values when compared to the experimental ones. Therefore, the reaction involved in the present adsorption system is not of the first-order.

In contrast, the pseudo-second-order model showed the best fit to the experimental data with the highest squared correlation coefficients ($R^2 = 0.999$). In addition, as shown in Table 3, the pseudo-second order predicted adsorbed masses, Q_{eII} , determined from the plots intercepts of t/Q versus t , agree very well with the experimental data. Thus, these results suggest that the pseudo-second-order model, based on the assumption that the rate limiting step might be chemical adsorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate, and provides the best correlation of the data [12].

The intraparticle diffusion analysis of the adsorption of orthophosphate onto POF showed that the depicted two-phase plot suggests that the adsorption process proceeds by surface adsorption at the earlier stages and by intraparticle diffusion at later stages, especially, for the high concentrations (over 30 mg L^{-1}). For a solid-liquid adsorption process, the solute transfer is usually characterized by either external mass transfer (boundary layer diffusion) for non-porous media or intraparticle diffusion for porous matrices, or both combined. To identify which case is suitable to the orthophosphate adsorption onto POF, the two coefficients of film D_f and particle D_p diffusion were calculated from the slopes of the curves Q_t/Q_e vs. \sqrt{t} and $\ln(1 - Q_t/Q_e)$ vs. t , determined by the film and intraparticle diffusion model, respectively. The values of diffusion coefficients given in Table 4 indicate that the intraparticle diffusion is greater than the diffusion through the boundary layer, which confirms that film diffusion significantly controls the rate of adsorption of orthophosphate.

3.7. Adsorption isotherm

The Langmuir, Freundlich and Temkin adsorption constants estimated from the isotherms at 20°C and the corresponding correlation coefficients are listed in Table 5. The highest regression correlation coefficient (0.990) was observed for Freundlich model, followed by Temkin (0.986), Langmuir (0.985) and DR (0.916) models. This indicates that the three first models are suitable for describing the adsorption equilibrium of orthophosphate onto POF. The maximum adsorption capacity (Q_m) determined from the Langmuir isotherm was calculated to be 7.45 mg g^{-1} . This rela-

Table 4
Diffusion kinetic parameters for phosphorus adsorption onto POF at different initial concentration.

Adsorbent	Initial concentration (mg L ⁻¹)	Film diffusion D_f (m ² s ⁻¹)	Particle diffusion D_p (m ² s ⁻¹)
POF	15	1.429E-12	3.725E-12
	30	1.339E-12	5.131E-12
	50	1.799E-12	5.125E-12
	80	3.030E-12	9.178E-12
	100	3.508E-12	4.712E-12
	Average (m ² s ⁻¹)	2.221E-12	5.574E-12

tively high adsorption capacity shows the strong electrostatic force of attraction between orthophosphate molecules and adsorbent bending-sites [12,30].

In order to understand the adsorption type, equilibrium data was applied to DR isotherm. Constants k and Q_m of DR isotherm were calculated from the slope and intercept of the plot of $\ln Q$ against ε^2 and were given in Table 5.

The mean free energy of adsorption (E), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the k -value using the equation [25]

$$E = -(2k)^{-0.5} \quad (17)$$

The calculated value of E was 9.69 kJ mol⁻¹. It is known that magnitude of E is useful for estimating the type of adsorption and if this value is between 8 and 16 kJ mol⁻¹ adsorption type can be explained by ion exchange [25]. Thus, the adsorption of orthophosphate onto POF can be explained by both chemisorption and ion exchange. This indicated that the bonds formed between orthophosphate and POF are strong which may allow the valorization of the complex orthophosphate-POF as organic fertilizer.

In order to predict the adsorption efficiency of the process, the dimensionless equilibrium parameter RL was determined. The calculated RL value for an initial aqueous concentration of 15 and 100 mg L⁻¹ were estimated to 0.711 and 0.269, respectively, which confirms that the used adsorbent is favourable for orthophosphate adsorption. Furthermore, the value of Freundlich exponent $n = 1.95$ in the range of 1–10, indicates a favourable adsorption.

In order to situate our novel natural adsorbent among those used to remove orthophosphate from aqueous solutions, a comparison based on adsorption capacity (mg g⁻¹) was made. The results, illustrated in Table 6, had shown that the POF could be considered as a promising material to remove orthophosphate when compared with the common natural materials. Indeed, the adsorption capacity of POF is 44 times higher than dolomite [9], 24 times than limestone [11], 17 times than sand [31], 7 times than apatite [6] and 2.5 times than bauxite [8]. In comparison with other lignocellulosic fibers the adsorption capacity of POF is about 2 times higher than wood fiber [32] and date palm fibers [26]. Thus, raw POF could be considered as the most efficient natural material for the removal

Table 5
Adsorption isotherm constants for phosphorus adsorption onto POF.

Isotherm	Constants	
Freundlich	n	1.953
	K_F	0.55
	R^2	0.990
Langmuir	Q_m (mg g ⁻¹)	7.45
	b (L mg ⁻¹)	0.027
	R^2	0.985
Temkin	A (L g ⁻¹)	1.69
	B	0.246
	c	0.986
DR	Q_m (mg g ⁻¹)	4.562
	k (mol ² kJ ⁻²)	0.00532
	R^2	0.916

of orthophosphate with Wollastonite [33], Shellsand [12] and Maerl [34].

3.8. Adsorption mechanism

With regards to further adsorption characteristics of orthophosphate on the surface of POF, the result of the effect of anions on adsorption capacity is particularly useful in determining whether the orthophosphate is associated with the surface of POF as an inner-sphere or outer-sphere complex. It is important to distinguish between outer-sphere and inner sphere complex in order to understand the different stability of adsorbed ion, and the various chemical and physicochemical properties of POF. In this study, the insignificant effects of Cl⁻ at different concentrations and SO₄²⁻ at concentrations lower than 150 mg L⁻¹ on the adsorption capacity (see Section 3.5) reflect that the ionic strength does not affect the adsorption behaviour, indicating an inner-sphere complex. Therefore, it is reasonable to speculate that the orthophosphate is adsorbed on the surface of POF by chemical bond.

Previous results from orthophosphate adsorption kinetics experiments agreeing with the pseudo-second-order equation suggested a chemisorption process. The attachment of orthophosphate must occur at the active sites on the surface of the POF. Therefore, the adsorption of orthophosphate species can be reasonably speculated to occur in two steps: (1) transfer of orthophosphate from the aqueous solution to the sites on the adsorbent; (2) chemical complexation/ion exchange at the active sites and precipitation on the adsorbent surface [39].

To highlight the mechanism of ion exchange in the case of the adsorption of orthophosphate onto POF, EDS analyses were carried out before and after the adsorption process (Fig. 6). The spectra before adsorption indicated the presence of two anions which are chloride and sulphide and the absence of orthophosphate (Fig. 6a). After adsorption, we note the appearance of orthophosphate peak, while, there was a total disappearance of chloride peak in addition to a slight decrease of the sulphide peak (Fig. 6b). This finding indicates that the process of ion exchange between the surface of

Table 6
Elemental analysis of raw POF before and after phosphorus adsorption (wt.%, dry basis).

Elemental analysis	Content (% dry basis)	
	Before	After
C	46.54	48.27
O	37.30	35.74
Na	0.19	0
Mg	0.53	0.64
Al	0.75	1.38
Si	1.85	2.44
P	0	0.38
S	2.24	2.10
Cl	0.41	0
K	0.49	0.70
Ca	5.94	4.31
Fe	3.75	4.04
Total	100.00	100.00

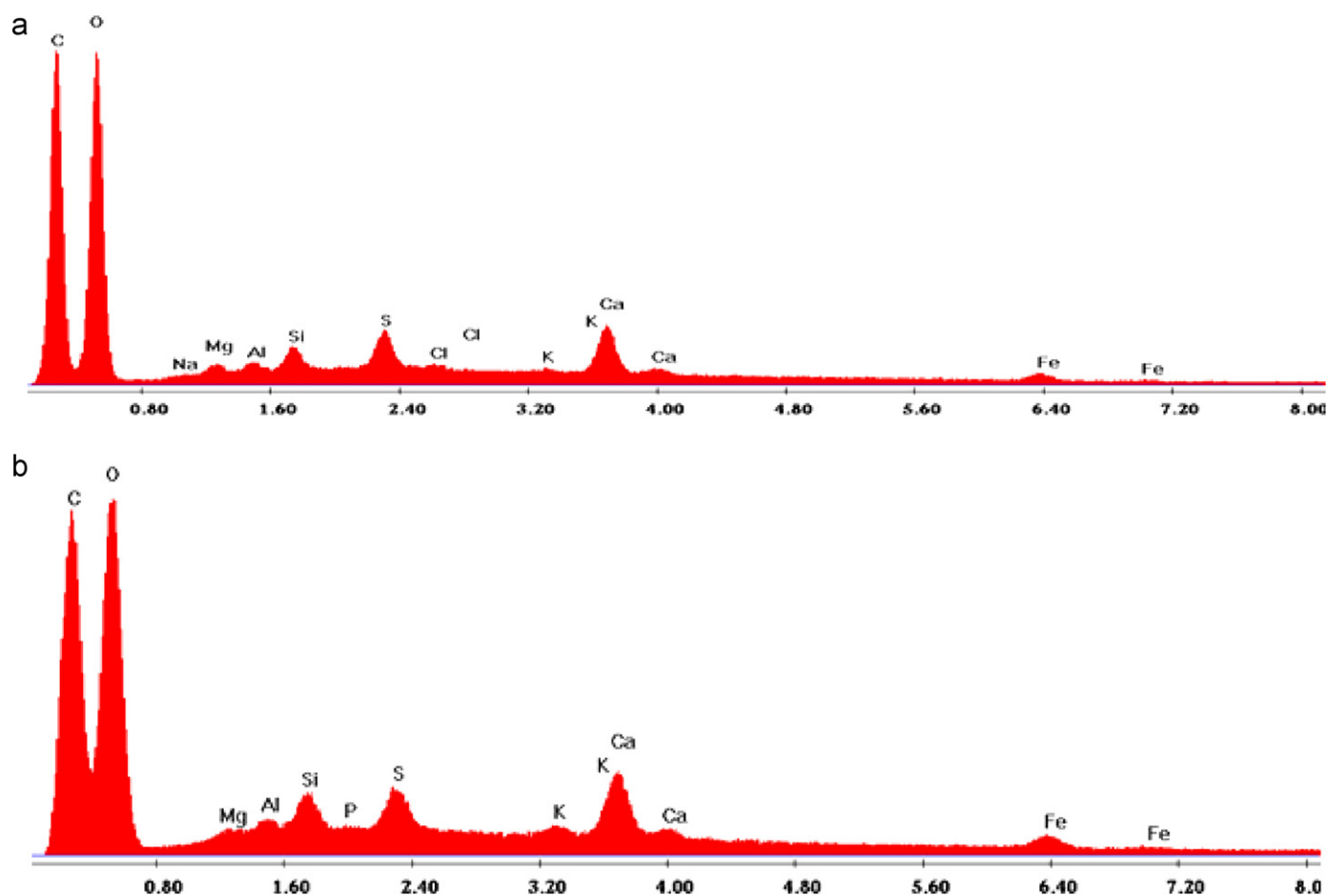
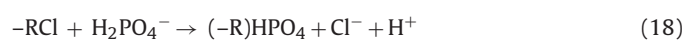


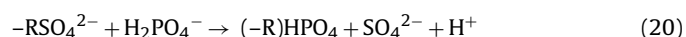
Fig. 6. EDS analysis of POF before (a) and after (b) adsorption of orthophosphate.

fibers and orthophosphate ions present in solution, may be one of the main processes involved for the adsorption of orthophosphate onto POF.

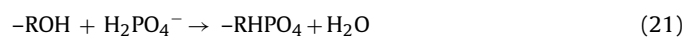
The ligand exchange between orthophosphate (in solution) and Cl^- can be realized by either acyl or alkyl chlorides accompanied with the release of H^+ to the solution, according to the following reactions;



The ligand exchange between orthophosphate (in solution) and SO_4^{2-} groups of hemicelluloses [12], 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 intramolecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin [12] can also be involved in the ligand exchange process, according to the following reactions:

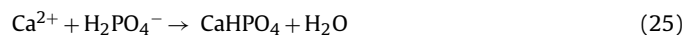


Furthermore, the presence of the Al–OH and Fe–OH functional groups could contribute to the adsorption of orthophosphate as described by [40]:



These different ligand exchange processes were also demonstrated by the difference in the elementary composition of POF before and after the adsorption process given in Table 7. From this table, it can be clearly noted that the percent of oxygen and sulphide has decreased. In addition, the chloride has completely disappeared.

On the other hand, the calcium content has decreased after adsorption of orthophosphate. The percent of Ca^{2+} ions was released to the solution via hydration and dissolution. Generally, the removal of orthophosphate is accompanied by a decrease in the Ca^{2+} ion concentration [41] which may lead to the precipitation of calcium orthophosphate, according to the following reaction;



The FTIR spectra before and after orthophosphate adsorption onto POF are shown in Fig. 7. The infrared (IR) spectrum of POF, displayed a number of absorption peaks, indicating the complex nature of the examined biomass. Shifts were registered in the bands located at 1276, 1385, 1432, 1644; 1816; and 2943 cm^{-1} . These shifts may be assigned to C–H bending, C–O stretching of COOH, carboxyl groups, the stretching vibrations of symmetrical or asymmetrical ionic carboxylic groups, acid halides groups and C–H stretching respectively [14]. This finding indicates that lig-

Table 7
Comparison of phosphorus adsorption onto POF with other natural adsorbents.

Material	C_0 (mg P L ⁻¹)	Adsorption capacity (mg P/g)	References
Apatite	0–500	4.76	[7]
Apatite	5–150	1.09	[6]
Bauxite	2.5–40	0.612	[35]
Bauxite	0–100	2.95	[8]
Dolomite	0–100	0.168	[9]
Gravels	5–1000	3.6	[10]
Limestone	5–25	0.3	[11]
Limestone	2.5–40	0.682	[35]
Maerl	0–5000	7.49	[34]
Opoka	5–25	0.1	[11]
Sand	0–100	0.417	[31]
Sand	0–320	3.941	[36]
Sand	5–1000	2.45	[10]
Shellsand	5–1000	4	[38]
Shellsand	5–1500	8	[37]
Shellsand	0–480	9.6	[12]
Soils	500–10,000	0.005	[13]
Spodosol	5–20	1	[11]
Wollastonite	0.8–1700	12	[33]
Zeolite	500–10,000	2.15	[13]
Wood fiber	0–100	4.3	[32]
Date palm fibers	10–110	4.35	[26]
POF	15–100	7.45	This study

and exchange mechanism between orthophosphate in solution and –OH on the surface of POF and also anion exchange process between orthophosphate and chloride anions previously demonstrated by EDS analysis might be present during phosphorus adsorption by POF.

Thus, we can conclude that different mechanisms such as ion exchange and precipitation have been involved in the adsorption of orthophosphate onto POF and could explain the removal of orthophosphate from aqueous solutions in such adsorption system. Furthermore the obtained complex orthophosphate–POF could be valorized as organic fertilizer.

3.9. Prospect of using POF to remove and recover orthophosphate

The dead sheets of *P. oceanica* are accumulated in considerable quantities, reaching a thickness of 1–2 m or more, on the most Mediterranean beaches between the end of spring and the end of summer, covering over 50 000 km² [16]. These fibers are not appreciated by the swimmers, because of the smell which may be emitted, but especially because they assimilate these accumulation as pollution. Huge quantities of these wastes are either transported (or possibly buried) in landfills, or piled up in adjacent areas to beaches or even re-immersed in the sea. In recent years, this natural material was investigated as a low-cost adsorbent to

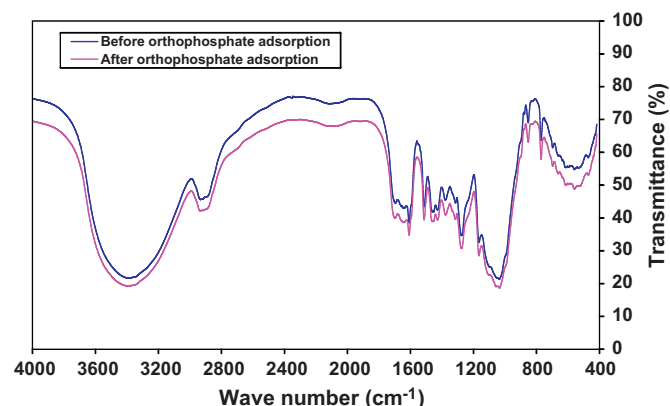


Fig. 7. FTIR analysis of POF before (a) and after (b) adsorption of orthophosphate.

Table 8
Comparison of phosphorus adsorption capacity of POF with other common pollutants.

Pollutant	C_0 (mg L ⁻¹)	Adsorption capacity (mg g ⁻¹)	References
Dyes (Methylene Blue)	50–300	5.51	[43]
Aromatic compounds (Phenol)	20–100	5.08	[43]
Heavy metals (ChromiumVI)	5–50	2.4	[42]
Nutrients (Ammonium)	10–50	2.11	[15]
(Phosphorus)	15–100	7.45	This study

remove a variety of pollutants from aqueous solution, e.g. heavy metals [42], dyes and phenol [43]. From Table 8, it is clear that the POF are more efficient to remove orthophosphate than dyes, heavy metals and phenols. Furthermore, the regeneration of the saturated POF with orthophosphate does not required while the agronomic reuse is possible. Thus, desorption and recovery processes could be avoided and the related costs reduced. This is not the case for the saturated POF with dyes or heavy metals or phenols where the regeneration process is required which may increase the costs. Consequently, for environmental, economic and operational considerations, the use of POF for the removal of orthophosphate and other nutrients appears to be more interesting. In addition, orthophosphate in wastewater represents a considerable renewable resource ready for technological exploitation, worth some 250 000 tones annually in Western Europe alone, comparable with the requirements of the orthophosphate industry [1] and there is no environmental or technical reason which impedes recycling of orthophosphate. 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 [1]. Thus, it is very important to develop a recovery process of orthophosphate from orthophosphate-containing wastewater systems as alternative resources of orthophosphate to compensate for such global exhaustion of high grade phosphate ores. Consequently, the removal of orthophosphate from wastewater by POF 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.

4. Conclusion

The present work has showed that POF could be considered as a promising low-cost material to remove and recover orthophosphate when compared with common natural materials. The maximum adsorption capacity (Q_m) determined from the Langmuir isotherm was calculated to be 7.45 mg g⁻¹ which could be considered as one of the highest capacities recorded for the adsorption of orthophosphate. The high adsorption capacity shows the strong electrostatic force of attraction between orthophosphate and the adsorbent bending-sites. The energy dispersive spectroscopy (EDS) before and after adsorption of orthophosphate onto POF showed that the main involved mechanisms are ligand exchange between orthophosphate (in solution) and Cl⁻, SO₄²⁻ and OH⁻ and precipitation with calcium. The obtained complex POF–orthophosphate is strongly banded which encourage its valorization as organic fertilizer. The use of POF presents an interesting option for both tertiary wastewater treatment (as a possible non-conventional adsorbent for the removal of orthophosphate), and waste recycling (as a fertilizer and compost).

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