



Review

Biosorption characteristics of phosphates from aqueous solution onto *Phoenix dactylifera* L. date palm fibers

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ABSTRACT

Phosphates are very important basic materials in agricultural and other industrial applications. The removal of phosphates from surface waters is generally necessary to avoid problems, such as eutrophication, particularly near urban areas. This paper is focused on the sorption of PO_4^{3-} ions from aqueous solution onto date palm fibers as a raw, natural and abundantly materials. A series of batch tests were conducted and the influence of contact time, initial phosphate concentration, pH of the solution and adsorbent dosage on PO_4^{3-} specie removal was investigated. FT-IR spectroscopy, scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM) analysis of the date palm fibers before and after phosphates biosorption and desorption studies were investigated to confirm the mechanism of the retention of phosphates. Results indicate that PO_4^{3-} uptake increased with increased initial phosphate concentration and decreased with increased pH values. The results showed that the highest phosphates adsorption capacity (4.35 mg/g) was found at pH 6.8, for an adsorbent dosage of 6 g/L, initial phosphate concentration of 50 mg/L, under a constant temperature of $18^\circ\text{C} \pm 0.2$, and the equilibrium state was reached within 120 min of exposure time. The relatively low cost and high capabilities of date palm fibers make them potentially attractive adsorbents for the removal of phosphate from aqueous solution.

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1. Introduction

Phosphate is often present in wastewater in low concentrations mostly as phosphates including organic phosphate, inorganic phosphate, oligophosphates and polyphosphates (particulate P). A typical raw domestic wastewater has a total phosphorus concentration of approximately 10 mg P/L with orthophosphate as the principal form of phosphate (5 mg P/L) in addition to small amount of other forms of phosphate [1], but a typical effluent total unfiltered phosphorus target is between 0.8 and 1.0 mg P/L [2]. Eutrophication of waters caused by nitrogen and phosphorus has recently become a matter of focus, and development of remediation technology has become important. Nitrogen and phosphorus were known as a significant nutrient to induce eutrophication, which was reported that phosphorus is especially limiting factor to control this phenomena [3]. These nutrients are directly responsible for extraordinary growth of algae as a result of excess nutrients in water bodies of rivers, lakes, and seas worldwide [4,5]. Removal of these nutrients, especially phosphorus by advanced treatment is necessary in areas where the regulations on effluent standards are strict [6,7]. For that reason, newly built wastewater treatment systems have been equipped with simultaneously removing nitrogen and phosphorus, or conventional activated-sludge (AS) processes being modified to adapt it.

Recently, alternative methods of phosphorus removal in water and wastewater treatment have been attracting increasing attention. 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 high capital cost [8]. A suitable method to remove these nutrients, principally phosphorus, to the requirement would compare with regard to effectiveness and economic point of view. The broad categories of phosphate effluent treatment include physical [9], chemical [10], biological [11] and crystallization methods [12]. Also, flotation has been used to remove phosphates from aqueous solutions [13]. Chemical removal techniques are the most effective and well established methods up to date, including phosphate precipitation with calcium, aluminium and iron salt [14]. However, the cost associated with the use of metal salts may hinder the widespread application.

The *Phoenix dactylifera* L. date palm is one of the most cultivated palms around the world. It is commonly found in the Afro-Asiatic dry-band, which stretches from North Africa to the Middle East [15,16]. It has a good tolerance to cold and dry-hot climates. In the Maghreb countries, particularly in Tunisia, oases cover almost 40,000 ha and represent an original form of human development in very harsh climatic conditions [17]. Among these, date-palm by-products (DPBP), date palm surface fibers were chosen in this study as it seemed most suitable for exploitation. After annually trimming operations, enormous quantities of date palm fibers wastes are thrown away, except in smaller scales for artisan products [18,19]. Date palm fibers could offer an appreciable economic and environmental potential, which should be in a position to effectively

contribute to their use as reinforcement in hot dry climates [20,21] and to the valorisation of such as date-palm by-products for tertiary domestic wastewater treatment [22]. Others by-products derived from date cultivation, such as leaves, and floral stems supporting date regimes may be useful in animal feeding because of the nutritive value of mainly wasted dates and stones [23] or as a biomonitor of high metals in arid environments [24,25].

This paper studies biosorption characteristics of orthophosphates species (PO_4^{3-}) onto *P. dactylifera* L. date palm fibers used as a raw, natural and abundantly materials in batch mode investigating the effect of the key process parameters. The effects of various parameters such as contact time, pH of solution, initial phosphate concentration and adsorbent dosage were examined. FT-IR spectral, scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM) analysis of the date palm fibers before and after phosphates biosorption and desorption studies were investigated to confirm the mechanism of the retention of phosphates.

2. Materials and methods

2.1. Preparation of the materials

The natural fibers used in this research are from the surface of *P. dactylifera* L. date palm turn obtained from Mednine (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 surface 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.

2.2. Adsorption kinetic measurements

Phosphate adsorption kinetics study was carried out with different initial concentrations of phosphate and a fixed concentration of the adsorbents at room temperature ($18^\circ\text{C} \pm 02$). Before the start of each kinetic experiment, 1000 mg of the sample was loaded in a 1 L. Six levels of initial phosphate concentrations (10, 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 H_2SO_4 and/or NaOH solutions. The flask was capped and stirred magnetically at 200 rpm for 240 min to ensure approximate equilibrium. Several mL of reaction solution was sampled for intervals between 0 and 240 min of adsorption. At the end of the adsorption period, the solution was filtered through a 0.45 μm membrane filter and then analyzed for PO_4^{3-} . The quantity of adsorbed phosphate was calculated from the decrease of the phosphate concentration in solution. The triplicate experiments demonstrated the high repeatability of this adsorption method and the experimental error could be controlled within 5%.

Table 1
Chemical components of date palm fibers.

Component	Percentage (wt.%)
Carbon	75.86
Oxygen	20.45
Hydrogen	2.20
Cobalt	0.62
Calcium	0.20
Magnesium	0.15
Sulphur	0.12
Siliceous	0.12
Iron	0.09
Nitrogen	0.07
Aluminium	0.07
Phosphorus	0.05

2.3. Desorption experiments

To evaluate phosphate desorption from the samples, the residual solids retained on the filter paper were collected in a 250 mL erlenmeyer flask after filtration of the suspension from an adsorption test. The flask was covered with magnetic stirring at 200 rpm for 3 h while pH was maintained at the same value as in the adsorption experiment. The suspension solution was filtered and analyzed for desorbed phosphate in a similar way described previously. The quantity of desorbed phosphate was determined by the amount of phosphate in solution after the desorption experiment.

The desorbability is expressed according to the capacity of desorption q_d (mg/g) and the capacity of adsorption q_a (mg/g) of adsorbate, as follows:

$$\text{desorbability}(\%) = \frac{q_d}{q_a} \times 100$$

2.4. Characterisation of the materials

2.4.1. Fourier transform infrared (FT-IR) spectroscopy analysis

Infrared absorption spectra of date palm fibers before and after phosphates biosorption were obtained using an EQUINOX FT-IR 55 spectrometer. The samples were ground with 200 mg of KBr (spectroscopic grade) in a mortar and pressed into 10 mm diameter disks less than 10 tonnes of pressure and high vacuum for FT-IR analysis. The conditions used were 64 scans at a resolution of 4 cm^{-1} measured between 4000 and 400 cm^{-1} .

2.4.2. Scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS) analysis

Date palm fibers made in this work were characterised by scanning electron microscopy (SEM) in the environmental mode (ESEM). Energy dispersive spectroscopy (EDS) was used to analyze the chemical composition of the date palm fibers surface by using QUANTA 200 FEI. The elemental composition of raw date palm fibers was determined from the peak areas and is summarized as shown in Table 1. Data represent the mean value of three independent quantification EDS spectrums tests. It was found that carbon and oxygen were the only consistent components in these materials. Other minor constituents in trace that were obtained from the analyses included hydrogen, iron, cobalt, magnesium, aluminium, siliceous, sulphur, nitrogen, phosphorus and calcium.

2.4.3. Transmission electron microscopy (TEM) analysis

After glutaraldehyde fixation at 50%, the samples were washed twice with sodium cacodylate 0.2 M (pH 7.4). Cells were post-fixed with 2% osmium tetroxide for 30 min. Cells were dehydrated for 10 min in ethanol in a series of solutions: 30%, 50%, 60%, 70%, 80%, 90%, 95% and 100%. The cells were then allowed to dehydrate in 100% acetone for a further 10 min. The dehydrated cells were infil-

trated with increasing concentrations of agar low viscosity resin (Epoxy Epon 812), a replacement for Spurr's resin, over 3 days. The polymerisation of the resin to form specimen blocks was accomplished in an oven at 60°C for 24 h. The specimen blocks were hand trimmed with a razor blade and sectioned with a glass knife using a Reichert Ultracut E Ultramicrotome. Microtome sections of 60–70 nm were placed on 150 mesh copper grids. The sections were stained with 2% uranyl acetate and lead citrate, and viewed with a JEOL 1010 transmission electron microscope operating at 80 kV.

2.5. Phosphates analysis

The phosphate species stock solution containing 1000 mg P/L was prepared by dissolving potassium dihydrogenophosphate (KH_2PO_4) powders (analytical reagent grade) in bidistilled water. Phosphate working solutions in different concentrations were prepared by diluting the PO_4^{3-} stock solution with distilled water. The pH of the solution was adjusted using minimum volume of 0.1 M H_2SO_4 and/or NaOH. The total volume added for pH adjustment never exceeded 1% of the total volume. The analysis of phosphate (as orthophosphate anions) was done spectrophotometrically at 880 nm, following the ascorbic acid method [26]: 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. Each analysis point was an average of three independent parallel sample solutions. Triplicate tests showed that the standard deviation of the results was $\pm 5\%$.

2.6. Phosphates uptake

The PO_4^{3-} uptake was calculated following the concentration difference method. The initial concentration C_i (mg/L) and leftover PO_4^{3-} concentration at different time intervals, C_e (mg/L), were determined and the PO_4^{3-} uptake q_e (mg PO_4^{3-} adsorbed/g adsorbent) was calculated from mass balance equation as follows:

$$q_e = \frac{C_i - C_e}{M} \times V$$

where V is the volume of the solution in L and M is the mass of sorbent in g.

The extent of sorption in percentage is found from the relation:

$$\text{sorption}(\%) = \frac{C_i - C_e}{C_i} \times 100$$

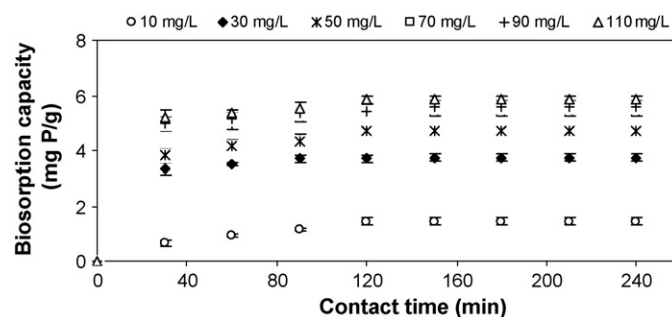


Fig. 1. Phosphates biosorption onto date palm fibers as a function of initial concentration (temperature at $18^\circ\text{C} \pm 0.2$, adsorbent dose at 6 g/L, agitation speed at 200 rpm and pH at 5).

2.7. Statistical analysis

Measurements were made in triplicates for the analysis of PO_4^{3-} parameter and data were recorded when the variations in two readings were less than 5%. In this paper, all data represents an average of three independent experiments ($N=3$) and data represent the mean value. For the determination of inter-group mean value differences, each parameter was subjected to the standard deviation, to the confidence intervals and to the Student's *t*-test for significance level ($p < 0.05$) [27]. All statistical analysis was done using Microsoft Excel 2003 version office XP.

3. Results and discussion

3.1. Effect of initial phosphate concentration and contact time

Experiments were undertaken to study the effect of varying initial concentration (10–110 mg/L) on orthophosphates specie removal onto date palm fibers. The experiments were carried out at $18^\circ\text{C} \pm 0.2$, an adsorbent dose at 6 g/L, an agitation speed at 200 rpm and pH at 5 for a contact period of 240 min. Fig. 1 indicates that all curves have the same shape. The results show that adsorption process is clearly time dependent. From this figure, it is observed that most of the orthophosphates specie uptake occurs within a time of 30 min at 88.9% of the totally biosorbed for an initial phosphates concentration of 110 mg/L. 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. Also, the outcome is generally in line with previous similar studies [28,29], such as the adsorption of phosphates onto some natural and low cost adsorbent attains equilibrium at about 1–2 h. Further increase in retention time does not seem to have any impact on the equilibrium concentration. Hence all the adsorption experiments were carried in 120 min.

The PO_4^{3-} uptake increased with increasing initial phosphate concentration from 1.45 mg/g for 10 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 increase in contact between adsorbent and adsorbate at higher [P] concentrations [30].

3.2. Effect of pH on phosphate adsorption

The pH of the aqueous solution is an important variable that influences the biosorption of ions at the solid–liquid interfaces. The pH value of the phosphate solution plays an important role in the whole biosorption process and particularly on the biosorption capacity.

With a similar procedure, the effect of pH on orthophosphates specie adsorption onto date palm fibers was examined in a series of experiments that used the same initial phosphate concentration (50 mg P/L) while maintaining pH at different values between 1.4 and 10.4. The effect of pH on orthophosphates adsorption onto date palm fibers is illustrated in Fig. 2. The results show that the uptake of orthophosphates specie adsorption onto date palm fibers tends to decrease with the increase of pH from 7.85 mg P/g at pH 1.4 to 3.43 mg P/g at pH 10.4. This can be attributed to the fact that a higher pH value leads the surface to carry more negative charges and thus would more significantly repulse the negatively charged species in solution. Therefore, at higher pH value, the decrease of phosphate adsorption capacity resulted from an increased repulsion

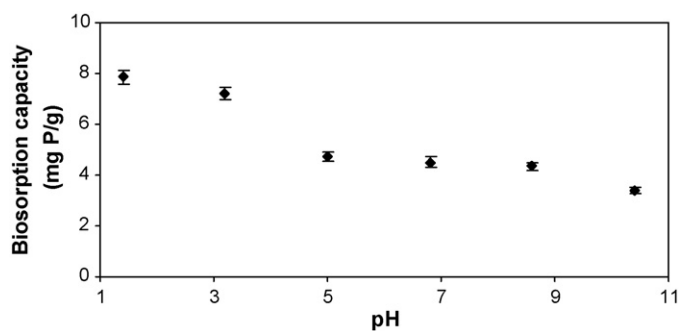


Fig. 2. Effect of pH on phosphates biosorption onto date palm fibers (temperature at $18^\circ\text{C} \pm 0.2$, adsorbent dose at 6 g/L, agitation speed at 200 rpm, $[\text{PO}_4^{3-}]_0$ at 50 mg/L and contact time at 120 min).

between the more negatively charged PO_4^{3-} anions and negatively charged OH^- anions charged surface adsorbent sites. So with increasing acidity of the solution, the surface becomes more positively charged; consequently, higher removal is expected at low pH values [28,30].

3.3. Effect of adsorbent dosage

To achieve the maximum adsorption capacity of the adsorbent for orthophosphates ions, the dose of date palm fibers materials was varied from 2 to 12 g/L and it was found that a dose of 6 g/L was sufficient for the maximum uptake of orthophosphates ions under the reported experimental conditions. These findings are shown in Fig. 3 and a perusal of this figure indicates that the PO_4^{3-} uptake adsorption increase from 3.75 mg/g (2 g/L adsorbent dose) to 4.69 mg/g (6 g/L adsorbent dose). It is also seen from this figure that a further increase in adsorbent dose (greater than 6 g/L) affects the uptake of phosphates adsorption greatly: the PO_4^{3-} uptake adsorption decreases from 4.69 mg/g (6 g/L adsorbent dose) to 1.75 mg/g (12 g/L adsorbent dose). This result is related to the fact that for significant doses of date palm fibers, the fibers were rolled up the ones on the others and consequently there is not a good contact with the orthophosphates ions dissolved in the followed solution.

3.4. Fourier transform infrared (FT-IR) spectroscopy investigations

FT-IR is a rapid analytical technique ideal for the initial classification of organic residues into groups with broadly comparable chemical composition. General determination of the nature of the samples can be made through comparison with reference spectra of known materials.

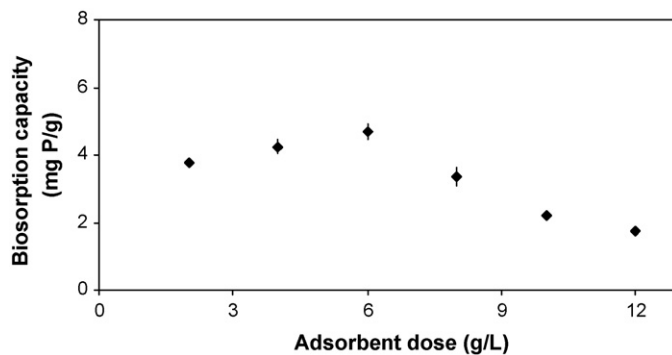


Fig. 3. Effect of adsorbent dosage on phosphates biosorption onto date palm fibers (temperature at $18^\circ\text{C} \pm 0.2$, agitation speed at 200 rpm, $[\text{PO}_4^{3-}]_0$ at 50 mg/L, contact time at 120 min and pH at 5).

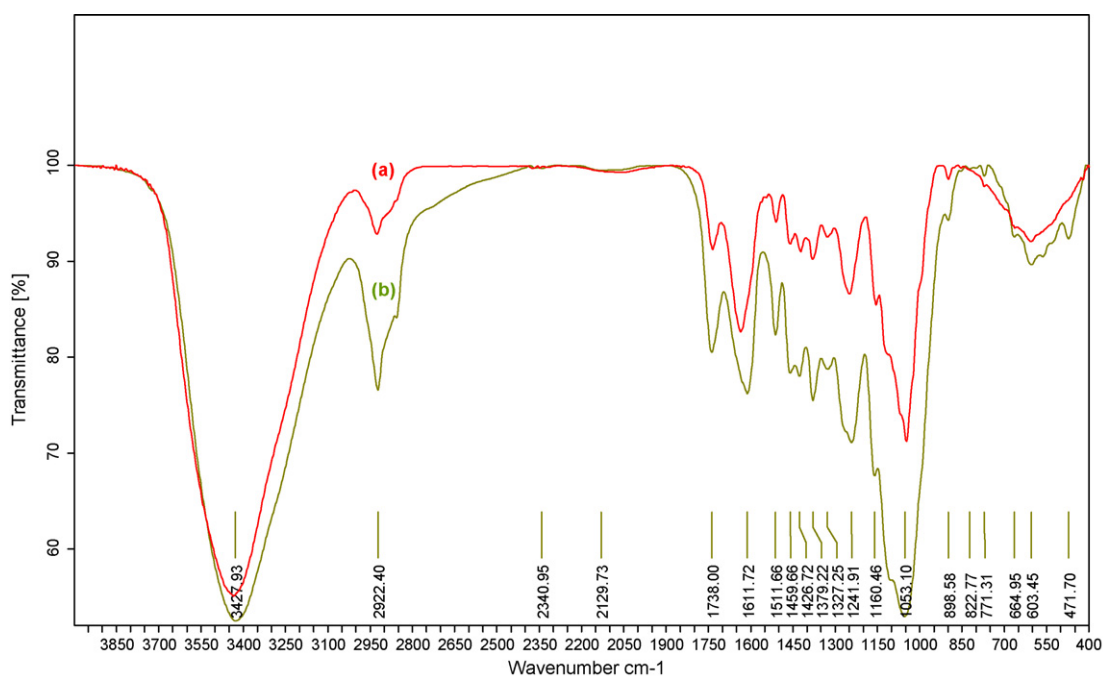


Fig. 4. (a) The FT-IR spectra of date palm fibers before phosphates biosorption. (b) The FT-IR spectra of date palm fibers after phosphates biosorption.

The FT-IR spectra before and after biosorption of phosphates onto date palm fibers are shown in Fig. 4a and b. The functional groups before and after biosorption of phosphates onto date palm fibers and the corresponding infrared absorption bands are shown in Table 2. As shown in Fig. 4a and b and Table 2, the spectra display a number of absorption peaks, indicating the complex nature of date palm fibers. These band shifts indicated that three major absorption bands at 3428, 2922 and 1053 cm^{-1} corresponding to the bonded $-\text{OH}$ groups, aliphatic $\text{C}-\text{H}$ out of plane groups bending and $\text{P}-\text{O}-\text{C}$ groups stretching were especially played a major role in phosphates biosorption onto date palm fibers.

3.5. Scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS) analysis

Scanning electron microscopy (SEM) micrographs and energy dispersive spectroscopy (EDS) spectra obtained before and after PO_4^{3-} biosorption onto date palm fibers are presented in Fig. 5a and b. These micrographs indicated clearly the presence of new shiny bulky particles adhering on the surface of date palm fibers cells. These particles are not seen in the date palm fibers before phosphate biosorption. This observation was confirmed by EDS analysis which revealed P signals after phosphates biosorption.

Table 2

The FT-IR spectral characteristics of date palm fibers before and after phosphates biosorption.

IR peak	Absorption bands (cm^{-1})			Assignment
	Before biosorption	After biosorption	Differences	
1	3435	3428	-07	Bonded hydroxyl groups (OH^-)
2	2926	2922	-04	Aliphatic $\text{C}-\text{H}$ groups
3	1735	1738	+03	$\text{C}=\text{O}$ stretching "keto" form
4	1509	1512	+03	Aromatic $\text{C}=\text{C}$ skeletal stretching
5	1380	1379	-01	$-\text{CH}_3$ bending
6	1250	1242	-08	$\text{P}-\text{O}-\text{C}$ stretching
7	1047	1053	+06	$\text{P}-\text{O}-\text{C}$ stretching
8	898	899	+01	$-\text{C}-\text{C}-$ groups
9	605	603	-02	$\text{C}-\text{H}$ out of plane bending

3.6. Transmission electron microscopy (TEM) analysis

Transmission electron microscopy is used to investigate the internal structure of date palm fibers cells. Thin ($<60-70$ nm) sections were made from cells embedded in resin to observe any possible microstructural changes resulting from phosphates biosorption onto date palm fibers.

Only internal cell changes after phosphates biosorption onto date palm fibers were visible in the micrographs. Transmission electron micrographs of date palm fibers after this treatment showed that when compared to untreated controls (Fig. 6a), we can see that well-dispersed, spherical particles occurred as both discrete and aggregated nanoparticles onto the internal walls of cells (Fig. 6b–e). It is thus evident that biosorption of phosphates onto date palm fibers had an effect on the cell boundaries and the microstructures of the cells. The extent of internal cell accumulation of phosphates may be induced by intraparticle diffusion of adsorbate to internal cell leading to high P deposition yield identified as a gray and black precipitates. Phosphates provide a useful indicator of bioaccumulation tendency. Thus the TEM data provide insight on the type and magnitude of bioaccumulation of phosphates due to the biosorption treatment.

On the other side, the sorption of phosphates onto *P. dactylifera* L. date palm fibers may be controlled by surface sorption (chemisorption interactions-type) and especially by intraparticle diffusion process. Kinetic studies may help to identify the sorption process, predicting the mechanisms are required for design purposes.

3.7. Desorption study

The tests of phosphate desorption were conducted with six initial phosphate concentrations (10, 30, 50, 70, 90 and 110 mg P/L) at pH 5 as shown in Table 3. The P desorbability can be defined as the ratio of the desorbed P over the total adsorbed P by the adsorbent. Therefore, the desorbability of P can be used to indicate the amount of the desorbed P in percentage from P loaded onto date palm fibers materials. The data in Table 3 show that the desorbability of P is about 10–13% for all samples, regardless of the initial

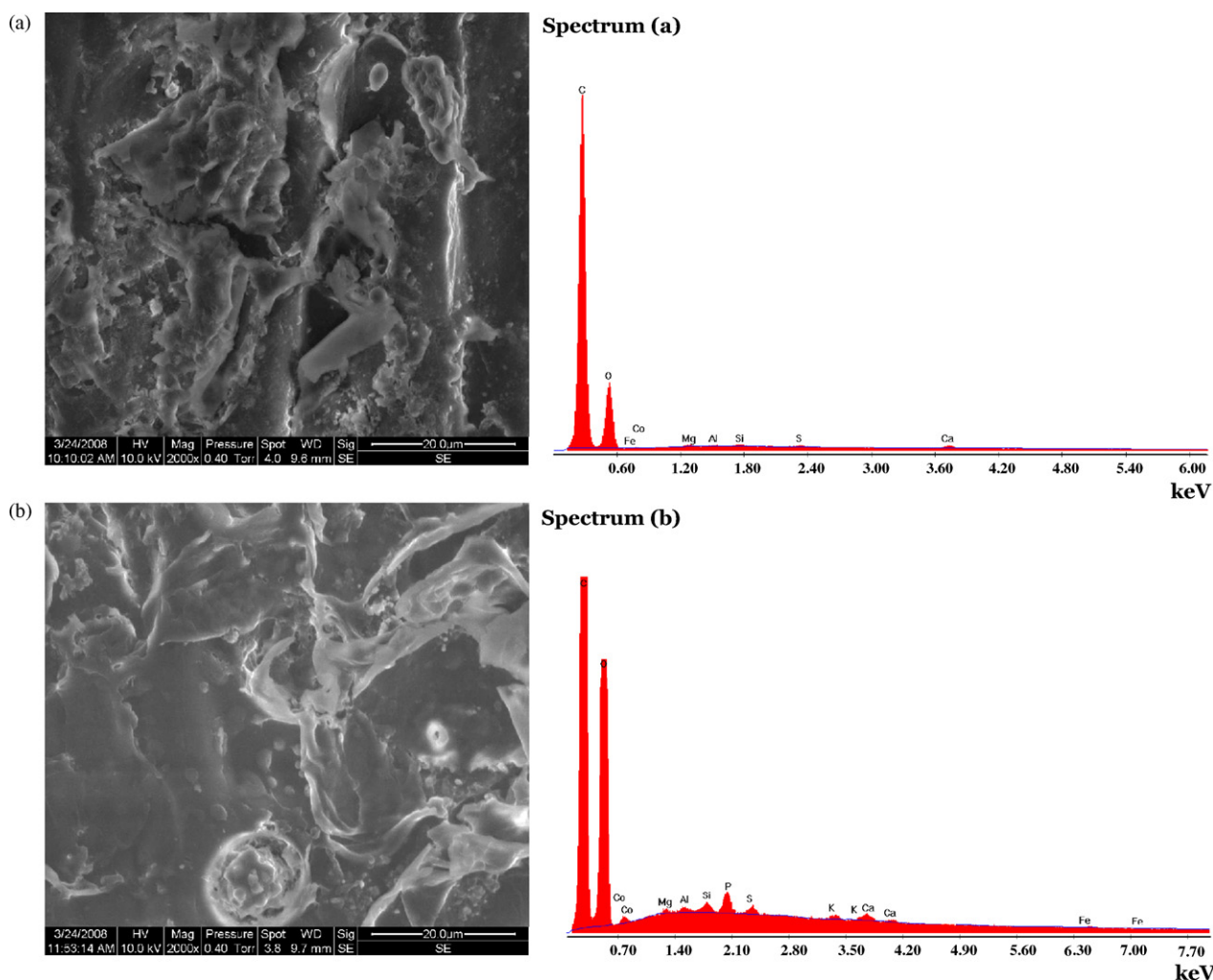


Fig. 5. (a) SEM photograph and EDS spectra of date palm fibers before phosphates biosorption. (b) SEM photograph and EDS spectra of date palm fibers after phosphates biosorption.

phosphate concentrations used for the batch adsorption experiments. The amount of the desorbed P is slightly increased with the increase of the adsorbed P. These results indicate that the P adsorption onto date palm fibers is not completely reversible and the bonding between the sample particles and adsorbed PO_4^{3-} is likely strong. It is relatively difficult for the adsorbed PO_4^{3-} to be desorbed from the samples.

3.8. 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. It can be found that the phosphate adsorption onto date palm fibers tends to decrease with the increase of pH, from 7.85 mg P/g at pH 1.4 to 3.4 mg P/g at pH 10.4. The pH of the aqueous solution is an important variable that influences the adsorption of anions and cations at the solid–liquid interfaces. As can be seen from Table 4, the pH value of the phosphate solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. Similar trends were also observed for phosphate adsorption on others adsorbents [28–35]. In Table 4, some common adsorbents for phosphates removal are presented and their reported phosphate adsorption capacities (mg P/g adsorbent) are given.

Akaganéite and layered double hydroxides appeared to have higher phosphate adsorption capacities respectively 59.6 and 42.4 mg/g than other materials, which may be attributed to the chemical precipitation, a more significant contributory phenomenon to the removal of PO_4^{3-} than physical adsorption. However, quartz sand seemed to have a minor phosphate adsorption capacity than other materials. In comparison with some mineral and organic materials the orthophosphate species seem to be efficiently removed from aqueous solutions using date palm fibers as natural adsorbent. The orthophosphate species uptake (4.35 mg/g) from aqueous solutions using date palm fibers as a cheap and abundant natural adsorbent was reached at pH 6.8.

3.9. The prospect of using date palm fibers to remove phosphates

Typical removal methods for high concentration of phosphorus consist of biological treatments such as the conventional activated-sludge process, chemical treatments, such as precipitation with Al, Fe and Ca components, or a combination of both treatments. However, in the case of a low concentration of phosphorus, bio treatment and precipitation are not effective. Fixed-bed processes using adsorption methods are recommended as the most effective removal processes for low concentrations [36–38].

The results reported herein indicate that date palm fibers could be successfully used to remove phosphates from aqueous solution

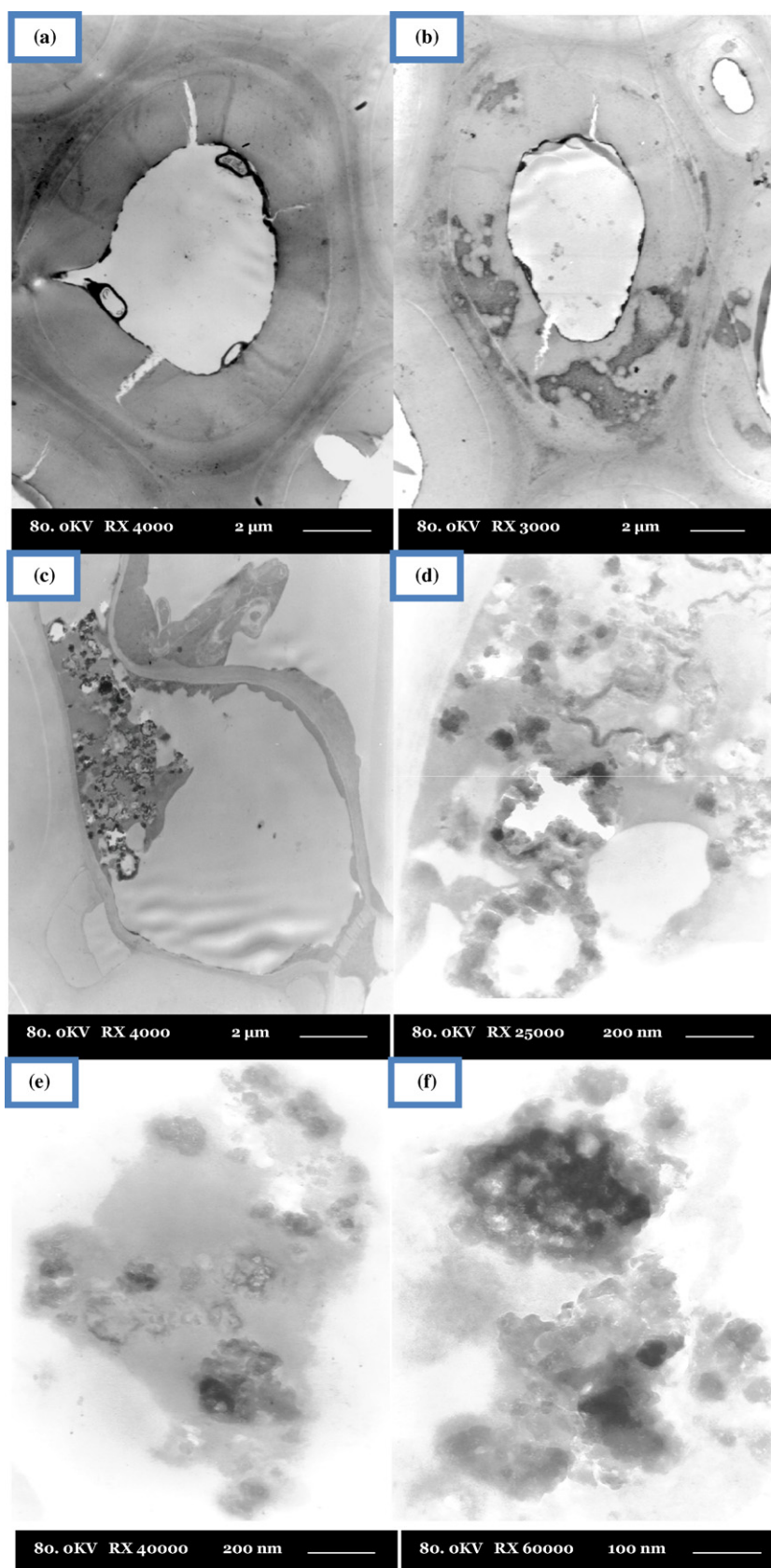


Fig. 6. (a) TEM photograph of date palm fibers before phosphates biosorption. From (b) to (f) TEM photographs of date palm fibers after phosphates biosorption at different magnifications. (b) (3000×), (c) (4000×), (d) (25,000×), (e) (40,000×), (f) (60,000×).

Table 3
Desorbability in percent of the biosorbed phosphates onto date palm fibers.

Initial concentration (mg P/L)	Biosorbed P (mg P/g)	Desorbed P (mg P/g)	Desorbability (%)
10	1.45 ± 0.14	0.15 ± 0.02	10.34 ± 0.43
30	3.75 ± 0.14	0.45 ± 0.01	12.00 ± 0.20
50	4.70 ± 0.20	0.52 ± 0.00	11.06 ± 0.53
70	5.35 ± 0.11	0.67 ± 0.00	12.52 ± 0.28
90	5.60 ± 0.20	0.74 ± 0.02	13.21 ± 0.13
110	5.85 ± 0.14	0.78 ± 0.01	13.33 ± 0.16

Table 4
Phosphates sorption capacities of different low cost and easily available materials.

Material	Adsorption capacity (mg P/g)	pH	Reference
Natural palygorskite	4	7.2	[28]
Layered double hydroxides	42.4	6	[31]
Akaganéite	59.6	7	[32]
Fe-oxides-coated quartz sand	0.62	5.3	[33]
Al-oxides-coated quartz sand	0.54	5.3	[33]
Calcite	1.9	8.2	[34]
Quartz sand	0.04	8.3	[35]
Amorphous slag	8	8.2	[29]
Calcined metal hydroxide sludge	16.48	6.95	[30]
Date palm fibers	4.35	6.8	This study

by sorption process. The biosorption of PO_4^{3-} onto date palm fibers may not be completely reversible and the bonding between the sample particles and sorbed PO_4^{3-} is likely strong. Consequently, the date palm fibers that adsorbed, accumulated phosphates may be a friendly material to the environment, as it does not require further treatment for regeneration because of its potential application to acid soils fertilization in arid climate such as southern of Tunisia.

4. Conclusions

Removal of PO_4^{3-} from aqueous solution onto date palm fibers was carried out at room temperature. Results indicate that pH, initial phosphate concentration and adsorbent dosage impacted orthophosphate specie removal: the PO_4^{3-} uptake increased with the increase of initial phosphate concentration and decreased with increasing pH values. It is also seen that a further increase in adsorbent dose (greater than 6 g/L) affect the uptake of phosphates biosorption greatly.

The conditions of maximum biosorption of the orthophosphates ions were optimized. In nature and in normal treatments, the treated waters are usually at pH from 5 to 8, so the adsorption capacity of PO_4^{3-} is about 4.35 mg P/g at pH 6.8, for an adsorbent dosage of 6 g/L, initial phosphate concentration of 50 mg/L, under a constant temperature of $18^\circ\text{C} \pm 02$, and the equilibrium state was reached within 120 min of exposure time.

The FT-IR spectroscopy, SEM/EDS and TEM analysis data provides a useful indicator on the mechanism of phosphates retention by adsorption and bioaccumulation onto date palm fibers due to the biosorption treatment. Kinetic studies help to identify the sorption process, predicting the mechanisms is required for design purposes. For a solid-liquid sorption process, the solute transfer is usually characterised by either external mass transfer (boundary layer diffusion) for non-porous media or intraparticle diffusion for porous matrices, or both combined [39]. The amount of PO_4^{3-} desorbed was 11–13% means to relatively difficult for the adsorbed PO_4^{3-} to be desorbed from the samples. Consequently, the date palm fibers may be a friendly material to the environment, as it does not require further treatment for regeneration because of its potential application to acid soils fertilization in arid climate such as southern of Tunisia.

The results of present investigation show that the relatively low cost and high capabilities of the date palm fibers make them potentially attractive adsorbents for the removal of phosphate from aqueous solution. Further experiments need to be conducted to test the dynamic sorption of PO_4^{3-} onto date palm fibers in fixed-bed column.

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