Removal of phosphorus from aqueous solution by *Posidonia oceanica* fibers using continuous stirring tank reactor

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ABSTRACT

The present study aims to develop a new potentially low-cost, sustainable treatment approach to soluble inorganic phosphorus removal from synthetic solutions and secondary wastewater effluents in which a plant waste (*Posidonia oceanica* fiber: POF) is used for further agronomic benefit. Dynamic flow tests using a continuous stirred tank reactor (CSTR) were carried out to study the effect of initial concentration of phosphorus, amount of adsorbent, feeding flow rate and anions competition. The experimental results showed that the removal efficiency of phosphorus from synthetic solutions is about 80% for $10 \, g \, L^{-1}$ of POF. In addition, the variation of the initial concentration of phosphorus from 8 to $50 \, mg \, L^{-1}$ increased the adsorption capacity from 0.99 to $3.03 \, mg \, g^{-1}$. The use of secondary treated wastewater showed the presence of competition phenomenon between phosphorus and sulphate which could be overcoming with increasing the sorptive surface area and providing more adsorption sites when increasing the adsorbent dosage of POF. Compared with columns studies, this novel CSTR system showed more advantages for the removal of soluble phosphorus as a tertiary treatment of urban secondary effluents with more adsorption efficiency and capacity, in addition to the prospect use of saturated POF with nutriment as fertilizer and compost.

1. Introduction

The release of phosphorus from municipal wastewater effluents into the environment is one major cause of eutrophication in receiving water bodies [1,2]. Phosphorus removal in conventional small-scale wastewater treatment systems is a critical issue that has not yet been sufficiently solved. In general, primary and secondary treatment is effective in removing particulate phosphorus. However, phosphorus in the secondary effluents is mostly soluble and is consumed for phytoplankton growth causing eutrophication in surface water bodies [3]. Consequently, tertiary treatment of secondary municipal effluents to remove soluble phosphorus has become increasingly necessary to meet environmental regulations worldwide.

There are a wide range of technologies available to remove phosphorus from wastewaters, such as chemical precipitation, biological treatment, constructed wetlands, and a number of wastewater-and-sludge-based methods [4,5], which typically require considerable capital investment and maintenance costs for infrastructure and reagents. Among all the approaches proposed,

adsorption is one of the most popular methods and is currently considered as an effective, efficient, and economic method for water purification. The assessment of a solid–liquid adsorption system is usually based on two types of investigations: batch adsorption and dynamic adsorption studies. Batch mode, which is usually limited to the treatment of small quantities of wastewater, is useful in providing information about effectiveness of sorbate–sorbent system. However, due to its very low scale and its static flow conditions, the data obtained under batch conditions are generally not applicable to most real treatment systems. In the practical operation of full-scale adsorption processes, continuous-flow fixed bed columns are often used. Fixed bed columns are known to be efficient in the removal of both biological oxygen demand (BOD_5) and total suspended solids (TSS) from wastewater. However, nitrogen (N) and phosphorus (P) removal is known to be somewhat problematic [6,7]. Indeed, clogging was a big issue when using reactive media in filtration systems. This was mainly associated to the use of fine media size, to biofilm development caused by large amount of TSS and chemical oxygen demand (COD) in the supplied effluent, and in a minor extent, to carbon dioxide (CO_2) capture and precipitation under calcium carbonate ($CaCO_3$) inside media, and to the flow rate. To overcome the clogging phenomenon, several solutions have been proposed including the use of prefilter to remove suspended solids and organic carbon [8], and the use of larger sized media (more than 5 mm medium diameter, e.g. [9]). However, all

these solutions do not seem to be efficient and sufficient to reduce the risk of clogging and to allow the use of finer reactive filter media with higher sorption capacity.

Continuous stirred tank reactor (CSTR) is another type of dynamic continuous-flow adsorption system which could be used for the removal of soluble phosphorus with less operational problems than column. There is little information available in the literature on the development of CSTR system for the removal of phosphorus from aqueous solution, especially by lignocellulosic materials. In this study, we have developed a novel laboratory reactor for the removal of soluble phosphorus from aqueous solutions using a plant waste material, *Posidonia oceanica* fiber (POF) as a low cost adsorbent. Due to their unique chemical composition, these abundant, renewable, biodegradable and eco-friendly materials could ensure the removal and the recovery of soluble phosphorus. The resulting saturated fibers with phosphorus can be reused as compost and fertilizer for agricultural purposes.

The main focus of this study is to evaluate the effect of certain parameters such as amount of adsorbent, initial concentration of phosphorus and feeding flow rate on phosphorus removal from synthetic solutions. Additional experiments were also made to assess the efficiency of such CSTR system to remove phosphorus from secondary wastewater effluents. The efficiency of this novel CSTR system for the removal of phosphorus was compared with many columns studies.

2. Materials and method

2.1. Adsorbent preparation and characterization

P. oceanica fibers (POF) is an endemic marine magnoliophyta found in the Mediterranean Sea, known for its great production of biomass and it is considered as one of the most abundant plant waste [10]. In many areas, very conspicuous wedge-shaped deposits of POF together with balls of fibrous material known as aegagropili, can be found covering vast areas of coast from a few centimetres in the water to several meters inshore. Those residues can develop cushions up to 4 m high, covering over 50,000 km² [11]. According to Duarte [12], the annual deposition per meter of beach is about 125 kg of dry matter per kilometre of sea meadow which corresponds to a great amount of POF. These deposits when occurring along the esplanades and tourist beaches are considered a nuisance by citizens and bathers especially because of the bad smell coming from the uncontrolled decomposition of the organic matter [13]. This problem is usually solved by removing and disposing those residues to landfill, to date the main and often unique solution applied. 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 [11]. Our purpose is to develop a new method to better manage this renewable important biomass as a novel non-conventional adsorbent for the removal of phosphorus as well as fertilizer and compost rather than disposing those residues to landfill. In this study, POF were collected from the conspicuous wedge-shaped deposits of POF (residues of rhizomes and decomposed leaves) covering vast areas of the sandy beach of Borj Cedria (North Eastern coast of Tunisia). The aegagropili was used as sources of POF in this study. The fibers are 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 biomass was stored in a desiccator for further use. The dried fibers were converted into fine powder by grinding with a *Retsch* mechanical grinder. The powder was sieved and the size fraction lower than 150 μm was used in these experiments.

The particle size distribution of the used fraction was determined using a *Malvern Mastersizer STD06* laser granulometer. The elemental composition of the POF was achieved by energy dispersive spectroscopy (EDS) using a *Quanta-200-Fei* apparatus. The BET specific area was determined using a *Quantachrom Autosorb 1 sorptiometr*. Finally, to give a qualitative and preliminary analysis of the main chemical groups present on the cell wall of biomass, this lignocellulosic 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*.

2.2. Phosphorus solutions preparation

The phosphorus species stock solution containing $1000 \, mg \, L^{-1}$ was prepared by dissolving potassium dihydrogenophosphorus (KH_2PO_4) powders (analytical reagent grade) in distilled water. Phosphorus working solutions in different concentrations were prepared by diluting the phosphorus stock solution with distilled water. The initial pH was adjusted to the desired value using 0.1 N HCl or NaOH.

2.3. Continuous adsorption studies

2.3.1. Laboratory CSTR presentation and experimental protocol

Continuous adsorption tests were carried out by using a CSTR for the removal of phosphorus from synthetic solutions and secondary wastewater effluents. A 1.2 L glass reactor was used to ensure the contact between POF and phosphorus in aqueous solutions. We have used a1.2 L glass reactor on the base of previous study performed to investigate such reactor for the removal of soluble contaminants [14–16]. At the start of the experiments, the desired fiber dosage was put in the reactor, which is then completely filled with the aqueous phosphorus solution at the desired concentration. Phosphorus-containing water was then continuously fed into the CSTR at different flow rate with a variable flow pump. In the same time, the adsorbent was also fed to the reactor in order to hold constant the POF mass in suspension and to achieve different fibers dosages (2, 5, or 10 g (dry weight) per liter).

The reactor was continuously stirred at 300 rpm using a magnetic stirrer. The system was continuously operated for about one hour until equilibrium was reached. This state is characterized by a quasi-stability of phosphorus concentrations at the outlet of the reactor.

The effluent was sampled at certain time intervals to determine the efficiency of this CSTR system for the removal of phosphorus. For each aqueous sample (10 mL), the suspension was filtered through 45 μm filter paper and the filtrate was analyzed in order to determine its dissolved phosphorus concentration. All the assays presented hereafter were conducted in triplicate and the mean values were reported in this study.

2.3.2. Effect of influent phosphorus concentration

Effect of influent phosphorus concentration on the adsorption of phosphorus onto the POF was investigated using four synthetic solution concentrations 8, 15, 30 and $50 \, mg \, L^{-1}$. The adsorbent dosage and flow rate were fixed to $5 \, g \, L^{-1}$ and $20 \, mL \, min^{-1}$, respectively.

2.3.3. Effect of the adsorbent dosage

Impact of the adsorbent dosage was determined for a constant concentration of the feeding synthetic solution and flow rate of $15 \, mg \, L^{-1}$ and $20 \, mL \, min^{-1}$, respectively. The used POF dosages tested were fixed to 2, 5 and $10 \, g \, L^{-1}$.

2.3.4. Effect of flow rate

Effect of the contact time between the POF and the phosphorus synthetic solution was evaluated for a constant feeding concentration and adsorbent dosage of $15\,mg\,L^{-1}$ and $5\,g\,L^{-1}$, respectively. The tested flow rates were fixed at 20 and $40\,mL\,min^{-1}$ using the peristaltic pump. These flow rates correspond to contact times of 1 and 0.5 h, respectively.

2.3.5. CSTR tests using secondary wastewater effluents and effect of anions competition

Secondary wastewater effluents from an activated sludge wastewater treatment plant (WWTP) for Soliman city (North East of Tunisia) were used to study the effectiveness of the continuous flow system in treating real wastewater. The phosphorus concentration in this wastewater was about $8\,mg\,L^{-1}$. These wastewater effluents typically have high levels of other anions, such as chloride and sulphate. The wastewater was used to study the effect of anion competition. In addition, two dosage of POF (5 and $10\,g\,L^{-1}$) were used to study the impact of increasing POF dosage on anion competition process.

2.4. Phosphorus analysis

The analysis of phosphorus was done by spectrophotometric measurement at 880 nm, following the ascorbic acid method [17] using a *Thermospectronic* (UV1) spectrophotometer: dilute solutions of phosphorus 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. Triplicate tests showed that the standard deviation of the results was ±5%.

2.5. Phosphorus uptake

The phosphorus uptake was calculated following the aqueous concentration difference method. The aqueous influent concentration C_0 ($mg\,L^{-1}$) and leftover phosphorus concentration at different time intervals, C_t ($mg\,L^{-1}$), was determined and the phosphorus uptake Q_t (mg phosphorus adsorbed/g adsorbent) was calculated from mass balance equation as follows:

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

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:

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

2.6. Evaluation of mass transfer characteristics

The determination of phosphorus mass transfer characteristics from aqueous solution to the adsorbent is a very important step in order to perform numerical studies and to carry out the up scaling of the used laboratory dynamic experimental devices such as columns or continuously fed reactors [14]. For reactors where the feeding solution is continuously renewed and the adsorbent mass is held constant, the rate of mass transfer (R) with respect to time is expressed as [14]:

$$R = V\frac{dC_w}{dt} \qquad (3)$$

where C_w is the phosphate concentration in the aqueous solution, V is the solution volume in the reactor and t is the contact time.

Table 1
Main physico-chemical characteristics of POF.

Particle size distribution	
d_{10} (μm)[a]	4
d_{60} (μm)[a]	27
UC[b]	6.18
d_{50} (μm)[a]	21
Elemental composition (%)	
Carbon	48.87
Oxygen	38.03
Sodium	0.21
Magnesium	0.56
Aluminum	0.60
Silicon	1.36
Sulphur	2.07
Chlorides	0.37
Potassium	0.37
Calcium	4.96
Iron	2.51
Specific area ($m^2\,g^{-1}$)	
Specific area, BET method	2

[a] d_x: mesh diameter that allows x% of the porous media to pass through.
[b] UC: uniformity coefficient: ratio of d_{60}/d_{10}.

Considering the concentration gradient in the external film around the particles, the rate of mass transfer across the boundary layer is equal to the adsorption rate:

$$V\frac{dC_w}{dt} = kS(C_s - C_w) \qquad (4)$$

where k is the mass transfer coefficient ($m\,s^{-1}$), C_s is the phosphate concentration onto the POF, S is the total interfacial area (m^2) of the adsorbent particles and V is the working solution volume in the reactor. Over small time scales, when C_s is much lower than C_w, the rate of mass transfer can be expressed by:

$$-V\frac{dC_w}{dt} = kSC_w \qquad (5)$$

Upon integration of Eq. (5), the following linearized equation is obtained:

$$\text{Ln}\left(\frac{C_t}{C_0}\right) = -\frac{kS}{V}t \qquad (6)$$

where C_0 and C_t and are the influent aqueous phosphate concentration and the effluent concentration at time t, respectively.

The mass transfer coefficients for all the experiments carried out in this study are determined from the slope of the plot of $Ln(C_t/C_0)$ vs. t.

2.7. Statistical analysis

Measurements were made in triplicates for the analysis of phosphorus 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 and to the confidence intervals methods. All statistical analysis was done using Microsoft Excel 2007 version office XP.

3. Results and discussion

3.1. Adsorbent characterization

From Table 1, the POF is a very fine solid porous media and could be use as a fine reactive filter media with good sorption capacity. Since POF is an organic material, the elemental composition analysis shows that carbon and oxygen are the main components of
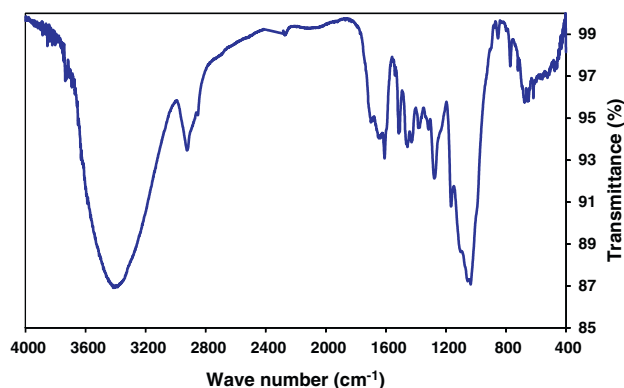
Fig. 1. FTIR analysis of POF surface.

Fig. 2. Effect of influent aqueous concentration on phosphorus removal by POF (pH = 7; adsorbent dosage = 5 g L^{-1}, temperature = 18 ± 2 °C; flow rate = 20 mL min^{-1}; error analysis = ±5%).

Fig. 3. Effect of POF dosage on phosphorus removal (pH = 7; initial phosphorus concentration = 15 mg L^{-1}, temperature = 18 ± 2 °C; flow rate = 20 mL min^{-1}; error analysis = ±5%).

fibers. In addition, POF as a vegetal biomaterial, constituted principally by lignin and cellulose as major constituents, can be viewed as natural ion-exchange materials that primarily contain weak acidic and basic groups on the surface [11,18]. The presence of anions such as chloride and sulphate may play an important role in the anion exchange processes with phosphorus. Furthermore, the presence of a non-negligible portion of iron, silicon and aluminum hydroxides can also be involved in the ligand exchange processes. Since the Ca content is important for the removal of phosphorus via sorption and precipitation processes, the POF which contain about 6% of Ca (Table 1), could be considered as a promising adsorbent for the removal of phosphorus.

Functional groups on the surface of POF that can be involved in the adsorption of phosphorus ions species are usually determined by Fourier transform infrared (FTIR) spectroscopy. The infrared (IR) spectrum of POF, displayed a number of absorption peaks, indicating the complex nature of the examined biomass. The result presented in Fig. 1 revealed adsorbent heterogeneity, evidenced by different characteristic peaks with the possible presence of phenolic (2934; 2095 cm^{-1}), carboxylic (1663; 1517; 1432; 1385 cm^{-1}), hydroxyl (3422 cm^{-1}) and carbonyl (1707 cm^{-1}) groups.

It is well indicated from FTIR spectrum of POF that carboxyl and hydroxyl groups are present in abundance. In addition, the peak attributed to pectin (1385 cm^{-1}) confirms the high quantity of calcium cations. In fact, pectin molecules have carboxyl functions which provide the ability to exchange ions. In the case of plant cell wall, these ions are mainly calcium ions formed by the apoplasmic movement. These divalent ions have the ability to form calcium bridges between two carboxyl groups of two adjacent molecules of pectin. This egg-box dimmer formation, resulting from the interaction between calcium ions and carboxylate groups is an electrostatic interaction highly influenced by temperature and pH [11,18].

3.2. Effect of influent phosphate concentration

The changes of phosphorus effluent concentration vs. time for different influent concentrations (8–50 mg L^{-1}) are presented in Fig. 2. From this figure, the results show that adsorption process is clearly time dependent. The effluent phosphate concentration decreases rapidly and reaches a quasi-equilibrium state after a contact time of about 10 min. From 10 to 70 min, the uptake is further increased but with a much slower rate. This kinetic adsorption process is explained by the fact that at the beginning, the phosphorus ions were adsorbed by the exterior surface of POF, the adsorption rate was fast. When the adsorption of the exterior surface reaches saturation, the phosphate ions enter into the POF particles and are adsorbed by the interior surface of the particles.
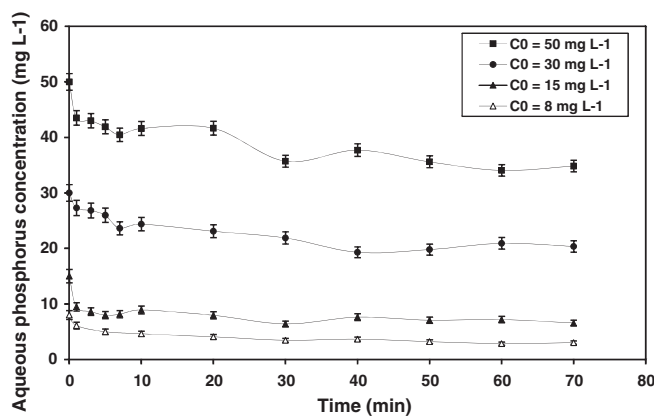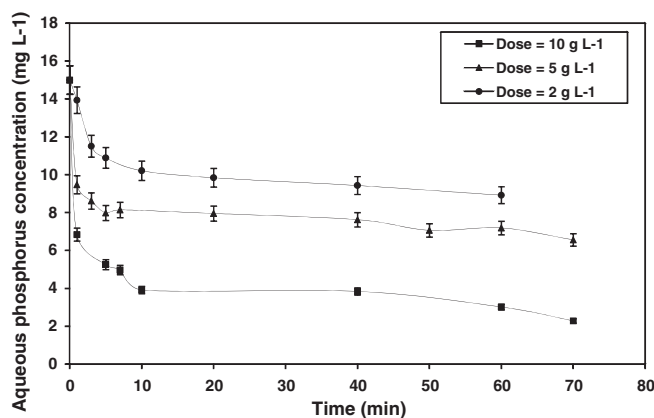
The phosphorus uptake increases with increasing initial phosphorus concentration. In fact, raising the influent phosphorus concentration from 8 to 50 mg L^{-1} allows the POF to increase their adsorption capacities from 0.99 to 3.03 mg g^{-1}. This finding is certainly due to the fact that at a fixed adsorbent dose, the number of active adsorption sites to accommodate the phosphorus ion remains unchanged while with higher adsorbate concentrations, the adsorbate ions to be accommodated increase. Thus, corresponding cumulative removal is higher at higher initial concentrations. Furthermore, phosphorus concentration gradient between aqueous solutions and adsorbent increase privileges the phosphorus adsorption process onto POF.

3.3. Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of phosphorus ions was investigated at dosages range of 2–10 g L^{-1} of POF. The result displayed in Fig. 3, shows that an increase in the biomass quantity causes a decrease in the residual phosphorus concentration and consequently an increase in the adsorption removal efficiency. Indeed, the adsorption removal efficiency values increased from 40% to 80%, as the biomass dose was increased from 2 to 10 g L^{-1}. Such a trend is mainly attributed to an increase in the sorptive surface area and the availability of more adsorption sites.
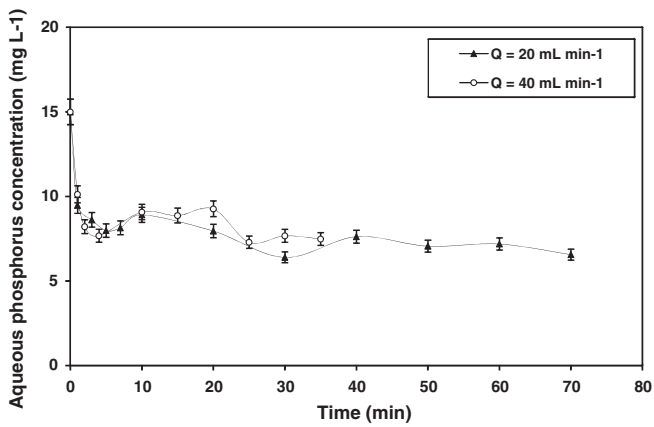
Fig. 4. Effect of flow rate on phosphorus removal by POF (pH = 7; initial phosphorus concentration = 15 mg L^{-1}, adsorbent dosage = 5 g L^{-1}; temperature = 18 ± 2 °C; error analysis = ±5%).
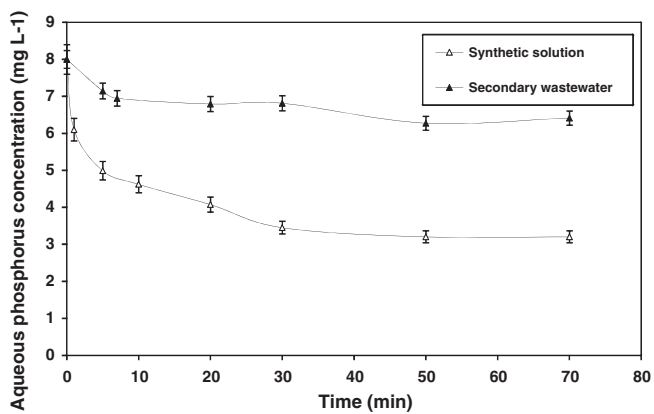

Fig. 5. Comparison of the removal efficiency of this CSTR system using synthetic solution and Soliman secondary wastewater (pH = 7; initial phosphorus concentration = 8 mg L^{-1}, adsorbent dosage = 5 g L^{-1}; temperature = 18 ± 2 °C; error analysis = ±5%).

3.4. Effect of phosphate feeding flow rate

The hydraulic residence time (HRT) in the reactor is generally considered as an important factor conditioning the pollutant removal under dynamic conditions. As cited in Section 2.3.4, two theoretical HRT of 1 and 0.5 h were investigated for a constant POF dosage of 5 g L^{-1}. The experimental results (Fig. 4) show that either the curve shape or the final effluent phosphorus concentrations at equilibrium are almost the same for the tested HRT. Thus, HRT does not affect phosphate removal performance by POF for the range of the tested flow rates. Consequently, phosphorus removal using such large-scale dynamic systems should more tolerate flow rate fluctuations than phosphate concentrations or adsorbent dosage [15,16].

3.5. CSTR tests using secondary wastewater effluents and effect of anions competition

To study the effectiveness of such continuous flow system to treat real wastewater and the competition processes between phosphorus and other anions present in wastewater, CSTR tests using secondary wastewater effluents from the WWTP of Soliman city was carried out and compared with synthetic solutions at the same influent phosphate concentration, 8 mg L^{-1}. The results displayed in Fig. 5, show that the phosphorus removal efficiency of this CSTR system decreases when using secondary wastewater efflu-

Table 2
Main characteristics of the used secondary treated wastewater from the WWTP of Soliman city.

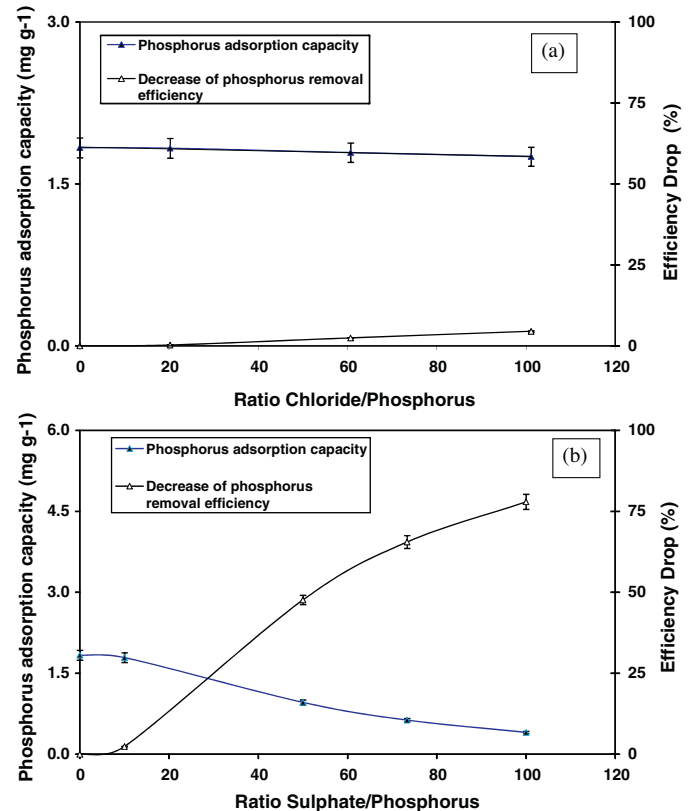| Parameters	Values
pH	7.3
Temperature (°C)	23
Salinity (g L^{-1})	1.6
Suspended solids (mg L^{-1})	73
COD (mg L^{-1})	90
BOD5 (mg L^{-1})	32.5
Ammonium (mg L^{-1})	30.2
Sulphate (mg L^{-1})	452.5
Chloride (mg L^{-1})	1190.9
Phosphorus (mg L^{-1})	8

Fig. 6. Impact of chloride (a) and sulphate (b) anions on the removal capacity and efficiency of phosphorus (pH = 7; initial phosphorus concentration = 15 mg L^{-1}, adsorbent dosage = 2 g L^{-1}; temperature = 18 ± 2 °C; error analysis = ±5%).

ents compared to synthetic solution. Indeed, phosphorus removal efficiency obtained with secondary wastewater is about 40% lower than the removal efficiency obtained with synthetic solution. The decrease of the phosphorus removal efficiency is mainly due to the presence of a competition phenomenon between phosphorus and other soluble anions present in secondary wastewater. Characteristics of secondary wastewater effluents from the WWTP of Soliman city given in Table 2 indicate the presence of a high concentration of chloride (1190.9 mg L^{-1}) and sulphate (452.5 mg L^{-1}).

In order to determine which anion from chloride and sulphate significantly affect the phosphorus removal efficiency by POF, batch adsorption tests were carried out by addition of chloride (303; 910 and 1517 mg L^{-1}) and sulphate (150; 750; 1100 and 1500 mg L^{-1}) with 15 mg L^{-1} of phosphorus for 60 min. The results presented the phosphorus adsorption capacity and the impacts of anions on the removal efficiency are given in Fig. 6. The results presented in Fig. 6a show that chloride anions cause minimal interference with the adsorption of phosphorus onto POF. In fact, for chlo-
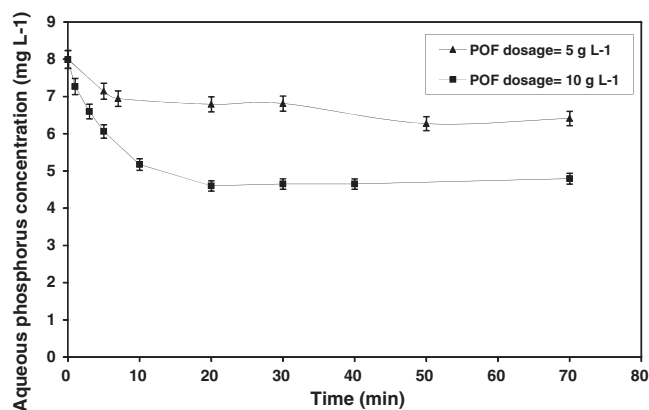
Fig. 7. Impact of increasing adsorbent dosage on the reduction of competition phenomenon (pH = 7; initial phosphorus concentration = 8 mg L^{-1}, temperature = 18 ± 2 °C; error analysis = ±5%).

ride/phosphorus ratio equal to 100 the decrease of the phosphorus adsorption capacity is about 5%. However, for the case of sulphate the increase in the sulphate concentration from 150 to 1500 mg L^{-1} results in a great drop of phosphorus adsorption. Indeed, for sulphate/phosphorus ratio lower than 20, the average decrease of the phosphorus adsorption capacity is about 5% and attained 75% for sulphate/phosphorus ratio equal to 100 (Fig. 6b). This indicated that the decrease of phosphorus removal efficiency obtained with secondary wastewater is mainly due to competition process between phosphorus and sulphate anions. Indeed, sulphate anions present in Soliman secondary wastewater at concentration of 452.5 mg L^{-1} which corresponding to sulphate/phosphorus ratio about 55. At this ratio, the adsorption capacity of phosphorus decrease about 40% using Soliman secondary wastewater (Fig. 5) and about 50% using aqueous solution of phosphorus in the presence of sulphate anions (Fig. 6b) which confirm the competition effect with sulphate. This phenomenon has been reported by several works which studied the adsorption of phosphorus by different materials such as cationized solid wood residues [19] Lanthanum(III) doped mesoporous silicates material [20] and various calcined layered double hydroxides [21].

For overcoming this competition effect, another CSTR test was made to study the impact of increasing the POF dosage from 5 to 10 g L^{-1} on phosphorus removal efficiency. The results presented in Fig. 7 indicate that the increase of POF dosage increase the phosphorus removal efficiency and reduce the competition effect with sulphate anions. In fact, the increase of the POF dosage from 5 to 10 g L^{-1} increased the phosphorus removal efficiency about 16%. This finding can be explained by the fact that increasing the dosage of POF increases the number of adsorption sites available to adsorb phosphorus which in turn reduces the competition effect with sulphate. Thus, more the number of adsorption sites, less is the effect of competition between phosphorus and sulphate.

3.6. Evaluation of mass transfer characteristics

In order to determine the effect of initial phosphorus concentration, adsorbent dosage and flow rate on the rate transport of phosphorus species from the bulk to the solid–liquid interface in synthetic solution, the mass transfer coefficients were determined by plotting Ln (C_t/C_0) with residence time and the results are given in Table 3. The results show that the mass transfer increased about 10 times with increasing the initial phosphorus concentration from 15 to 50 mg L^{-1}. This is due to the increase of phosphorus ions in solution which make their transport to the solid–liquid interface faster than lower concentration containing less phos-

phorus molecules. Similarly, increasing adsorbent dosage from 5 to 10, leads to the increase of the mass transfer from the bulk to the solid–liquid interface. This observation can be imputed to the increase in adsorption sites. For the effect of flow rate, it was demonstrated in Section 3.4 that the increasing of flow from 20 to 40 did not affect the adsorption capacity nor the equilibrium state, however, the values of the mass transfer coefficients indicate a slight increase of the rate transport of phosphate species from the bulk to the solid–liquid interface when the flow rate rises from 20 to 40 mL min^{-1}. This observation may be due to the decrease of the resistance in mass transfer when the flow rate is increased.

In order to determine the effect of anions competition, the mass transfer coefficients of synthetic solution and Soliman wastewater were determined at 5 g L^{-1} dosage and were found to be 1.06×10^{-3} m s^{-1} and 5.6×10^{-4} m s^{-1}, respectively. This result indicates that the rate transport of phosphate species to the solid–liquid interface in synthetic solution is faster than in wastewater. This finding is due to the presence of high concentrations of sulphate anions in the used wastewater, which compete with phosphorus anions for adsorption sites. The mass transfer coefficient of Soliman wastewater at 10 g L^{-1} dose was found to be 9.86×10^{-4} m s^{-1} which is comparable to the one found for the synthetic solution at POF dosage of 5 g L^{-1}. This indicates that the rise in adsorbent amount leads to an increase in the sorptive surface area and the availability of more adsorption sites. Thus, for overcoming the effect of competition in wastewater and to get a satisfactory adsorption capacity, it is recommended to increase the adsorbent dosage.

3.7. Prospect of using POF to remove and recover phosphate using CSTR system

Phosphorus removal from aqueous solutions onto POF using a continuous stirred tank reactor (CSTR), could be considered as the first study using plant waste to adsorb soluble phosphorus using CSTR mode. Thus, it is important to compare the adsorption capacity of POF with other used materials (organic and inorganic) and the efficiency of CSTR system with other types of dynamic continuous-flow adsorption system. For this aim, a comparison was made and presented in Table 4.

The results show that the POF could be considered as a very attractive and promising material to remove phosphorus from aqueous solutions when compared with the common natural materials. Indeed, the phosphorus adsorption capacity of POF is very important compared to many mineral materials such as bauxite, shale, burnt oil shale, limestone, zeolite, fly ash [22], Danish sands [27], dolomite [29] and some organic materials such as skin split waste [31] and peat [33]. Thus, POF could be considered as the most efficient natural material for the removal of phosphorus with Oyster shell [28].

In addition to the high adsorption capacity of POF, the use of CSTR system is more efficient than column mode. In fact, the high efficiency obtained in this study (80%) is higher than the efficiency obtained for the most column studies (average 50%) indicated in Table 4. Furthermore, the use of such CSTR system could ensure many operational, environmental and economic advantages. From a practical stand point, the amount of adsorbent material used in CSTR is less than in column. The contact between the particle of adsorbent and the soluble pollutants is more homogenous and the rate transport of phosphate species to the solid–liquid interface is faster than in column mode.

In cases in which column systems are used, where all contaminants (SS, BOD, TN, TP etc.) are removed in one filter bed, the clogging of substratum active particle surfaces and pore spaces, with organic matter (litter, biofilm etc.), can lead to decreasing soluble phosphorus removal. However, in CSTR just the soluble

Table 3
Determination of the phosphorus species mass transfer coefficients for the CSTR experiments carried out (*: POF dosage = 5 g L^{-1}, pH = 7, flow rate = 20 mL min^{-1}; ◆ : influent phosphorus concentration = 15 mg L^{-1}, pH = 7, flow rate = 20 mL min^{-1}; ⚎ : influent phosphorus concentration = 15 mg L^{-1}, pH = 7, POF dosage = 5 g L^{-1}).

	Influent phosphorus concentration (mg L^{-1})*			POF dosage (g L^{-1})◆		Flow rate (mL min^{-1})⚎	
	15	30	50	5	10	20	40
k (m s^{-1})	1.23×10^{-3}	9.4×10^{-3}	3.1×10^{-2}	1.23×10^{-3}	4.71×10^{-2}	1.23×10^{-3}	7.87×10^{-3}

Table 4
Comparison of phosphorus adsorption capacities and efficiencies of different adsorbent materials using different types of dynamic continuous-flow adsorption system.

Adsorbent material		Experimental conditions	Adsorption capacities and efficiencies		References
			Q (mg/g)	Efficiency (%)	
Bauxite Shale Burnt oil shale Limestone Zeolite Fly ash	Column	20 g of the adsorbent 2.5–40 mg L^{-1} KH$_2$PO$_4$ 2.1–2.8 mL min^{-1} HRT 12–24 h	0.650–0.730	–	[22]
Alum sludges	Column	1 kg of the adsorbent 1.68 mg L^{-1} KH$_2$PO$_4$ HRT 3 h	2.66	45%	[23]
Wollastonite	Column	5–30 mg L^{-1} KH$_2$PO$_4$	0.467–1.8	51.10%	[24]
Shellsand	Column	5–1000 mg P L^{-1} KH$_2$PO$_4$	3.5	–	[25]
EAF steel slag	Column	18.3 kg of the adsorbent 20 mg L^{-1} KH$_2$PO$_4$ HRT 12–24 h	1–2.2	80%	[26]
Sands (Danish)	Column	10 mg L^{-1} KH$_2$PO$_4$ HRT 12–14 h	0.052–0.165	50%	[27]
Oyster shell	column	100 g of the adsorbent 50 mg L^{-1} KH$_2$PO$_4$ HRT 4 h	0.180–7.925	–	[28]
Sand	Column	330 mg L^{-1} KH$_2$PO$_4$	0.7–0.8	37%	[29]
Dolomite			0.2	44%	
Sand	Column	0.5–2.0 mg L^{-1} HRT 2 h; HLR 7.2–86.4 L d^{-1}	–	40%	[30]
Skin split waste	Column	1.7 mg L^{-1} Industrial wastewater 40 mL h^{-1} HRT 0.5 h	0.17	–	[31]
Peat	Biofilter	Domestic wastewater Biofilter 70–258 L m^2 d^{-1}	–	12–44%	[32]
Peat	Pilot-scale	Municipal Wastewater 4.9 mgP L	0.081	58%	[33]
POF	CSTR	10 g adsorbent 1.2 L CSTR 50 mgP L KH$_2$PO$_4$ HRT 0.5^{-1} h	3.03	80%	This study

phosphorus and other soluble pollutants can be removed. The clogging phenomenon affects the lifetime of filter bed, however, in CSTR the adsorbent material are in suspension and the saturated adsorbent could be regenerated continuously.

In addition, there are many potential environmental and economic benefits such as the minimization and the management of the great amount of POF accumulated annually on the beaches of the Mediterranean and which causes a series of economic and environmental problems. At present they are dumped as waste, which result in the loss of enormous mass of organic material. The use of POF as a novel non-conventional and low-cost adsorbent for the removal of phosphorus using CSTR, can be an effective method for the removal of soluble phosphorus from wastewater and consequently the control of eutrophication in lakes and similar confined water bodies. Moreover, the recovery of phosphate-containing wastewater could be considered as an alternative resource of phosphorus in order to compensate the global exhaustion of high grade phosphate ores. The enriched POF with phosphorus and other nutrients could be reused as compost and fertilizer for agricultural purposes and as a consequence reduces the use of chemical fertilizer.

3.8. Costs estimation

The use of POF as a novel non-conventional and low-cost adsorbent for the removal of phosphorus using CSTR system could be considered as a suitable method to treat hotel effluents which are characterized by high content of phosphorus due to the excessive use of detergents. In fact, a major part of the drinking water stream is used in bathtubs, showers, hand-washing basins, laundry machines, kitchen sinks, etc., has a low content of organic matter and pollutants [34]. The amount of this wastewater was estimated about 28 m^3 day^{-1} for a hotel where the maximum occupancy is on the order of 1000 clients [35].

Table 5
Estimation of the capital and operation costs.

Item	Cost, €
Capital costs (€)	
Pumps	10,526
Tanks	1,360
Piping	26,315
CSTR reactor	5,350
Total	43,551
Operating costs (€/m³)	
Labour	0.32
Energy	0.108
Transport	0.02
Maintenance	0.01
Total	0.458

The low cost and the simplicity of the current treatment system and the abundance of POF on the Mediterranean coasts allow the application of this technique to treat this amount of wastewater which could be reused for flushing toilets as useful strategy for saving water [34] and for watering the green and the gardened area.

The estimation of the capital and the operating costs for the treatment of $30 \, m^3 \, day^{-1}$ is presented in Table 5. On the basis of the results of this study, the capacity of the reactor was estimated to $1.25 \, m^3$ to treat a flow of $30 \, m^3 \, day^{-1}$. One collection tank of $1.25 \, m^3$ is also needed to collect the treated water. The piping costs included the piping used for wastewater treatment and for the reuse of treated for flushing toilet [35]. Concerning the operating costs, energy costs were calculated from the energy requirements for pumping feed water and for stirring the reactor (power demand is about $0.54 \, kWh/m^3$). Transport costs corresponded to the transport of the enriched POF to the composting unit. The costs of adsorbent, chemicals and sludge disposal are null. The calculated total treatment cost is $0.458 \, €/m^3$.

In addition to the economic advantages, there are many environmental benefits such as the reduction of water consumption in hotels by the reuse of the treated wastewater for flushing toilet and watering green area. This may reduce the pressure on the tap water demand especially in arid or semiarid regions (like Tunisia) where water demand exceeds the natural available resources. The recovery of the great amount of phosphorous and valorization of the abundant and renewable POF is a promising strategy for the management of natural resources on the coastal regions.

4. Conclusions

This study shows that POF can be considered a tenable material for phosphorus removal and recovery from aqueous solutions compared to various other materials. The main parameter influencing the phosphorus adsorption capacity of POF is the adsorbent dosage, with greater POF concentration yielding greater adsorption. The phosphorus removal efficiency from synthetic solutions exceeds 80%. The use of secondary treated wastewater showed the presence of competition phenomenon with sulphate which could be overcome by increasing the adsorbent dosage of POF. The CSTR system could be used as a tertiary treatment for urban secondary effluents with the added benefits of reducing inputs to landfills and reusing nutrient saturated POF as fertilizer and compost. Large scale pilot studies are recommended in order to confirm the promising results obtained at laboratory scale.

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