



Phosphate mine wastes reuse for phosphorus removal from aqueous solutions under dynamic conditions

Salah Jellali^{a,*}, Mohamed Ali Wahab^a, Makram Anane^a, Khalifa Riahi^b, Latifa Bousselmi^a

^a Water Research and Technologies Centre (CERTE), Wastewater Treatment and Recycling Laboratory, Soliman, Tunisia

^b School of Engineering in Rural Equipment of Medjez El Bab, Laboratory of Chemistry and Water Quality, Medjez El Bab, Tunisia

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ABSTRACT

Phosphate mine slimes (PMS), an abundant waste generated from phosphate mines, was used in this study as a cost-effective adsorbent to investigate the phosphate anions removal from synthetic and urban secondary treated wastewater solutions. Dynamic experiments using laboratory reactors were carried out to study the effect of phosphate influent concentration, PMS dosage and feed flow rate on phosphate removal and a kinetic model was used to determine the phosphate mass transfer coefficients. The results show that the phosphate removal increases with influent phosphate concentration and PMS dosage. The feed flow rate has no significant effect. On the other hand, the phosphate removal from wastewater is less efficient than the synthetic solution due to anions competition process. The evaluation of phosphates mass transfer coefficients confirms the presence of anion competition phenomena and the necessity of increasing PMS dosage to provide more adsorption sites. The cost-effective and high adsorptive capability of PMS make them attractive materials for phosphate anions removal and recovery from secondary treated wastewaters with the possibility of agronomic reuse as fertilizer.

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1. Introduction

Phosphate is often present in wastewater mostly as organic phosphate, inorganic phosphate, oligophosphates and polyphosphates [1]. Its release into water bodies can disturb the balance of aquatic organisms and affects water quality due to eutrophication process, consequence of decrease of dissolved oxygen availability and excessive algae growth [2]. In many countries, stringent regulations have limited discharged phosphorus level in urban wastewater to 0.05 mg L^{-1} and emphasize the need of adapted techniques for its removal [3].

Various biological, physical and chemical methods have been developed to remove phosphate from wastewaters. The formers are very difficult to operate in wastewater treatment plants because they require strict anaerobic and aerobic conditions and highly skilled operation regarding microbial adaptation [4]. Physical methods, such as reverse osmosis and electro-dialysis, developed to fulfill the strict standards of wastewater disposal, have the drawback of high costs [5]. Precipitation process with lime, aluminum and iron salts, is the most widely used chemical technique for phosphate removal. However, it requires a large amount of chemicals and produces a great quantity of waste sludge [6]. Anion exchange-

ers are other commonly used chemical methods but they have low selectivity in presence of competing anions [7].

In the last decade, considerable attention has been paid to developing effective and low-cost adsorbents from natural materials for phosphate adsorption with agricultural reuse potential [8,9]. The tested materials include apatite [10,11], dolomite [12,13], limestone [14], zeolite [15,16], coal acid mine drainage sludge [17], wood particles [18] and date palm fibers [9].

Phosphate mine slimes (PMS) are wastes generated abundantly by phosphate mining industry and discharged into the environment [19]. Each ton of manufactured phosphate produces about 1 T of PMS, causing a very serious waste disposal problem for many countries [19,20,21]. To date, in Mediterranean countries, very little work has been carried out regarding the reuse of mine sludges in agricultural activities [19,21]. No significant research work has been reported on the reuse of PMS for urban or industrial wastewaters treatment in general and phosphates removal in particular. However, it could present a potential for phosphate removal given the wide range of studies reporting the efficiency of fine porous media to treat urban wastewater [17,22]. The success of such treatment is environmentally beneficial by reducing water bodies' eutrophication and the resulting material could offers a subsequent use for soil amendment if of course PMS do not release any toxic elements such as heavy metals [8,17].

On the other hand, the peer-reviewed scientific literature indicates that the majority of phosphate removal studies were carried out with either synthetic solutions or very small scale devices

* Corresponding author at: CERTE, B.P. 273, 8020 Soliman, Tunisia.

Tel.: +216 79325044; fax: +216 79325802.

E-mail addresses: salah.jellali@certe.rnr.tn, sj194@yahoo.fr (S. Jellali).

(batch mode), which make their extrapolation for real application very difficult. Only very few experiments have been done using real wastewaters and/or laboratory columns [23,24]. They are confronted to the clogging phenomenon caused by suspended solids filtration and micro-organisms population growth. This phenomenon induces a significant decrease of the treatment efficiency and of the measured flow rate at the columns outlet [25–27]. The laboratory reactors are other techniques used to tackle these problems by treating an important amount of wastewater and ensuring continuous renewal of both the aqueous solution and the adsorbents. The need of using this technique at laboratory or field scale has been pointed out by several authors [17,28].

This research work presents a significant practical and industrial interest in the valorization of an abundant waste for wastewater treatment. It has two original aspects which are the reuse of PMS as a low-cost adsorbent and the recovery of nutrients (phosphates and nitrogen) from urban wastewater respectively. Moreover it offers a double environmental solution since it avoids the water bodies' eutrophication and reduces the discharged PMS wastes amounts. Thus, this research work can be considered as a very interesting contribution to the preservation of the environment in particular for countries rich in phosphates.

The main goal of this work is to study, under different experimental conditions, the efficiency of PMS as an abundant and low-cost waste for phosphate removal from synthetic solutions and secondary treated wastewater, using laboratory reactors technique. The comparison of the capability of this adsorbent with those presented in literature and its prospect use in agriculture is also discussed.

2. Materials and methods

2.1. Adsorbent preparation and characterization

The used adsorbent was obtained from the discharged sludges of Metlaoui phosphate extraction manufactures, located at around 350 km at the south of Tunis, Tunisia. The annual average amount discharged is about 3.5 millions m^3 [29]. These sludges are a mixture of 86% of water and 14% of solid phase (PMS).

In this study, PMS were separated from water after natural settling during 5 days period, and then air-dried during one week. The resulting product was crashed and sieved mechanically using a set of sieves. Only the particles with diameter inferior to $63 \mu\text{m}$ were used. This fraction was chosen in order to have a good mixing between PMS particles and the aqueous phase when the reactor is stirred with the magnetic stirrer and consequently to ensure a good contact between aqueous phosphate species and the adsorbent. The particle size distribution of the used fraction was determined using a Malvern Mastersizer STD06 laser granulometer. Its mineralogical composition was performed by X-ray analysis with a Philips PAN Analytical, X Pert PRO-MPD model. The elemental composition of the PMS was achieved by energy dispersive spectroscopy (EDS) using a Quanta-200-Fei apparatus. Finally, the BET specific area was determined using a Quantachrom Autosorb 1 sorptometer.

2.2. Synthetic phosphate solutions preparation and analysis

Potassium dihydrogen phosphate (KH_2PO_4), acquired from Fisher Scientific, was used in adsorption tests as the source of phosphate ions. A stock phosphate solution of 1000mg L^{-1} was prepared with distilled water and used throughout the study. The analysis of phosphate species contents was performed spectrophotometrically at 880 nm, following the ascorbic acid method [30].

2.3. Dynamic adsorption studies

2.3.1. Experimental set up and protocol

The used experimental set up is given by Fig. 1. The contact between the phosphate species and the PMS was ensured in a 1.2 L glass reactor. At the beginning of the experiments, the used reactor was rapidly filled with both the desired aqueous phosphate solution and the PMS dose. Afterwards, using a variable flow peristaltic pump (Masterflex, Cole-Parmer Instrument Company, USA), the aqueous solution containing dissolved phosphate species was continuously fed to the reactor at a predefined flow rate, corresponding to the desired contact time (Fig. 1). In the same time, an accurate adsorbent mass, determined on the basis of preliminary experiments, was also fed to the reactor each 10 min in order to compensate its losses through the overflow and consequently to keep constant the PMS dosage. The reactor was continuously stirred at 300 rpm using a magnetic stirrer (Agimafic-S, I. P. Selecta Company) for a while after the equilibrium is reached. The equilibrium corresponds to phosphate concentrations stability at the reactor outlet.

The efficiency of the system on the phosphate removal was followed through the effluent phosphate concentrations progress measure by the analysis of 10 mL aqueous solutions sampled at different times. For each aqueous sample, the suspension was filtered through $45 \mu\text{m}$ filter paper and the filtrate was analyzed in order to determine its dissolved phosphate concentration. All assays presented hereafter were conducted in duplicate and the mean values were reported.

2.3.2. Effect of the influent phosphate concentration

The influent phosphate concentrations effect on their adsorption onto the PMS was carried out through kinetics and equilibrium studies. Three influent phosphate concentrations were used: 15, 30 and 50mg L^{-1} and their progress in time were followed until 70 min. The adsorbent dosage, pH and aqueous flow rate were fixed at 5g L^{-1} (dry amount), 7 and 20mL min^{-1} respectively.

2.3.3. Effect of the adsorbent dosage

The impact of the adsorbent dosage was determined for a constant concentration of the feed synthetic solution, pH and flow rate of 15mg L^{-1} , 7 and 20mL min^{-1} respectively. The used PMS doses were fixed to 2, 5 and 10g L^{-1} .

2.3.4. Effect of the feeding flow rate

The effect of the contact time between the PMS and the phosphate synthetic solution was evaluated for a constant influent concentration, pH and adsorbent dosage of 15mg L^{-1} , 7 and 5g L^{-1} respectively. The tested flow rates were fixed to 20 and 40mL min^{-1} using the peristaltic pump. These flow rates correspond to contact times of 1 and 0.5 h respectively.

2.3.5. Effect of anions competition

During this study, two types of phosphate solutions were used. The first one, corresponded to synthetic solutions at a concentration of 8mg L^{-1} prepared, as cited above, by diluting the phosphate stock solution with distilled water. The second type of phosphate solutions with also an average concentration of 8mg L^{-1} came from an activated sludge wastewater treatment plant (WWTP) of Soliman city (North East of Tunisia). Its quality depends on the importance of the industrial proportion in the raw wastewater received in the WWTP entrance. However, the average values of some physico-chemical parameters are: 73mg L^{-1} of suspended solids (SS), 90mg L^{-1} of biological oxygen demand (BOD_5), 32.5mg L^{-1} of total organic carbon (TOC), 7.3 of pH, 1.6g L^{-1} of salinity and 8mg L^{-1} of phosphate species. This effluent does not

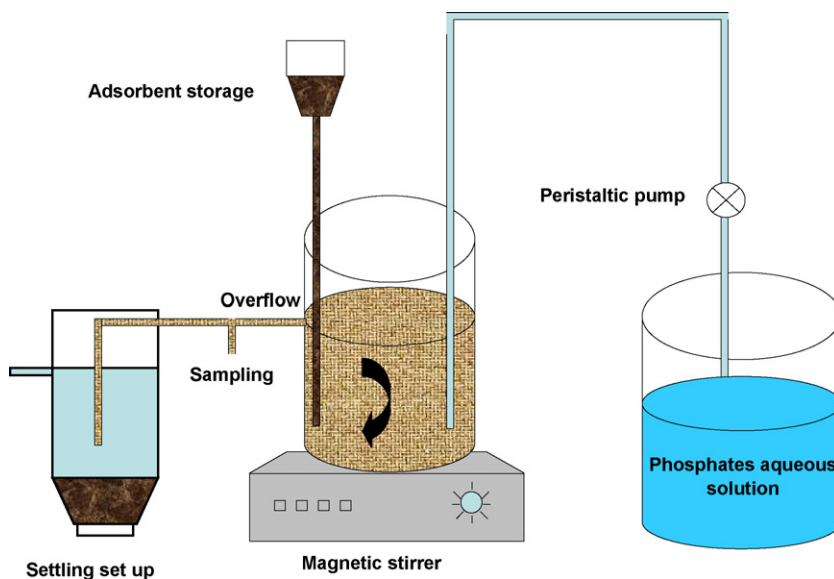


Fig. 1. Schematic representation of the used device for the study of phosphate adsorption onto PMS in dynamic mode.

conform to the Tunisian discharges norms, which are 30 mg L^{-1} for both BOD_5 and SS and 0.05 mg L^{-1} for phosphate [27].

2.3.6. Phosphate removal parameters calculation

The quantity of the adsorbed phosphate was calculated from the decrease of the phosphate concentration in the aqueous solutions. At a giving time, t , the amount of adsorbed phosphate onto the PMS, Q_t , (mg g^{-1}) was obtained as follows:

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

where C_0 and C_t are the influent aqueous phosphate concentration and the effluent concentration at time t , respectively, V the total volume of the aqueous solution (L) and M is the mass of the used dried adsorbent (g).

The adsorption removal efficiency (ARE), at time t , is calculated from the relation:

$$\text{ARE}(\%) = \frac{(C_0 - C_t)}{C_0} 100 \quad (2)$$

2.4. Evaluation of mass transfer characteristics

The determination of phosphate mass transfer characteristics from the aqueous solution to the adsorbent is a very important step for the up scaling of the used laboratory dynamic experimental devices such as columns or continuously fed reactors or also to perform the numerical studies [17,28]. For reactors where the feed solution is continuously renewed and the adsorbent mass is held constant, the rate of mass transfer (R) with respect to time is expressed as [28]:

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

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

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:

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

where, k is the mass transfer coefficient (m s^{-1}), C_s the phosphate concentration onto the PMS, S the total interfacial area (m^2) of the

adsorbent particles and V is the working solution volume in the reactor. At short times, when C_s is very lower than C_w , then the rate of mass transfer can be expressed by:

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

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

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

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 were determined from the slope of the plot of $\text{Ln}\left(\frac{C_t}{C_0}\right)$ vs. t .

2.5. Heavy metals leaching test

Since Tunisian PMS could contain some heavy metals [19], two leaching experiments were carried out to determine if certain metals could be solubilized in the aqueous phase from the PMS during the phosphate adsorption process. The tests were performed by agitating 100 mL distilled water dosed with 0.5 g of PMS for 120 min at pH 7. After agitation, samples were filtered through a $45 \mu\text{m}$ membrane, and then the concentrations of the main dissolved metals (Cd, Zn, Cr, Cu, Fe, Mn and Ni) in the filtrate were determined using an Elemental Analysis Spectrometer Inductively Coupled Plasma (Jokin Ywon Ultimac).

3. Results and discussions

3.1. Adsorbent characterization

The physico-chemical PMS matrix characterization shows that they are formed with a very fine solid porous media with a relatively high surface area (Table 1). Moreover, they are essentially composed by dolomite (50%) and clays (39%) which should have an important impact on the aqueous phosphate removal [12–13,17]. The elemental composition analysis shows that oxygen; calcium; silicon and iron are the main components of the PMS. Other constituents with percentage lower than 5% are also present in the PMS including carbon; phosphorus; aluminum; magnesium; chlorides;

Table 1

Main physico-chemical characteristics of the used Mine phosphate slimes (1) d_x : mesh diameter that allows $x\%$ of the porous media to pass through; (2) UC: uniformity coefficient: ratio of d_{60}/d_{10} .

Particle size distribution	
d_{10} (μm) ¹	4
d_{60} (μm) ¹	27
UC ($-$) ²	6.18
d_{50} (μm) ¹	21
Mineralogical composition (%)	
Calcite	2
Dolomite	50
Smectite	10
Illite	12
Kaolinite	17
Fluorapatite	7
Helvite	1
Gypsum	1
Elemental composition (%)	
Carbon	4.35
Oxygen	38.69
Sodium	0.74
Magnesium	2.94
Aluminum	3.50
Silicon	13.81
Phosphorus	4.06
Sulphur	0.83
Chlorides	1.08
Potassium	0.79
Calcium	23.83
Iron	5.37
Main heavy metals contents (mg/kg) [19]	
Cadmium	48.2
Zinc	311.5
Chromium	352.0
Copper	28.1
Specific area ($\text{m}^2 \text{g}^{-1}$)	
Specific area, BET method	40.82

sulfur; potassium and sodium (Table 1). On the other hand, the heavy metals analysis in the PMS showed that they are relatively rich in cadmium and chromium [19].

3.2. Dynamic experiments results

3.2.1. Effect of the influent phosphate concentration

According to the experimental conditions detailed in Section 2.3.2, the results show that for a constant PMS dosage of 5 g L^{-1} , the phosphate adsorption process is clearly time dependent (Fig. 2). The effluent phosphate concentration decreases rapidly and reaches a quasi-equilibrium state after a contact time of about 10 min. From

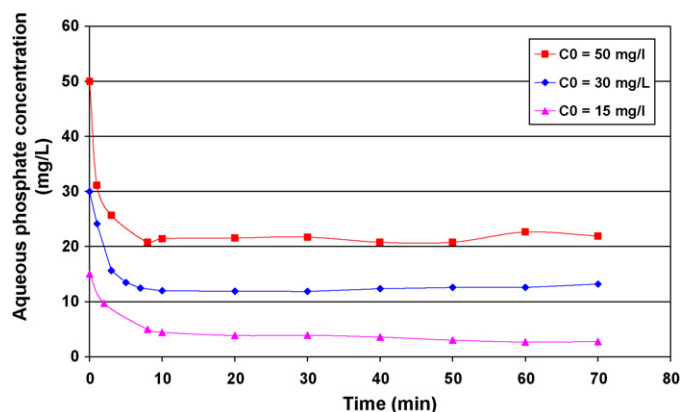


Fig. 2. Effect of influent aqueous concentration on phosphate removal by PMS (pH 7; adsorbent dosage = 5 g L^{-1} , temperature = $18 \pm 2 \text{ }^\circ\text{C}$; flow rate = 20 mL min^{-1}).

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 phosphate ions were adsorbed by the exterior surface of PMS, so the adsorption rate was fast. When the exterior surface sites reach saturation, the phosphate ions enter into the PMS particles and were adsorbed by the interior surface of the particles [9]. Thus, a minimum contact time of 10 min seems to be sufficient to reach an equilibrium state between the adsorbent and the phosphates species contained in the aqueous solution. This relatively small contact time is due to the high stirring forces in the reactor which facilitate the contact between PMS particles and the phosphates species and increase the rate transport of phosphate species from the aqueous solution to the solid–liquid interface. In addition, the use of fine porous media size ($<63 \mu\text{m}$) increase the sorptive surface area and the availability of more adsorption sites. It is important to underline that this contact time is comparable to the ones found for adsorbents having relatively similar mineralogical composition (dolomite and/or clays). For example, Karaca et al. [13] showed that in batch mode, 10 min is sufficient to reach an equilibrium state between phosphate species and dolomite originated from Turkey. Moreover, Boujelben et al. [31] showed that this equilibrium time was evaluated to 15 min when they studied the orthophosphates removal by Tunisian iron oxide crushed brick.

The final measured effluent phosphate concentrations for influent feed aqueous concentrations of 50, 30 and 15 mg L^{-1} were determined to be 21.8, 12.6 and 2.8 mg L^{-1} , respectively. These effluent concentrations are equivalent to phosphate removal efficiencies of about 56%, 58%, and more than 81%, respectively.

On the other hand, it appears that the phosphate uptake increases with increasing influent phosphate concentration. In fact, raising the influent phosphate concentration from 15 to 30 and 50 mg L^{-1} allows the PMS to increase their adsorption capacities from 2.44 to 3.48 and 5.64 mg g^{-1} respectively. This finding could be explained by the fact that higher is the initial aqueous phosphate concentrations, higher is the concentration gradient between aqueous solution and the solid phase which result in more important diffusion rates. Furthermore, for high initial aqueous concentrations, the contact probability between phosphates species contained in the aqueous phase and the adsorbent might be more privileged.

The phosphates adsorption process onto PMS was not yet illustrated. However, according to many phosphate adsorption studies using mineral adsorbents, this process might be essentially chemical [10,11,31]. The involved mechanisms might include both ligand ion exchange with chlorides, and sulphates anions (see Table 1) and sharing between phosphate species and some functional groups such as hydroxyl groups [31].

3.2.2. Effect of the adsorbent dosage

The impact of the PMS dosage on phosphate removal under the experimental conditions cited in Section 2.3.3, shows that the effluent phosphate concentrations decrease rapidly until a contact time of about 10 min (Fig. 3), then the phosphate removal is further increased but with a very slow rate. Furthermore, it is observed that higher is PMS dose, lower is the effluent phosphate concentrations and consequently higher is the removal efficiency. The effluent phosphate concentrations at equilibrium for PMS doses of 2, 5 and 10 g L^{-1} are determined to be 7.5, 2.8 and 0.8 mg L^{-1} , respectively (Fig. 3). These effluent concentrations are equivalent to phosphate removal efficiencies of about 50%, 81%, and more than 94%, respectively. Thus, under the studied experimental conditions, PMS adsorption capacity increases with increasing its dose. This trend has also been observed for the adsorption of phosphate onto dolomite [13] and onto coal acid mine drainage

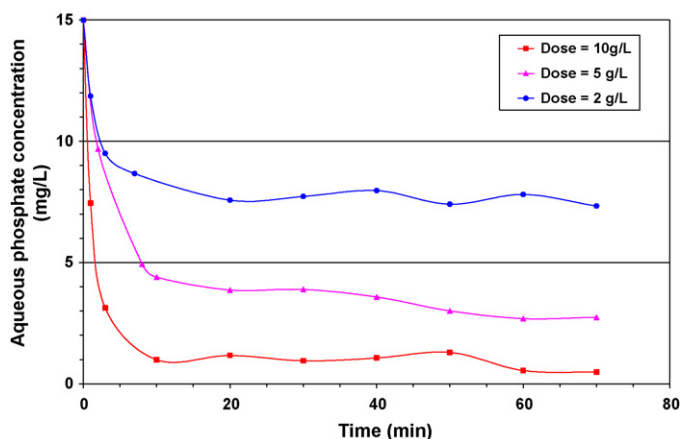


Fig. 3. Effect of PMS dosage on phosphate removal (pH 7; initial phosphate concentration = 15 mg L^{-1} , temperature = $18 \pm 2^\circ\text{C}$; flow rate = 20 mL min^{-1}).

sludge [17]. It confirms that the PMS dose increase induces an increase in the total available surface area of the adsorbent particles. The phosphate removal efficiency observed at PMS dose of 10 g L^{-1} is significantly high and indicates that they could be used as potential adsorbent for phosphate removal from aqueous solutions.

3.2.3. 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 PMS dosage of 5 g L^{-1} . The experimental results (Fig. 4) show that either the curve shape or the final effluent phosphate concentrations at equilibrium are almost the same for the tested HRT. At equilibrium, the phosphate removal efficiencies are calculated to be about 81% for the two tested flow rates. Thus, HRT does not significantly affect phosphate removal performance by PMS for the range of the tested flow rates. This is due to the fact that the two used HRT (1 and 0.5 h) are higher than 10 min, which is determined to be sufficient to reach equilibrium between the phosphate species in the aqueous phase and the PMS (see Section 3.2.1). This finding is in concordance with the results reported by Wei et al. [17] when they studied the phosphate removal from surface water from the Monongahela river (West Virginia, USA) by acid mine drainage sludge generated by coal mine. Consequently, phosphate species removal using such large-scale dynamic systems should more tolerate

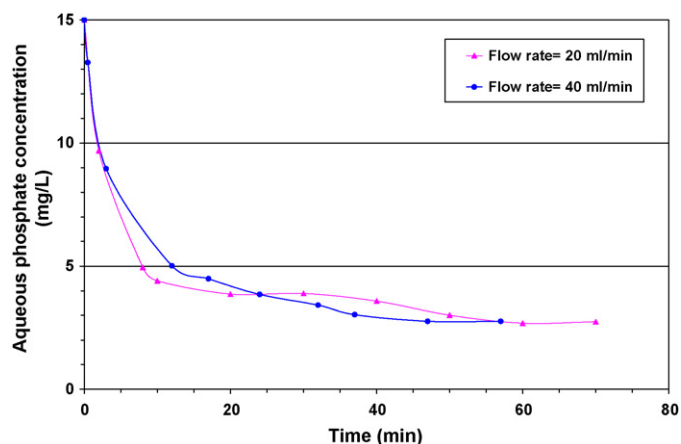


Fig. 4. Effect of flow rate on phosphate removal by PMS (pH 7; initial phosphate concentration = 15 mg L^{-1} , adsorbent dosage = 5 g L^{-1} ; temperature = $18 \pm 2^\circ\text{C}$).

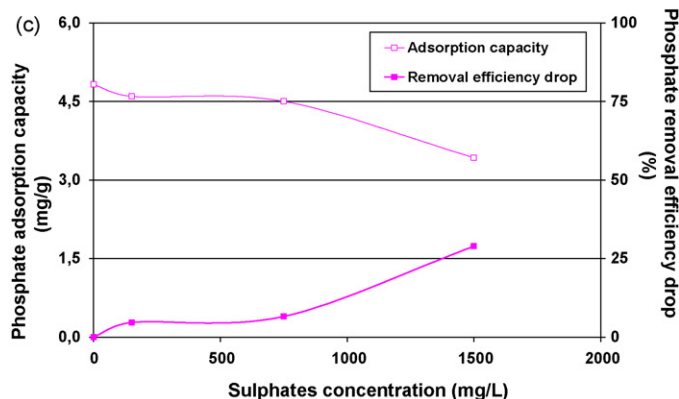
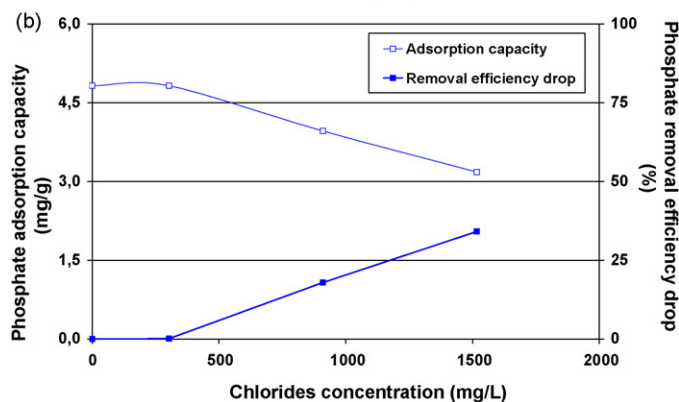
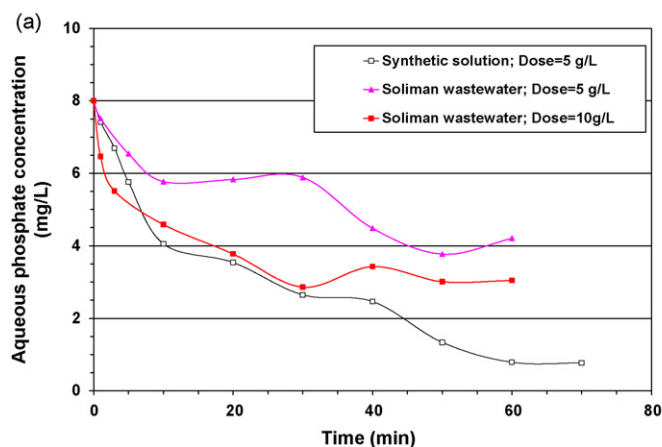


Fig. 5. Effect of anion competition on phosphate removal by PMS (a) Comparison between synthetic solution and Soliman secondary wastewater (pH 7; initial phosphate concentration = 8 mg L^{-1} , temperature = $18 \pm 2^\circ\text{C}$; flow rate = 20 mL min^{-1}); (b) Impact of chlorides anions in batch mode (pH 7; initial phosphate concentration = 15 mg L^{-1} , temperature = $18 \pm 2^\circ\text{C}$); (c) impact of sulphates anions in batch mode (pH 7; initial phosphate concentration = 15 mg L^{-1} , temperature = $18 \pm 2^\circ\text{C}$).

flow rate fluctuations than phosphate concentrations or adsorbent dosage.

3.2.4. Effect of anion competition

The impact of using the secondary treated wastewater of Soliman city instead of the synthetic solutions at the same influent phosphate concentration, 8 mg L^{-1} , is presented in Fig. 5a. This figure shows that PMS are more efficient to remove phosphate species from synthetic solution than from Soliman's urban wastewater. Indeed, for the same PMS dosage (5 g L^{-1}), the effluent concentrations at equilibrium are determined to be 0.8 and 4.2 mg L^{-1} for the synthetic solution and the wastewater respectively. The corresponding removal efficiencies are estimated to be about 90% and

Table 2

Determination of the phosphate species mass transfer coefficients for the dynamic experiments carried out (*: PMS dosage = 5 g L⁻¹, pH 7, flow rate = 20 mL min⁻¹; ◆: influent phosphate concentration = 15 mg L⁻¹, pH 7, flow rate = 20 mL min⁻¹; ▲: influent phosphate concentration = 15 mg L⁻¹, pH 7, PMS dosage = 5 g L⁻¹).

	Influent phosphate concentration (mg L ⁻¹)*			PMS dosage (g L ⁻¹)◆		Flow rate (mL min ⁻¹)▲	
	15	30	50	5	10	20	40
<i>k</i> (m s ⁻¹)	0.70 × 10 ⁻³	1.06 × 10 ⁻³	2.34 × 10 ⁻³	0.70 × 10 ⁻³	1.58 × 10 ⁻³	0.70 × 10 ⁻³	0.85 × 10 ⁻³

48% respectively. However, when the PMS dosage is increased to 10 g L⁻¹, the equilibrium phosphate concentration in the effluent decreases to 3.0 mg L⁻¹ (Fig. 5a) and the removal efficiency exceeds 62%.

The decrease of phosphate adsorption capacities by PMS is mainly due to the presence of relatively high contents of anions such as sulphates and chlorides in Soliman's wastewater. These two anions are present in the wastewater at concentrations of 452.5 and 1190.9 mg L⁻¹ respectively.

In order to determine the effect of chlorides and sulphates on phosphate species removal by PMS, synthetic batch adsorption assays with different contents of these two anions and a constant phosphorus concentration of 15 mg L⁻¹ were carried out. The tested chlorides and "sulphates" concentrations were fixed to 303; 910 and 1517 mg L⁻¹ and "150; 750; 1100 and 1500 mg L⁻¹" respectively. The results (Fig. 5b and c) show that taking into account the Soliman wastewater quality, the chlorides anions have a much higher efficiency in lowering phosphate species adsorption onto PMS. Indeed, for chlorides and sulphates concentrations of 1517 and 750 mg L⁻¹ respectively, the phosphate species removal efficiency decreases with about 34% and 7% respectively. This finding confirms that the decrease of phosphate removal efficiency obtained with the used secondary wastewater is mainly due to competition process between phosphate species and chlorides anions.

This phenomenon has also been reported by Karthikeyan et al. [32] when they studied the adsorption of phosphate onto cationized solid wood residues. In this context, Jellali et al. [27] showed that the use of real wastewater containing high contents of calcium and magnesium highly affects the ammonium adsorption onto a sandy soil.

3.3. Evaluation of mass transfer characteristics

The mass transfer coefficients were determined as cited in Section 2.4 for all experiments carried out in this study (Table 2). The results show that the mass transfer coefficient increases about 3 times when the influent phosphate concentration rises from 15 to 50 mg L⁻¹. This is mainly due to the increase of phosphate ions in the solution in case of high phosphate concentrations which enhances their transport to the solid–liquid interface. Similarly, increasing adsorbent dosage from 5 to 10 g L⁻¹ increases twice the mass transfer coefficient. This finding could be linked to the increase of the active adsorption sites. Concerning the effect of flow rate, 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.

The mass transfer coefficients of the phosphate experiments onto PMS from Soliman's wastewater are compared to the one of the synthetic solution and presented in Fig. 6. The mass transfer coefficients of the synthetic solution and Soliman's wastewater at the same PMS dosage of 5 g L⁻¹ are found to be 3.15 × 10⁻⁴ m s⁻¹ and 1.68 × 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 relatively faster than in the case of the wastew-

ater. This observation is mainly due to the presence of other anions in wastewater which compete with phosphate anions. The mass transfer coefficient of Soliman's wastewater at 10 g L⁻¹ dose was found to be 3.26 × 10⁻⁴ m s⁻¹ which is comparable to the one found for the synthetic solution at PMS dosage of 5 g L⁻¹. This finding indicates that the rise in adsorbent dosage 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 consequently to improve the phosphate adsorption efficiency, it is recommended to increase the adsorbent dosage.

3.4. Metal leaching experiments

The aqueous phase analysis results after 120 min contact time between PMS and distilled water at pH 7 show that all the followed heavy metals concentrations of Cd, Zn, Cr, Cu, Fe, Mn and Ni are lower than the detection limits of the ICP/AES apparatus, which are 0.1, 5.0, 0.5, 0.5, 5.0, 0.2, 0.5 μg L⁻¹ respectively. Thus, it can be concluded that these heavy metals resolubilization from PMS (see Table 1) to the aqueous phase is not likely to be a major concern when phosphate removal by PMS is carried out at a pH range typical for secondary treated municipal wastewaters (6 < pH < 8). This finding could be explained by the fact that these heavy metals are mainly present in the residual, carbonates and oxy-hydroxides fractions [19]. The exchangeable fraction which could be easily resolubilized does not exceed 3% [19]. This result is in concordance with the one presented by Wei et al. [17] when they studied the phosphate adsorption by acid mine drainage generated by coal mine. Indeed, they showed that even for large pH game (between 5 and 9), no significant metal resolubilization from their adsorbent was observed.

3.5. Comparison with other adsorbents and prospect using of PMS in urban WWTPs

In order to situate the PMS efficiency among the materials used to remove phosphate from aqueous solutions, a comparison based on the adsorbed amount, was made with some common materials under dynamic conditions (Table 3). The results show that the PMS

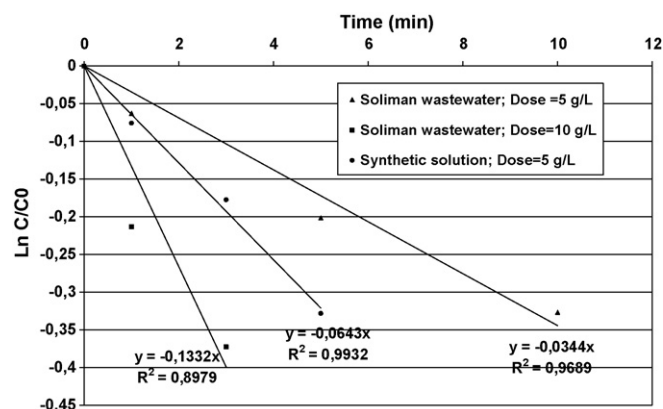


Fig. 6. Impact of the use of wastewater and adsorbent dosage on phosphates mass transfer coefficients

Table 3

Comparison of phosphate adsorption onto mine phosphates slimes with other natural adsorbents (✦ : batch mode; ✧ : dynamic mode).

Material	C_0 (mg L ⁻¹)	Adsorption capacity (mg g ⁻¹)	References
Opoka✦	5–25	0.10	[14]
Skin split waste✧	1.7	0.17	[23]
Dolomite✦	0–100	0.17	[12]
Limestone✦	5–25	0.30	[14]
Bauxite✦	2.5–40	0.61	[33]
Spodosol✦	5–20	1.00	[14]
Apatite✦	5–150	1.09	[10]
Polonite✧	4.11	1.3	[34]
Natural zeolite✦	500–10000	2.15	[15]
Natural zeolite✦	0.5–1000	2.19	[16]
Alum sludges✧	1.68	2.66	[24]
Wood fiber✦	0–100	4.32	[18]
Date palm fibers✦	10–110	4.350	[9]
Apatite✦	0–500	4.76	[11]
Maerl✦	0–5000	7.49	[35]
Shellsand✦	5–1500	8.00	[36]
Scallop shell✧	20	12.70	[37]
Phosphate mine slimes✧	50	5.63	This study

could be considered as promising materials to remove phosphate. Indeed, for an aqueous phosphate concentration of 15 mg L⁻¹, an adsorbent dosage of 5 g L⁻¹ and at pH 7, the adsorption capacity of PMS is about 34 times higher than skin split waste [23], 4 times than polonite [34] and 2 times than alum sludge [24].

This comparison has been extended to batch systems since only very few dynamic experiments were presented in literature (Table 3). Generally for a given adsorbent, the adsorbed phosphate amounts in dynamic mode are very lower than those obtained in batch mode [23,24]. Despite of this proved statement, the adsorbed amount by PMS in dynamic mode is found to be so much higher than those reported for other materials in batch mode (Table 3). Indeed, the adsorbed phosphate mass by PMS is more than 33 times higher than dolomite [12], 18 times than limestone [14], 5 times than apatite [10] and comparable to apatite [11] and lignocellulosic materials such as wood fibers [18] and date palm fibers [9].

Since PMS present a relatively high phosphate adsorption capacity, their use as a low-cost adsorbent could be considered as an attractive method for phosphate removal from urban wastewater. The phosphate adsorption process with PMS could be ensured by a separate set up at the outlet of the secondary treated wastewater plants as a tertiary treatment. The wastewater and the PMS will be continuously renewed and stirred in the set up allowing a reasonable contact time between nutrients and the adsorbent. After nutrients adsorption in this set up, the resulting enriched PMS could then be recovered from the effluent by settling operation in a separate device or by other solid–liquid separation method. The no resolubilization of heavy metals from the enriched PMS with nutrients encourage their reuse as fertilizer for agricultural purposes [8,17]. This operation will limit the derogatory effects on the environment of the non controlled discharging of urban wastewaters and phosphates mines sludges. However, further controlled large-scale experimental investigations are recommended in order to study the impact of physico-chemical and bacterial properties of the agricultural soils and also the added PMS dosage on the possible heavy metals transport in the subsurface.

4. Conclusions

This study demonstrates that phosphate mine wastes can be considered as promising materials for phosphate species removal and recovery from wastewaters. Indeed, even in dynamic mode, they present relatively high phosphate adsorption capacity compared to various other materials tested in batch mode. The main

parameter influencing the phosphate adsorption capacity of PMS is the adsorbent dosage. For neutral pH and PMS doses higher than 10 g L⁻¹, the phosphate removal efficiency from synthetic solutions exceeds 94%. The use of a secondary treated wastewater decreases this removal efficiency due to anion competition phenomenon with probably chlorides and sulphates anions. However, increasing the PMS dosage has significantly compensated this decrease. The no resolubilization of heavy metals from the enriched PMS with nutrients allows their reuse as fertilizer for agricultural purposes.

The used dynamic reactor shows high potentialities of PMS to be used as a tertiary treatment of urban secondary effluents which permits in the same time the prevention of water bodies eutrophication and the reuse of huge amounts of wastes. Large-scale pilot studies are recommended in order to confirm the promising results obtained at laboratory scale.

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