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Phosphates removal from aqueous solutions by powdered marble wastes under static conditions

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ABSTRACT

Powdered marble wastes (PMW) generated by marble industry with abundant amounts were used in this study as low-cost materials to investigate the phosphate anions removal from synthetic solutions. Batch assays were carried out to study the effect of some key parameters such as phosphates influent concentrations, contact time, PMW dosage, and pH on phosphate removal. The batch experiments results showed that PMW have relatively high phosphates adsorption capacity compared to several natural materials. Indeed, the adsorption capacity determined from Langmuir isotherm exceeds $35\,\mathrm{mg\,g^{-1}}$. Furthermore, the adsorption process is favored for acidic pH values and also when increasing initial aqueous concentrations and marble wastes dosage. For an initial aqueous phosphates concentration of $100\,\mathrm{mg\,L^{-1}}$, the removal efficiency is close to 90% for adsorbent dosage higher than $2\,\mathrm{g\,L^{-1}}$. On the other hand, the adsorption modeling studies showed that phosphates adsorption is well described by second-order model and was essentially controlled by the boundary layer diffusion process. The cost effective and high adsorptive capability of PMW make them attractive and promising materials for phosphates anions removal and recovery from secondary treated wastewaters with the possibility of agronomic reuse as fertilizer.

Keywords: Phosphates; Marble wastes; Batch; Removal

1. Introduction

Phosphorus is an essential element in the ecosystem. It has an important role in plant and animal physiology and exists in four forms according to the aqueous pH value (PO_4^{3-}; HPO_4^{2-}; $H_2PO_4^-$; H_3PO_4). The usual forms of phosphorus found in aqueous solutions include orthophosphates, polyphosphate, and organic phosphates [1]. Phosphates are used in many consumer products and are a principal factor for many industry applications such as detergents, clarifying sugar solution, fertilizers industry, and others. Their presence in wastewater with relatively high concentrations may cause eutrophication of water bodies by the excessive

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proliferation of algae and the depletion of dissolved oxygen contents [2]. A variety of biological and physicochemical treatment technologies have been proposed to remove the excessive phosphates ions in wastewaters. The biological methods generally require strict conditions in terms of sequences of aerobic and anaerobic conditions. Furthermore, under certain conditions, the removal efficiency does not exceed 30% [3]. The physicochemical methods such as precipitation in the presence of iron salts and aluminum are relatively expensive and lead to the formation of significant quantities of sludge. Phosphates adsorption using low-cost materials is one of the treatment technologies that permits an important phosphates removal efficiency with the minimum of cost. Many studies have been carried out using different local organic and mineral wastes materials for phosphates removal and recovery from aqueous solutions such as dolomite [4], limestone [5], iron coated natural materials [6], mine wastes [7], crab shells [8], apatite [9], wood fibers [10], and orange wastes [11].

Marble industry generates huge amounts of wastes, by which around 70% of this precious mineral resource, composed mostly of calcite (a crystalline form of calcium carbonate, $CaCO_3$), is wasted in the mining, processing, and polishing procedures. Around 40% of marble wastes are generated world widely during quarrying operations in the form of rock fragments and are essentially being dumped either in nearby empty pits, roads, sidewalks, or landfills [12]. The rest (30%) is associated with the processing and polishing actions in the manufactures and is constituted by crushed fragments and also marble in powder form. They are always discharged in empty pits or landfills without any reuse.

Very little work has been carried out regarding the use of crushed marble for urban wastewater treatment. The main studies concerned their reuse as porous media filter in subsurface flow constructed wetlands technique [13,14]. These studies showed that crushed marble mixed with gravel and sands could be efficiently used for phosphates removal from wastewater. However, no scientific work has been carried out regarding the valorization of Powdered marble wastes (PMW) for urban wastewater treatment in general and phosphates removal and recovery in particular.

The main objective of this work is to study the use of PMW as low-cost materials for phosphates removal from wastewater by varying some key parameters such as initial aqueous concentration, contact times, pH, PMW dosage, and the presence of other anions such as sulfates and chlorides.

2. Materials and methods

2.1. Adsorbent preparation and characterization

In this study, the PMW come from the manufacturing of large stones of "Bianco Gioia" marble. They were collected as a dry pure powder at the vicinity of the cutting and polishing devices from a marble manufacture located in Borj Cedria city which is situated at about 25 km at the south of Tunis, Tunisia. PMW were sieved mechanically using a sieve with a mean diameter of 2 mm in order to remove any existing fragments. Then, it was washed with distilled water and dried in an oven at 40°C for 48 h to a constant weight. The particle size distribution of the used PMW was determined using a Malvern Mastersizer STD06 laser granulometer. Phases present in the PMW were analyzed using an X-ray diffractometer Cu K_α radiation, PW 1710, Philips. Scans were conducted from 0 to 60° at a rate of 2θ/min. The elemental composition of the PMW was achieved by energy dispersive spectroscopy (EDS) using a Quanta-200-Fei apparatus. The BET specific area was determined using a Quantachrom Autosorb 1 sorptiometer. The determination of the pH of zero point charge (pH_{ZPC}) of PMW was performed according to the solid addition method [15] using 0.01 M KNO_3 solutions, 1 g of PMW for initial pH values of 2, 4, 6, 8, 10, and 12.

2.2. Phosphates solutions preparation and analysis

The phosphate stock solution containing 1,000 mg L^{-1} was prepared by dissolving potassium dihydrogen orthophosphate (KH_2PO_4), acquired from Fisher Scientific, in distilled water. Phosphate working solutions with different concentrations were prepared by diluting the stock solution with distilled water. The analysis of phosphates contents was performed spectrophotometrically at 880 nm following the ascorbic acid method [16].

All assays presented hereafter were conducted in triplicate and the mean values were reported.

2.3. Batch adsorption studies

Batch experiments consisted in analyzing the effect of initial aqueous concentration, contact time, solutions pH, adsorbent dosage, and the presence of other anions on phosphates adsorption onto PMW. These experiments were conducted at 22 ± 02°C in 120-mL capped flasks. During these assays, a predetermined amount of the adsorbent was shaken in 50 mL of phosphates solution during 960 min at 400 rpm using a Varimag-poly15 magnetic stirrer. This time is high enough to ensure an equilibrium state between aqueous phosphates and the PMW particles. The dissolved phosphates concentration was determined spectrophotometrically after the suspension filtration through filter paper.

2.3.1. Impact of initial phosphates concentrations and contact time

The influence of initial phosphate concentration and contact time on the adsorption of phosphates by MPW was carried out through kinetic and equilibrium studies. Five initial phosphates concentrations were chosen: 15, 30, 50, 80, and 100 mg L^{-1} and their progress in time were followed at 13 contact times: 1, 5, 10, 20, 40, 60, 90, 120, 180, 300, 420, 720, and 960 min. These experiments were conducted for an adsorbent dosage and pH of 4 g L^{-1} (dry amount) and 6.4 respectively.

2.3.2. Effect of initial pH solutions

The initial aqueous pH solution effect on phosphates adsorption was examined in a series of experiments varying pH between 4 and 10. During these assays, the initial phosphates concentration and the adsorbent dosage were fixed at 100 mg L^{-1} and 4 g L^{-1}, respectively. The pH adjustment was done using small volumes (lower than 1 mL) of 0.1 M HCl and NaOH solutions.

2.3.3. Impact of the adsorbent dosage

The impact of the adsorbent dosage on the phosphates adsorption onto PMW was determined by shaking 50 mL of aqueous phosphates solutions with different PMW amounts. The used initial phosphates concentration and pH were fixed to 100 mg L^{-1} and 6.4, respectively. The tested adsorbent doses were 0.2, 1, 2, 4, and 6 g L^{-1}.

2.3.4. Impact of competition with chloride and sulfates anions

In order to determine the competing effect of chlorides and sulfates anions on the phosphates removal efficiency by PMW, some specific synthetic batch adsorption tests containing both phosphates and chlorides or phosphates and sulfates were carried out. The used chlorides and sulfates concentrations cover a relatively large interval and take into account of exceptional variation of wastewater quality. Indeed, the used chlorides concentrations were fixed to 600, 1,200, 2,400, and 3,600 mg L^{-1} and sulfates ones to 200, 500, 1,000, 1,500 mg L^{-1}. For all these tests, the initial aqueous phosphates concentration and pH were fixed to 100 mg L^{-1} and 6.4, respectively.

2.3.5. Phosphates removal calculation

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

$$q_t = \frac{(C_0 - C_t)V}{M_{\text{MPW}}}$$

where C_0 and C_t (mg L^{-1}) are the initial and at a given time, t, aqueous phosphates concentrations, respectively, V the volume of the aqueous solution (L), and M_{MPW} is the weight of the used adsorbent (g).

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

$$\eta\ (\%) = \frac{(C_0 - C_t)}{C_0} \times 100$$

2.4. Modeling studies

2.4.1. Adsorption isotherms

The adsorption equilibrium defines the distribution of the solute between the liquid and the solid phases after the adsorption reaction reaches equilibrium. The amount of adsorbed solute vs. the amount of solute in solution at equilibrium is called adsorption isotherm. In this study, Langmuir and Freundlich models [17,18] which are the two most famous ones were investigated to fit the experimental adsorption isotherms. The used isotherms and their linear forms are given in Table 1.

2.4.2. Kinetic models

Adsorption of a given solute on a solid is a fairly complex mechanism. Indeed, the rate of adsorption is strongly influenced by several parameters such as the status of the solid matrix that has generally heterogeneous reactive sites and the physicochemical conditions under which the adsorption takes place. The study of adsorption kinetics is very useful for understanding the involved mechanisms and also for the design of future large-scale adsorption facilities. Many

Table 1
Used isotherms models and their linear forms (q_m is the maximum adsorption capacity ($\mathrm{mg\,g^{-1}}$); k_l the Langmuir constant related to the adsorption energy ($\mathrm{L\,mg^{-1}}$); K_F constant indicative of the adsorption capacity and $1/n$ is a constant relative to the adsorption intensity)

Isotherm	Equation	Linear form	Plot
Langmuir	$q_\mathrm{e} = \frac{q_\mathrm{m} k_l C_\mathrm{e}}{1+k_l C_\mathrm{e}}$	$\frac{C_\mathrm{e}}{q_\mathrm{e}} = \frac{1}{k_l q_\mathrm{m}} + \frac{1}{q_\mathrm{m}} C_\mathrm{e}$	$\frac{C_\mathrm{e}}{q_\mathrm{e}}$ vs. C_e
Freundlich	$q_\mathrm{e} = K_\mathrm{F} C_\mathrm{e}^{1/n}$	$\mathrm{Ln}\, q_\mathrm{e} = \mathrm{Ln}\, K_\mathrm{F} + \frac{1}{n} \mathrm{Ln}\, C_\mathrm{e}$	Ln q_e vs. Ln C_e

models are used to fit the kinetic sorption experiments. In this study, the most used ones which are the first-order, second-order, intraparticle, and film diffusion models were tested (Table 2).

3. Results and discussion

3.1. Characterization of the used adsorbent

The main physical and chemical properties of MPW are presented in Table 3. MPW can be considered as a very fine solid porous media and therefore used as a fine reactive filter media with probable high adsorption capacity. Indeed, the mean diameter is relatively low (22.6 µm). The BET specific area of the used PMW was estimated to $0.14\,\mathrm{m^2\,g^{-1}}$ which is comparable to commercial calcium carbonate [19] and dolomite [20]. The X-ray and EDS analyses indicate that PMW are exclusively formed by calcite with relatively high contents of Ca. Since Ca is important for the removal of phosphates via sorption and precipitation processes [21], the PMW should present an interesting capability of phosphates removal and recovery from aqueous solutions (Table 3). The $\mathrm{pH_{ZPC}}$ was determined to 8.11, which is very close to the value found for calcite with a purity of 98% in $\mathrm{CaCO_3}$ [22]. As a consequence, under the used experimental conditions (initial pH = 6.4), the PMW particles surface should be initially positively charged.

Table 3
Main physico-chemical characteristics of the used Marble powder wastes (1: dx: mesh diameter that allows x% of the porous media to pass through; 2: UC: uniformity coefficient: ratio of d_{60}/d_{10})

d_{10} (µm)^1	2.6
d_{60} (µm)^1	28.6
UC (−)^2	10.9
d_{50} (µm)^1	22.6
Ca (%)	32.9
Mg (%)	0.75
Specific area ($\mathrm{m^2\,g^{-1}}$)	0.14
pH of zero point charge ($\mathrm{pH_{ZPC}}$)	8.11

3.2. Bach experiments results

3.2.1. Effect of phosphates aqueous concentration and contact time

The effect of the initial aqueous phosphates concentration and contact time has been determined according to the experimental conditions given in Section 2.3.1. The experimental results show that all curves have globally the same shape (Fig. 1). Indeed, these curves are composed by two distinct parts: the first one is related to a kinetic behavior where the phosphates adsorption by the adsorbent highly increases in time, the second one corresponds to an equilibrium state which is characterized by relative

Table 2
Used kinetic models and their linear forms (k_1 ($\mathrm{min^{-1}}$) and k_2 ($\mathrm{g\,mg^{-1}\,min^{-1}}$) are the equilibrium rate constant of pseudo-first-order and pseudo-second-order models respectively. q_{eI} and q_{eII} are the theoretical phosphates equilibrium concentration onto PMW for the pseudo-first-order and pseudo-second order models respectively. D_f, D_{ip} are the film and intraparticle diffusion coefficients respectively. r is the average radius of the used particles)

Model	Equation	Linear form	Plot
Pseudo-first-order	$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1 (q_e - q_t)$	$\mathrm{Ln}\,(q_e - q_t) = \mathrm{Ln}\, q_{eI} - k_1 t$	$\mathrm{Ln}\,(q_e - q_t)$ vs. t
Pseudo-second-order	$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2 (q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 q_{eII}^2} + \frac{1}{Q_{eII}} t$	$\frac{t}{q_t}$ vs. t
Film diffusion		$\frac{q_t}{q_e} = 6 \left(\frac{D_f}{\pi r^2}\right)^{1/2} \sqrt{t}$	$\frac{q_t}{q_e}$ vs. $\sqrt{t}$
Intraparticle diffusion		$\mathrm{Ln}\left(1 - \frac{q_t}{q_e}\right) = \mathrm{Ln}\,\left(\frac{6}{\pi^2}\right) - \left(\frac{D_{ip}\pi^2}{r^2}\right) t$	$\mathrm{Ln}\left(1 - \frac{q_t}{q_e}\right)$ vs. t

constant adsorption capacities. The duration necessary to reach this equilibrium state is phosphates aqueous concentration dependent. In fact, it has been estimated to be about 720 min for an initial phosphate concentration of 15 and 30 mg L^{-1} and about 960 min for 50, 80, and 100 mg L^{-1}. However, it is important to underline that the maximum of adsorption capacity was achieved during contact times lower than 3 h. Indeed, as an example, for an initial aqueous phosphates concentration of 100 mg L^{-1}, more than 82% of the total adsorption capacity has been observed after only 2 h of contact time. As a consequence for industrial applications, a maximum contact time of 1.5–3 h could be adopted since it permits a relatively important phosphates removal compared to the one found after 16 h of contact time.

On the other hand, the phosphates uptake increased with increasing initial phosphates concentration. In fact, raising the initial phosphates concentration from 15 to 100 mg L^{-1} allows the PMW to increase their adsorption capacities from 3.3 to 22.42 mg g^{-1}, respectively. This finding could be explained by the fact that for high initial aqueous concentrations, the contact probability between phosphates species contained in the aqueous phase and the adsorbent might be more privileged. Furthermore, higher is the initial aqueous phosphate concentration; higher is the concentration gradient between aqueous solution and the solid phase which result in more important diffusion rates [20].

3.2.2. Influence of pH

The effect of pH on phosphates removal by the used adsorbent has been carried out according to the experimental conditions cited in Section 2.3.2. It appears that the adsorbed phosphates amount at equilibrium (q_e) increases with the decrease in pH values (Fig. 2). Indeed, for a constant initial aqueous concentration of 100 mg L^{-1}, the phosphates adsorption was evaluated to be equal to 14.3 mg g^{-1} at pH 10 and increased up to 23.9 mg g^{-1} at pH 4. This behavior could be explained by the fact that at a pH value of 10, which is higher than the pH_{PZC} of the used adsorbent (see Table 3), the PMW surface carry more negative charges and consequently would more repulse the negatively charged phosphates ions. On the other hand, the phosphates adsorption decrease for alkaline pH can be also attributed to the competition between hydroxyl ions and phosphates anions for adsorption sites [23]. On the contrary, at low pH values, especially those lower than the value of the pH of point of zero charge which has been evaluated to 8.11 (see Table 3), the surfaces of the adsorbent particles were positively charged which would favor the adsorption of phosphates anions onto the positively charged surfaces of marble particles.

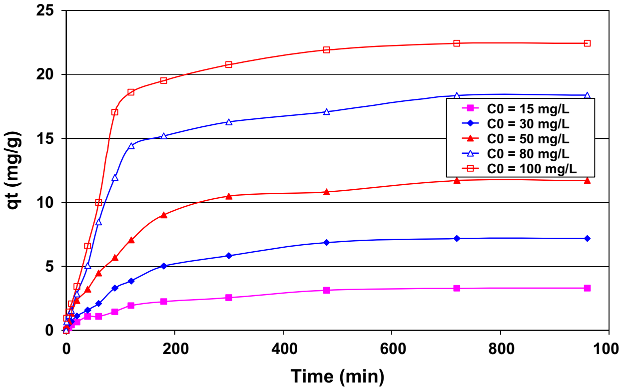

Fig. 1. Effect of initial aqueous phosphates concentrations and contact time on its removal by MPW (adsorbent dose = 4 g L^{-1}; initial pH = 6.4; temperature = 22 ± 2˚C).

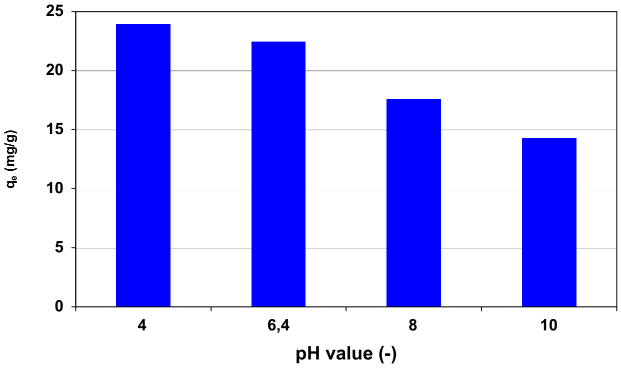

Fig. 2. Effect of pH on the adsorption capacity of phosphate onto MPW (PMW dose = 4 g L^{-1}; initial phosphate concentration = 100 mg L^{-1}; temperature = 22 ± 2˚C).

3.2.3. Effect of the adsorbent dosage

The effect of MPW dosage on the removal of phosphates from the aqueous solutions is given by Fig. 3. The experimental results showed that the dose of the adsorbent plays a significant role in the phosphate removal from the synthetic solutions. Indeed, the efficiency of phosphates removal from the aqueous solutions highly increases from about 49% to more than 86% for adsorbent doses of 0.2 and 2 g L^{-1}, respectively. For doses higher than 2 g L^{-1}, the phosphate uptake is further increased but with a much slower rate. Thus, under the studied experimental conditions, PMW present a relatively high phosphates removal

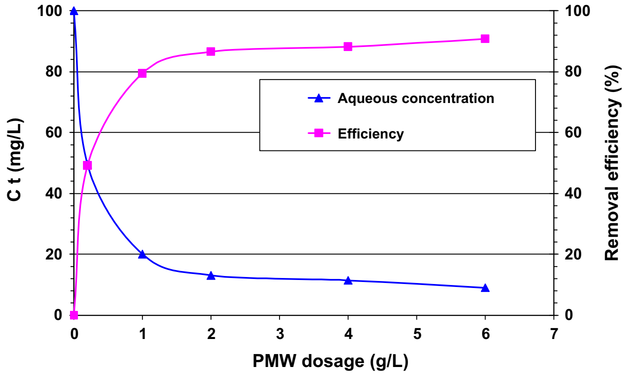

Fig. 3. Effect of adsorbent dosage on phosphates adsorption onto MPW (initial aqueous concentration = $100\,\mathrm{mg\,L^{-1}}$; initial solution pH = 6.4; temperature = 20 ± 2℃).

from aqueous solutions for doses equal or larger than $2\,\mathrm{g\,L^{-1}}$. This trend has been observed also for the adsorption of phosphates onto dolomite [20], phosphates mine slimes [7], and iron hydroxide-eggshell waste [24] and confirms that the PMW dose increase induces an increase in the total available surface area of the adsorbent particles.

3.2.4. Effect of competitive anions

Real wastewaters always contain many anions other than phosphate; these anions may affect the phosphate removal through their adsorption competition on the existing sorption sites. In order to assess the competing effect of other anions on phosphate removal by PMW, batch adsorption tests of phosphate were carried out by the addition of chlorides or sulfates at different aqueous concentrations as described in Section 2.3.4. As shown in Figs. 4 and 5 it appears that for an initial phosphate concentration of $100\,\mathrm{mg\,L^{-1}}$, the chlorides anions did not compete with phosphate species until a concentration of about $1{,}200\,\mathrm{mg\,L^{-1}}$. However, further increase in chlorides concentrations results in a drop of phosphates adsorption by about 5.8 and 13.4% for initial chlorides concentration of 2,400 and $3{,}600\,\mathrm{mg\,L^{-1}}$, respectively. On the other hand, the presence of sulfates anions under the studied experimental conditions (concentrations varying between 200 and $1{,}500\,\mathrm{mg\,L^{-1}}$) did not affect the phosphate removal by PMW. Chlorides effect on the removal efficiency of phosphate is more pronounced than sulfates which should be due to its relatively higher mobility and smaller atomic size [7]. These results prove that the MPW have an important selectivity and affinity toward the phosphates anions and then could be efficiently used for its removal and recovery from aqueous solutions without a significant adsorption capacity reduction due to the presence of other anions in the wastewater.

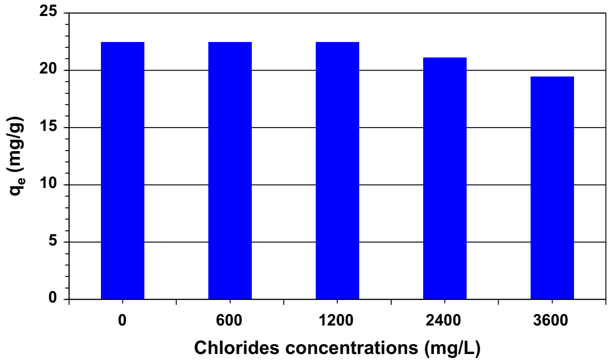

Fig. 4. Effect of chlorides ions on phosphate removal by marble wastes (pH = 6.4; initial phosphate concentration = 100 $\mathrm{mg\,L^{-1}}$, PMW dose = $4\,\mathrm{g\,L^{-1}}$; temperature = 22 ± 2℃).

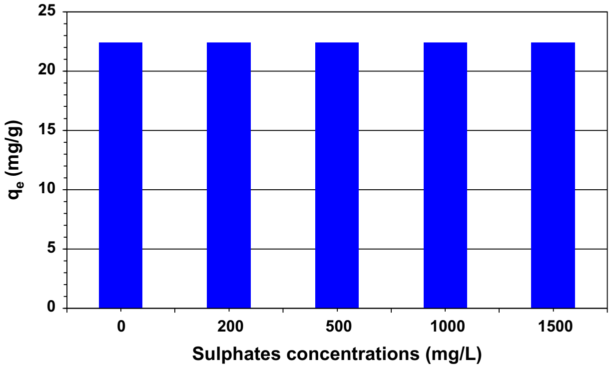

Fig. 5. Effect of sulphates ions on phosphate removal by MPW wastes (pH = 6.4; initial phosphate concentration = $100\,\mathrm{mg\,L^{-1}}$; PMW dosage = $4\,\mathrm{g\,L^{-1}}$; temperature = 22 ± 2℃).

3.3. Modeling studies

3.3.1. Adsorption isotherms

The Langmuir and Freundlich adsorption constants estimated from the isotherms at 22℃ and the corresponding correlation coefficients are presented in Table 4. The calculated value of Freundlich exponent $n = 1.32$ is in the range of 1–10, which indicates a favorable adsorption of phosphates onto PMW. The maximum adsorption capacity (q_m) determined from the Langmuir isotherm was estimated to be $35.12\,\mathrm{mg\,g^{-1}}$ at pH 6.4. This relatively high adsorption capacity is indicative of strong electrostatic forces of attraction between the phosphates molecules and the adsorbent bending sites. On the other hand, the Langmuir parameter, R_L, for an initial aqueous concentra-

Table 4
Adsorption isotherms constants for phosphates adsorption onto PMW (pH = 6.4; PMW dosage = 4 g L^{-1}; temperature = 22 ± 02 °C)

Isotherm parameters	Freundlich			Langmuir		
	n	K_F	R^2	q_m (mg g^{-1})	k_l (L mg^{-1})	R^2
MPW	1.32	3.437	0.945	35.12	0.17	0.991

tion of 15 and 100 mg L^{-1} was estimated to 0.28 and 0.06, respectively. These values are lower than 1, which confirms that the used material is favorable for phosphates adsorption. The Langmuir model presents better correlation coefficient compared to the Freundlich model. The validity of Langmuir model suggests a monolayer adsorption process onto relatively homogenous surfaces of the adsorbent where interactions between adsorbed molecules are negligible and the adsorption sites have equal affinities for the adsorbate molecules [25].

3.3.2. Kinetic studies

The parameters of the three used models: pseudo-first-order, pseudo-second-order, and intraparticle diffusion models are presented in Table 5. The correlation coefficients for the first-order model obtained for some used initial phosphates concentrations were relatively low and the theoretical adsorbed masses, q_{eI}, did not give acceptable values when compared to the experimental ones. Therefore, the reaction involved in the present adsorption system is not of firstorder. At the contrary, for the second-order model, the correlation coefficients were close to 1. Furthermore, the calculated adsorbed masses, q_{eII}, agree very well with the experimental ones (Table 5). Thus, these results suggest that the pseudo-second-order model, based on the assumption that the rate limiting step might be chemical adsorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate, is the most suitable model for the studied experimental conditions.

The analysis of the adsorption of phosphates onto PMW with film and intraparticle diffusion models showed that the depicted two-phase plot suggests that the adsorption process proceeds by surface adsorption at the earlier stages and by intraparticle diffusion at later stages. The values of diffusion coefficients given in Table 5 indicate that except for an initial phosphates concentration of 80 mg L^{-1}, the intraparticle diffusion coefficients are greater than those of the film diffusion

Table 5
Kinetic rate parameters of the adsorption of phosphates onto MPW at different initial aqueous concentrations (pH = 6.4; adsorbent dosage = 4 g L^{-1}; temperature = 22 ± 02 °C)

Initial phosphates aqueous concentration (mg L^{-1})					
	15	30	50	80	100
Experimental q_e (mg g^{-1})	3.30	7 .18	11.71	18.37	22.42
First-order model					
K_1 (min^{-1})	0.0011	0.0101	0.0092	0.0133	0.0128
Calculated q_{eI} (mg g^{-1})	3.31	7.12	10.24	17.87	18.36
R^2	0.995	0.939	0.951	0.991	0.976
Second-order model					
K_2 (g mg^{-1} min^{-1})	0.0027	0.0010	0.0008	0.0006	0.0005
Calculated q_{eII} (mg g^{-1})	3.31	7.28	11.83	18.60	22.90
R^2	0.992	0.987	0.994	0.991	0.989
Film and intraparticle diffusion models					
D_f ($\times10^{-14}$ m^2 s^{-1})	2.41	2.13	3.08	4.19	4.82
R^2	0.885	0.906	0.973	0.948	0.945
D_{ip} ($\times10^{-14}$ m^2 s^{-1})	8.27	8.65	4.65	4.00	7.10
R^2	0.991	0.994	0.885	0.969	0.971

Table 6
Comparison of phosphate adsorption onto PMW with other natural adsorbents under static conditions

Material	Adsorption capacity ($\mathrm{mg\,g^{-1}}$)	Reference
Opoka	0.10	[4]
Dolomite	0.17	[26]
Limestone	0.30	[4]
Sand	0.42	[27]
Limestone	0.67	[5]
Apatite	1.09	[9]
Natural zeolite	2.19	[28]
Wood fiber	4.32	[10]
Phosphate mine slimes	7.45	[7]
Maerl	7.49	[29]
Shellsand	9.60	[30]
Wollastonite	12.00	[31]
Powdered marble wastes (PMW)	35.12	This study

through the boundary layer. This finding confirms that in case of PMW, the film diffusion process controls significantly the rate of adsorption of phosphates ions. The same finding has been registered for phosphates removal by phosphates mines slimes [7].

3.4. Comparison with other adsorbents and prospect using of PMW for phosphates removal and recovery from wastewaters

The comparison of the phosphate adsorption capacity by MPW and other materials under static conditions is given by Table 6. It can be concluded that PMW could be considered as attractive natural materials for the removal and recovery of phosphates from aqueous solutions. Indeed, PMW adsorption phosphate capacity (q_m) is several hundred times more than opoka [4] and dolomite [26] and several 10 times more than limestone [4,5], sands [27], apatite [9]. It is also several times higher than natural zeolite [28], phosphate mine slimes [7], maerl [29], shellsand [30], and wollastonite [31].

In real cases, the phosphate removal process with PMW could be ensured by a separate device at the outlet of the secondary treated wastewater plants as a tertiary treatment. The wastewater and the PMW should be continuously renewed and stirred in this device in order to ensure a sufficient contact time between PMW particles and the dissolved phosphates or other nutrients such as nitrogen and potassium. After nutrients adsorption in this setup, the resulting enriched PMW could then be recovered from the effluent and then reused in agriculture as low cost fertilizer. However, further controlled large-scale experimental investigations seem to be necessary in order to study the impact of the PMW adding onto the soil's physicochemical and bacterial properties.

4. Conclusions

Based on the experimental results of this study, it appears that PMW present high selectivity and efficiency toward the removal of dissolved phosphates from synthetic aqueous solutions. The adsorption process effectiveness increased with increasing adsorbent dosage and initial concentrations and decreased with increasing pH values. The phosphates removal might be controlled by complexation with some specific functional groups and also precipitation with calcium cations. The use of PMW as a low-cost material for phosphates removal and recovery ensures both efficient tertiary wastewater treatment and waste recycling as a fertilizer. Further investigations will be conducted to study the mechanisms involved in the phosphates removal by PMW and to appreciate the effects of using the resulting P-enriched solid matrix as fertilizer on the physicochemical and hydrodynamic soil proprieties and also plants physiology.

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