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Powdered marble wastes reuse as a low-cost material for phosphorus removal from aqueous solutions under dynamic conditions

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ABSTRACT

In this study, phosphorus anions removal efficiency from synthetic aqueous solutions and urban secondary treated wastewater solutions by powdered marble wastes (PMW) as an effective low-cost material has been investigated using continuous stirring reactors (CSTRs). The experimental results showed that the phosphorus removal from the synthetic solutions is dependent on the PMW dosage and especially on the influent feeding flow rate. Indeed, for an influent aqueous concentration of $100\,\mathrm{mg\,L^{-1}}$ and a PMW dose of $12\,\mathrm{g\,L^{-1}}$, the average phosphorus removal efficiency increases from about 35 to 79% when the feeding flow rate was decreased from 10 to $2.5\,\mathrm{mL\,min^{-1}}$. For a relatively high phosphorus influent concentration ($100\,\mathrm{mg\,L^{-1}}$), the highest removal efficiency, more than 88%, was observed for two CSTRs disposed in serial mode, a feeding flow rate of $4.5\,\mathrm{mL\,min^{-1}}$ and a PMW dose of $12\,\mathrm{g\,L^{-1}}$. The cost-effective and high phosphorus removal capability of PMW, compared to many natural or industrial byproducts, make them very promising materials for phosphorus removal and recovery from secondary treated wastewaters with the possibility of reuse as a fertilizer in agriculture.

Keywords: Marble wastes; Phosphorus; Removal; Dynamic; CSTR

1. Introduction

Phosphorus is an essential nutrient that is required for the growth of organisms in most ecosystems; however, if it exits in excess, it can cause the eutrophication of not only the surface fresh water bodies but also marine dead zones [1]. Indeed, discharged phosphorus into surface waters, which occurs principally from both agriculture activities and discharged domestic and industrial wastewaters, can disturb the balance of organisms present in water and affect water quality mainly through the depletion of the dissolved oxygen level as the algae decay [2]. On the other hand, phosphate rock is a non renewable and a critical resource on which modern society is highly dependent. Due to a constant increase demand of phosphates to satisfy the food's need of the world population, production of phosphate rock is estimated

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to peak around 2035, after which demand would outstrip supply [3]. Thus, phosphorus recovery from renewable resources such as wastes and wastewaters has become this last decade an innovative research option [4,5].

The main technologies allowing phosphate recovery from municipal wastewater and their possible reuse in agricultural field are both spontaneous or enhanced struvite crystallization and sorption onto natural materials technologies [3,6]. Since the struvite generation in wastewater treatment systems requires highly skilled operation regarding the suspended solids concentrations, pH values, and artificial supplementary magnesium adding [6,7], great attention has been paid this last decade to the development and the use of effective and low-cost organic and/or mineral materials for phosphorus recovery from aqueous solutions. The tested materials include date palm fibers [8]; Poseidonia oceanica fibers [9]; calcite [10]; apatite [11,12]; dolomite [13]; limestone [14]; shellsand [15]; zeolite [16]; coal acid mine drainage sludges [17]; and phosphates mines slimes [18]. These studies have proved that the highest phosphorus removal capacities were reported for filter materials having relatively high CaO or Ca contents and for pH values higher than 7 [19].

Marble is a nonfoliated metamorphic rock resulting from the metamorphism of limestone, composed mostly of calcite. Marble products, which are naturally rich in Ca, are used principally in construction, interior and exterior decoration. The overall marble amount produced in the world was estimated to be about 81 million tons y^{-1} [20]. Marble industry generates huge amounts of wastes, by which around 70% of this precious mineral resource is wasted in the mining, processing, and polishing procedures. Around 40% of marble wastes is 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 [21]. The rest (30%) is associated to processing and polishing actions in the manufactures and is constituted by crushed fragments and also marble in powder form (PMW). PMW, which are generally mixed with water as sludges, as well as the crushed fragments, 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 [10,22]. However, no scientific work has been carried out regarding the valorization of PMW for urban wastewater treatment in general and phosphorus removal and recovery in particular in column or continuous stirred tank reactor (CSTR) mode. The success of such operation is environmentally beneficial since it avoids the water bodies' eutrophication, reduces the discharged PMW amounts in landfills, and permits the recycling of the resulting complex low-cost material phosphorus in agriculture as fertilizer which consequently reduces the use of synthetic chemical fertilizers that has sextupled between 1950 and 2000 [23].

The main goals of this experimental study are to test the use of PMW for phosphorus removal and recovery from synthetic aqueous solutions and to evaluate the effect of certain key parameters such as PMW dosage, influent feeding flow rate and aqueous phosphorus concentration using CSTRs technique. The use of this technique is technically very interesting since it permits to overcome the problems of batch system results extrapolation for real applications due to their small scales and also the clogging phenomenon met when using fixed bed columns [18,24,25].

2. Materials and methods

2.1. PMW preparation and characterization

In this study, the used solid matrix is constituted by powdered marble wastes resulting 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. In this study, PMW were sieved mechanically 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 1,710, 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 sorptiometr. The pH of zero point charge (pH_{ZPC}) of PMW was performed according to the solid addition method [26] using 0.01 M KNO_3 solutions (CAS number: 7757–79-1), 1 g of PMW for initial pH values of 2, 4, 6, 8, 10, and 12.

2.2. Synthetic phosphorus solutions preparation and analysis

Potassium dihydrogen phosphate (KH_2PO_4, (CAS number: 7778–77-0), acquired from Fisher Scientific, was used in CSTR tests as the source of phosphorus ions. A stock phosphorus solution of 1,000 mg L^{-1} was prepared with distilled water and used throughout the study. The analysis of phosphorus species contents was performed spectrophotometrically at 880 nm, following the ascorbic acid method [27]. For all the synthetic experimental studies cited below, the initial pH of the used aqueous solutions was fixed to 6.4.

2.3. CSTR phosphorus removal studies

2.3.1. Laboratory CSTR presentation and experimental protocol

Continuous flow tests were carried out by using a CSTR system for the removal of phosphorus from synthetic solutions and real secondary treated wastewater effluents (Fig. 1). A 1.2 L glass reactor was used to ensure the contact between PMW and phosphorus in aqueous solutions. At the start of the assays, the desired PMW dosage was put in the reactor, which is then rapidly filled with the aqueous phosphorus solution at the desired concentration. Afterward, the phosphorus-containing water was continuously fed from a 10-L volume tank to the CSTR system with a variable flow pump (Masterflex, Cole-Parmer Instrument Company, USA) at different flow rates corresponding to the desired contact times. The reactor was continuously stirred at 300 rpm using a magnetic stirrer (Agimafic-S, I. P. Selecta Company) for several hours until equilibrium is reached. This state is characterized by a quasi-stability of phosphorus concentrations at the entrance of the settling setup (Fig. 1). The effluent was sampled at the entrance of the settling device 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 (containing water and PMW losses) was filtered through filter paper (0.45 μm) and the filtrate was analyzed in order to determine its dissolved phosphorus concentration.

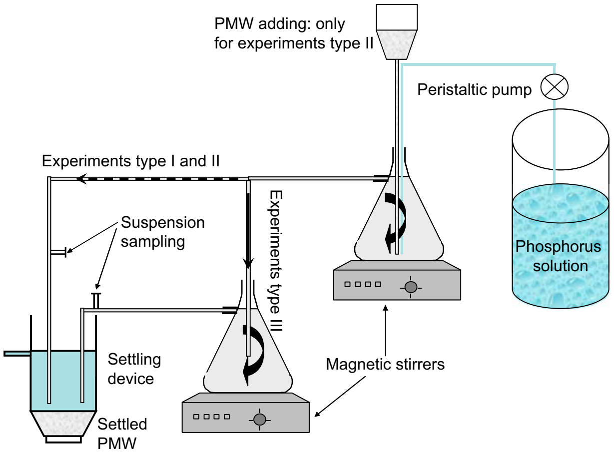

Fig. 1. Schematic representation of the CSTR used for the study of phosphorus removal by PMW.

During this study, in order to determine the effects of the PMW losses from the reactor′ outlet and also the CSTR system design, three types of assays were carried out (Fig. 1):

- First set of experiments (EXP-I): only one CSTR was used without any PMW adding;
- Second set of experiments (EXP-II): only one CSTR was used with adding of defined amounts of PMW each 10 minutes in order to compensate the corresponding losses from the reactor′ outlet;
- Third set of experiments (EXP-III): two CSTRs disposed in serial mode were used without any PMW adding. At the beginning of this kind of experiments, the PMW were put only in the first reactor and the second one was completely empty (Fig. 1).

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

2.3.2. Effect of the PMW dosage

The impact of the PMW dosage was determined for EXP-I at a constant concentration of the feeding synthetic solution of 100 mg L^{-1} and a flow rate of 4.5 mL min^{-1}. The used PMW dosages were fixed to 4, 12, and 20 g L^{-1}.

2.3.3. Effect of the influent feeding flow rate

The effect of the contact time between PMW and the phosphorus synthetic solution was evaluated for EXP-I at a constant feeding concentration and PMW dosage of 100 mg L^{-1} and 12 g L^{-1}, respectively. The tested feeding flow rates were fixed at 10, 4.5, and 2.5 mL min^{-1}. These flow rates correspond to theoretical hydraulic residence times in the reactor of 2.0, 4.4, and 8.0 h, respectively.

2.3.4. Effect of PMW adding

The effect of PMW adding (EXP-II) on the aqueous phosphorus removal has been investigated at two flow rates of 4.5 and 10 mL min^{-1}. The used synthetic solution feeding concentration and initial PMW dosage were fixed to 100 mg L^{-1} and 12 g L^{-1}, respectively. As indicated above, specified PMW amounts (determined on the basis of preliminary experiments) were added each 10 min to the reactor in order to compensate the losses from the reactor's outlet and consequently to keep its dosage constant.

2.3.5. Effect of the use of two CSTRs

The use of two reactors disposed in serial mode (EXP-III) aims to ensure a large contact time between the dissolved phosphorus and PMW (Fig. 1). Its impact on the aqueous phosphorus removal has been determined for a constant feeding concentration, an initial PMW dosage in the first reactor and influent flow rate of $100\,\mathrm{mg\,L^{-1}}$, $12\,\mathrm{g\,L^{-1}}$, and $4.5\,\mathrm{mL\,min^{-1}}$, respectively. It is worth mentioning that the second reactor was completely empty at the beginning of the experiments and no PMW adding was operated in the system.

2.3.6. Phosphorus removal parameters calculation

The phosphorus removal by PMW at equilibrium, q_e, (mg removed phosphorus $\mathrm{g^{-1}}$ PMW) was calculated from mass balance equation as follows:

$$q_e = \frac{M_{t_0} + M_{inj} - M_{t_f} - M_{recup}}{M_{MPW}} \quad (1)$$

where t_0 and t_f are the times corresponding to the start and the end of the experiment, respectively. M_{t0}, M_{inj}, M_{recup}, M_{t_f}, and M_{PMW} are the initial phosphorus mass existing inside the reactor before the start of the experiment; the injected mass in the reactor between t_0 and t_f; the recuperated mass at the outlet of the reactor during the same time period; the existing mass inside the reactor at the end of the experiment and the used PMW mass, respectively. These masses are calculated using the following equations:

$$M_{t_0} = C_0\,V_r \quad (2)$$

$$M_{inj} = C_0\,Q\,(t_f - t_0) \quad (3)$$

$$M_{t_f} = C_f\,V_r \quad (4)$$

$$M_{recup} = \int_0^{V_{tot}} C(t)\,dv \quad (5)$$

where C_0, $C(t)$, and C_f, are the influent, at time t and final aqueous phosphorus concentration measured at the outlet of the reactor, respectively. Q is the applied flow rate. V_r and V_{tot} are the reactor volume and the total solution volume recuperated at the outlet of the reactor.

Eq. (5) was approximated using the trapeze method by the formula presented hereafter [25]:

$$M_{recup} = \frac{1}{2}\sum_{i=0}^{i=n} (C_{i+1} - C_i)\,(V_{i+1} - V_i) \quad (6)$$

where C_{i+1}, C_i, and "V_{i+1}, V_i" are the phosphorus aqueous concentrations and "recuperated volume at the outlet of the reactor" at the instants t_{i+1} and t_i, respectively.

The phosphorus removal efficiency at equilibrium (ARE) is calculated from the relation:

$$\mathrm{ARE}\,(\%) = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (7)$$

3. Results and discussions

3.1. PMW characterization

From Table 1, the PMW can be considered as a very fine solid porous media and therefore used as a fine reactive filter media with probable high removal 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 [28] and dolomite [13]. The X-ray and EDS analyses indicate that PMW are exclusively formed by calcite with relatively high contents of Ca. No Fe or Al is detected (Table 1). Since Ca is important for the removal of phosphorus via sorption and precipitation processes [19], so the PMW should present an interesting capability of phosphorus removal and recovery from aqueous solutions (Table 1). 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 $CaCO_3$ [29]. As a consequence, under the used experimental conditions (initial pH = 6.4), the PMW particles surface should be positively charged.

Table 1
Main physicochemical characteristics of the used marble powder wastes ((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})

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 ($\mathrm{m^2/g}$)	0.14
pH of zero point charge ($\mathrm{pH_{ZPC}}$)	8.11

3.2. Dynamic experiments results

3.2.1. Effect of PMW dosage

According to the experimental conditions presented in section 2.3.2, the results showed that for all the used PMW dosages, the phosphorus removal process is clearly time dependent (Fig. 2). Indeed, the aqueous phosphorus concentrations decreases rapidly for contact times lower than 160, 133, and 90 min for PMW dosages of 4, 12, and 20 g L^{-1}, respectively. From these times, equilibrium state, characterized by relatively stable aqueous phosphorus concentration, is attained. On the other hand, due to the presence of more sorption sites, higher is the PMW dosage; faster is the phosphorus removal kinetic. This observed kinetic removal process is partially explained by the fact that at the beginning, the phosphorus ions were partly adsorbed by the exterior surface of PMW, so the adsorption rate was fast. When the exterior surface sites reach saturation, the phosphorus ions enter into the PMW particles pores and were adsorbed by the interior surface of the particles. The found equilibrium times are comparable to materials relatively rich in Ca such as blast furnace slag discharged by steel factories [30] and red mud waste from alumina industries [31]. They are relatively higher than pure dolomite [13] and phosphate mine slimes [32].

On the other hand, the increase in the PMW dosages causes a decrease in the residual phosphorus concentration and consequently an increase in its removal efficiency (Fig. 2). Indeed, the phosphorus removal efficiencies values increased from about 53–75%, as the PMW dose was increased from 4 to 12 g L^{-1}. Such a trend is mainly attributed to both an increase in adsorption capacity—through an increase in the sorptive surface area and adsorption sites—and to the availability of more favorable conditions of calcium phosphates precipitation due to the dissolution of more Ca from PMW into the aqueous solutions [11,33]. The phosphorus adsorption process onto PMW might include both ligand ion exchange carbonates, sharing between phosphorus species and some specific functional groups [18,19]. In our case, the phosphorus removal from the aqueous solutions might include both adsorption and precipitation as calcium phosphates species because of the relatively high equilibrium pH of the effluent which was determined to vary between 7.4 and 8.3. This pH interval favors the chemical precipitation of the various forms of calcium phosphates [34]. In cases where the wastewater to be treated is more acid, the contents of other ions such as Mg, Fe, and Al may be more important as the precipitation reactions with these ions are favored at low pH values [34].

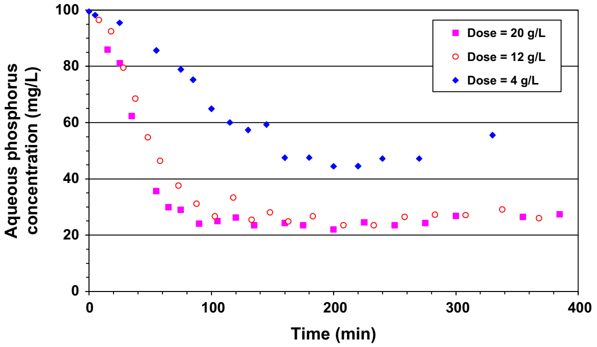

Fig. 2. Effect of PMW dosage on phosphorus removal from synthetic solutions for the first set of assays: EXP-I (influent phosphorus concentration = 100 mg L^{-1}, temperature = 20 ± 2°C; flow rate = 4.5 mL min^{-1}).

The phosphorus removal efficiency onto PMW remained quasi constant from a dose of 12 g L^{-1} and further dose augmentation (until 20 g L^{-1}) did not affect significantly the uptake of phosphorus from the aqueous solution (Fig. 2). This plateau corresponds to an average residual phosphorus concentration at equilibrium (C_f) of 24.8 mg L^{-1} and a removal efficiency of about 76%. Thus, under the studied experimental conditions, PMW present a relatively high phosphorus removal from aqueous solutions for doses equal or larger than 12 g L^{-1} compared to natural materials such as dolomite [13] and phosphate mine slimes [18].

3.2.2. Effect of feeding flow rate

The hydraulic residence time (HRT) in the reactor could be considered as an important factor conditioning phosphorus removal under dynamic conditions. As indicated in section 2.3.3, three theoretical HRTs of 2, 4.4, and 8 h were investigated for a constant PMW dosage of 12 g L^{-1}. The experimental results (Fig. 3) show that the phosphorus removal efficiency is relatively low for an influent feeding flow rate of 10 mL min^{-1} and becomes important for flow rates values of 4.5 and 2.5 mL min^{-1}. Indeed, at equilibrium, the residual average aqueous phosphorus concentration decreases from 65.8 to 21.6 mg L^{-1} for feeding flow rates of 10 and 2.5 mL min^{-1}, respectively. These concentrations correspond to phosphorus removal efficiencies of about 35 and 79%, respectively. Thus, for this flow rate interval, higher is the contact time between the PMW and aqueous phosphorus solution; higher is the effectiveness of the phosphorus removal and recovery. However, no significant difference on phosphorus removal performance by PMW was observed between flow rates of 4.5 and 2.5 mL min^{-1}

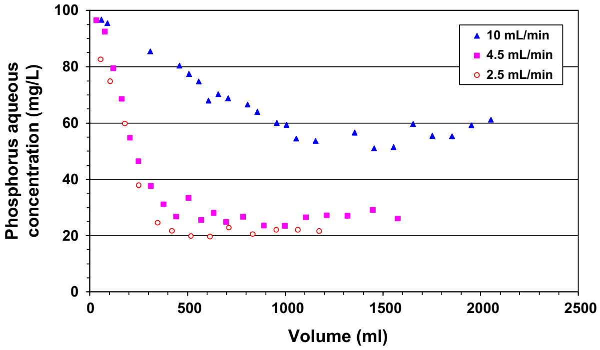

Fig. 3. Effect of influent feeding flow rate on phosphorus removal by PMW for the first set of assays: EXP-I (influent phosphorus concentration = 100 mg L^{-1}, adsorbent dosage = 12 g L^{-1}; temperature = 20 ± 2˚C).

(Fig. 3). This finding is attributed the fact that the HRTs of 4.4 and 8 h corresponding to the flow rates of 4.5 and 2.5 mL min^{-1} are so much higher than the required time to achieve equilibrium between the phosphorus species in the aqueous phase and the PMW (about 133 min, see § 3.2.1). The required HRT is very dependent on the physicochemical properties of the used low-cost material. Indeed, Brooks et al. [35], when studying phosphates removal by wollastonite (calcium metasilicate) using vertical up-flow columns, reported that removal efficiencies higher than 80% were obtained for residence times more than 1.7 days. Besides, Lin et al. [33] demonstrated in batch mode that the phosphorus removal efficiency by commercial calcite increases with the reaction time until the equilibrium was attained after 18 h. However, Wei et al. [17] found that HRT of only 1–2 h is sufficient to ensure an optimal phosphorus removal from surface water from the Monongahela river (West Virginia, USA) by an acid mine drainage sludge essentially formed by iron and aluminum hydroxides. It is worth mentioning that this HRT might be also dependent on the agitation intensity and the physical properties of the reactor such as total volume, position of the influent's inlet and outlet and its geometric form.

The average removed phosphorus amounts were determined using Eq. (1) to 7.9, 13.8, and 14.8 mg g^{-1} for feeding flow rates of 10, 4.5, and 2.5 mL min^{-1}, respectively. The value relative to the last flow rate is relatively important compared to many tested materials under dynamic conditions such as some Danish sands [36], phosphates mine slimes [18], shellsand [37], limestone which is, like PMW, mainly constituted by calcium carbonate [38] and Polish opoka, which contains about 50% of calcium carbonate [14].

The relatively low phosphorus removal efficiency at a feeding flow rate of 10 mL min^{-1} (Fig. 3) could be attributed not only to the low contact time between aqueous phosphorus and PMW but also to the high PMW amounts losses from the reactor's overflow. In fact, preliminary assays (data not shown) had indicated that the PMW losses from the reactor's outflow depend significantly on the used flow rate. Indeed, in the first 10 minutes, the lost PMW amounts for a flow rate of 10 mL min^{-1} were about 2 and 7 times higher than the ones observed for flow rates of 4.5 and 2.5 mL min^{-1}, respectively. Therefore, the PMW dosage inside the reactor and thereby the total number of available adsorption sites decrease significantly with time for higher influent feeding flow rates resulting in a net decrease in phosphorus removal percentage.

3.2.3. Effect of PMW adding

According to the experimental conditions detailed in section 2.3.4, the experimental results show that for a PMW dosage of 12 g L^{-1} and an influent feeding flow rate of 4.5 mL min^{-1}, the continuous PMW adding does not offer better phosphorus removal efficiency (Fig. 4(a)). In fact, the aqueous phosphorus concentration at the entrance of the settling device decreases slightly from 25.6 for EXP-I to 22.9 mg L^{-1} in case of EXPII. This result confirms the finding reported in section 3.2.1 mentioning that for a used influent feeding flow rate of 4.5 mL min^{-1}, the PMW dosage increase from 12 to 20 g L^{-1} does not improve significantly the phosphorus removal from the aqueous solutions (see Fig. 2). However, the PMW adding seems to be necessary for an influent flow rate of 10 mL min^{-1} in order to compensate the relatively high amounts of the used material lost from the reactor's outflow (Fig. 4(b)). Indeed, even if the phosphorus removal kinetics at the beginning of the experiments are quite similar for EXP-I and EXP-II, the phosphorus removal efficiency at equilibrium state increases from about 46% to 61% when PMW were added to the reactor.

As a consequence, Fig. 4(a) and (b) indicate that for relatively high applied influent flow rates, PMW amounts losses from the CSTR have to be compensated by continuous adding of raw PMW. However, other technological solutions could be used in order to decrease these losses and to optimize PMW addition into the reactor.

3.2.4. Effect of the use of two CSTRs

In order to improve the phosphorus removal efficiencies registered when using one reactor for flow rates of 10 and 4.5 mL min^{-1}, which are, respectively,

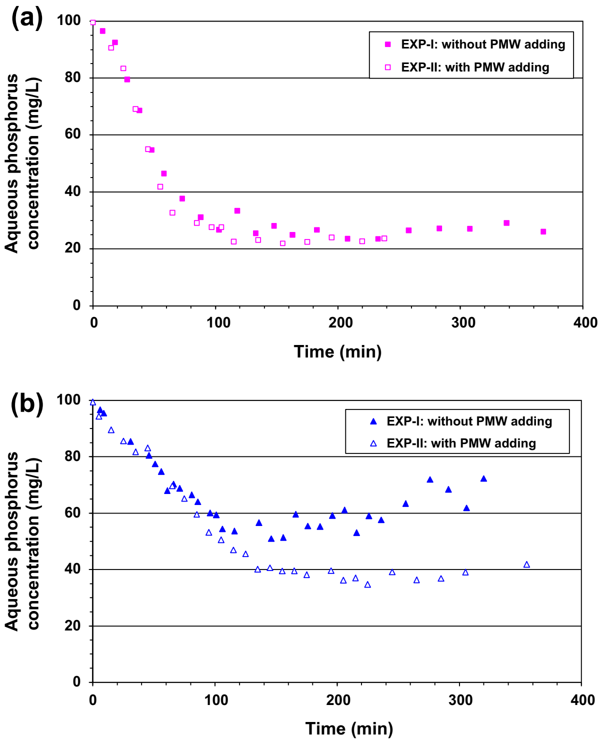

Fig. 4. Effect of continuous marble adding on phosphorus removal (influent phosphorus concentration = 100 mg L^{-1}, adsorbent dosage = 12 g L^{-1}; temperature = 20 ± 2°C). (a) flow rate = 4.5 mL min^{-1}; (b) flow rate = 10 mL min^{-1}.

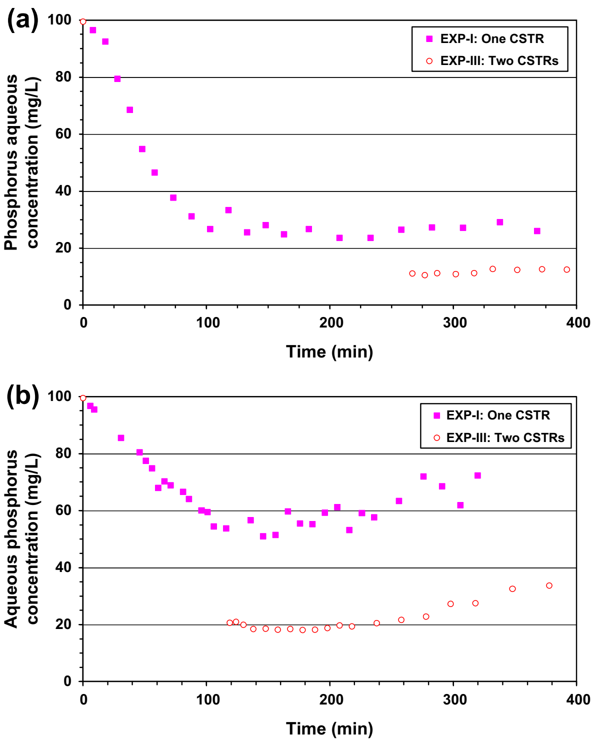

Fig. 5. Effect of the use of two CSTRs disposed in serial mode on phosphorus removal (a) flow rate = 4.5 mL min^{-1}; (b) flow rate = 10 mL min^{-1} (influent phosphorus concentration = 100 mg L^{-1}, adsorbent dosage = 12 g L^{-1}; temperature = 20 ± 2°C).

75% and 35% (See § 3.2.2), a second reactor has been disposed in serial mode (Fig. 1). Fig. 5(a) and (b) present the phosphorus aqueous concentrations at the entrance of the settling device for applied flow rates of 4.5 and 10 mL min^{-1}, respectively, when two reactors disposed in serial mode were used. As specified in section 2.3.5, the PMW dosage in the first reactor and influent phosphorus concentration were fixed to 12 g L^{-1} and 100 mg L^{-1}, respectively.

The experimental results show clearly that the use of two CSTR disposed in serial mode permits a significant decrease in the effluent phosphorus concentration. Indeed, when the initial HRTs were doubled and the PMW losses from the first reactor's overflow were collected into the second reactor (which was totally empty at the beginning of the experiments), the measured effluent phosphorus aqueous concentrations at equilibrium (C_f) decrease from 65.8 to 19.6 mg L^{-1} and from 25.6 to 11.7 mg L^{-1} for influent flow rates of 10 and 4.5 mL min^{-1}, respectively. The total phosphorus removal efficiencies for the two CSTRs system were evaluated to 80.3 and 88.3% for flow rates of 10 and 4.5 mL min^{-1}, respectively. The corresponding removed phosphorus masses per gram of PMW were evaluated using Eq. (1) to 15.9 and 17.0 mg g^{-1} for feeding flow rates of 10 and 4.5 mL min^{-1}, respectively. They are, respectively, 101 and 23% higher than the ones registered when using only one CSTR. Thus, to ensure high phosphorus removal efficiencies by PMW, the use of two CSTRs disposed in serial mode seems to be necessary especially in case of relatively high influent feeding flow rates. The best phosphorus removal efficiency of PMW (88.3%) is about 26% higher than the one found for crushed Norwegian marble [10]. This finding could be explained probably by both the low specific area and the difficulty of Ca^{2+} dissolution into water of their very coarse used medium compared to our PMW. For a feeding flow rate of 10 mL min^{-1}, the measured phosphorus aqueous concentration at the outlet of the second reactor increases slightly after a duration of about 250 min (Fig. 5(b)). This behavior is certainly due to the relatively important PMW losses observed at this flow rate. It is important to underline that for the tested flow rates, the use of two CSTRs offers better phosphorus removal efficiencies than the continuous adding of PMW in case of one CSTR. As a consequence, for PMW dosage higher than 12 g L^{-1}, phosphorus removal and recovery from wastewaters using real large-scale dynamic devices should more

Table 2
Comparison of phosphate adsorption onto PMW with other adsorbents under dynamic conditions (HRT: hydraulic residence time; HLR: hydraulic loading rate; d_x: mesh diameter that allows x% of the porous media to pass through; SA = specific area; CEC: cationic exchange capacity)

Material and main characteristics	Study type	Description of the study	Phosphorus retention characteristics	References
Natural materials				
Oyster shell. d_{10} = 0.9 mm; d_{60} = 1.5 mm Ca = 37.8%; Mg = 0.22%; Fe = 0.06%	Column	Synthetic solution: C = 50 mg P L^{-1}; HRT = 4 h; HLR = 0.3 L day^{-1}	Saturation value after 70 days = 7.925 mg P g^{-1}	[41]
Polonite. Particle size: 2–5.6 mm; Ca = 24.5%; Mg = 0.44%; Fe = 1.65%	Column	Synthetic solution: C = 5 mg P L^{-1}; HLR = 530 L m^{-2} day^{-1}	Retained P after 68 weeks = 96.7%	[46]
Danish sands. d_{10} = 0.2–1.4 mm; d_{60} = 0.6–3.7 mm; Ca = 0.06–6.99%; Mg = 0.008–0.223	Column	Synthetic solution: C = 10 mg P L^{-1}; HRT = 12–14 h; HLR = 0.24 L day^{-1}	Removal efficiency after 12 weeks: 0.052–0.165 mg P g^{-1}	[36]
Crushed Norwegian marble. d_{10} = 0.7 mm; d_{60} = 1.7 mm; Ca = 38.9%; Mg = 0.26%; Fe = 0.04%; Al = 0.09%	Column	Synthetic solution: C = 10 mg P L^{-1}; HRT = 12–14 h; HLR = 0.24 L day^{-1}	Removal efficiency after 12 weeks = 70%	[10]
Commercial calcite. d_{10} = 0.8 mm; d_{60} = 3.3 mm; Ca = 24%; Mg = 0.36%; Fe = 0.13%; Al = 0.35%	Column	Synthetic solution: C = 10 mg P L^{-1}; HRT = 12–14 h; HLR = 0.24 L day^{-1}	Removal efficiency after 12 weeks = 100%	[10]
Shellsand. Ca = 31.8%; Mg = 1.46%; Fe = 0.22%; Al = 0.15%	Column	Synthetic solution: C = 5–1,000 mg P L^{-1}; HLR = 100 L m^{-2} day^{-1}	Adsorption capacity after 32 days: 3.5 mg P g^{-1}	[37]
Shellsand. Particle size: 3–7 mm; Ca = 32.8%; Mg = 1.42%; Fe = 0.06%	Column	Synthetic solution: C = 10 mg P L^{-1}; HRT = 4.1 day; HLR = 4.5 L day^{-1}	Adsorption capacity after 303 days: 0.497 mg P g^{-1}	[15]
Wallastonite. Particle size: 1–3 mm; Ca = 15.1%; Mg = 1.33%; Fe = 2.15%; Al = 0.55%	Column	Synthetic solution: C = 5 mg P L^{-1}; HLR = 610 Lm-2 day^{-1};	P-removal efficiency after 68 weeks of operation = 51.1%	[46]
Posidonia oceanica fibers: d_{10} = 4 µm; d_{60} = 27 µm; Ca = 4.96%; Mg = 0.56%; Fe = 2.51%; Al = 0.6%; SA = 2 m^2/g	CSTR	Synthetic solution: C = 50 mg P/L; adsorbent dosage = 5 g L^{-1} HRT = 0.5–1 h	Adsorbed P amount = 3.03 mg g^{-1}; P-removal efficiency = 80%	[42]
Phosphate mine slimes: d_{10} = 4 µm; d_{60} = 27 µm; Ca = 23.83%; Mg = 2.94%; Fe = 5.37%; Al = 3.5%; SA = 40.82 m^2/g	CSTR	Synthetic solution: C = 50 mg P/L; adsorbent dosage = 5 g L^{-1} HRT = 0.5–1 h	Adsorbed P amount = 5.63 mg g^{-1}; P-removal efficiency = 81%	[32]
Powdered marble wastes (PMW). See Table 1 for the main characteristics	CSTR	Synthetic solution: C = 100 mg L^{-1}; adsorbent dosage = 12 g L^{-1}; HRT = 8.8 h	Adsorbed P amount = 17.0 mg g^{-1}; P-removal efficiency = 88.3%	This study
Industrial by-products				
Coal fly ash. Particle size: <12.6 mm; CEC = 9.3 cmol/kg;	Column	Synthetic solution: C = 35–42 mg P L^{-1}; HLR = 3 L day^{-1}	Adsorption capacity after 40 days: 0.3 mg P g^{-1}	[39]
Basic oxygen furnace slag. Particle size:<22 µm.	CSTR	membrane-filtered effluent from a membrane bioreactor in a sludge treatment process: C = 72.9 mg P L^{-1}; HRT = 2 h	P-removal efficiency after 30 days of operation = 52.4%	[47]

(*Continued*)

Table 2
(*Continued*)

Material and main characteristics	Study type	Description of the study	Phosphorus retention characteristics	References
Electric furnace steel slag. Particle size: 2.5–10 mm; CaO = 30.4%; Al_2O_3 = 4.67%; Fe_2O_3 = 34.7%; MgO = 13.1%	Column	Synthetic solution: C = 20 mg P L^{-1} for 114 day then 400 mg L^{-1} for 21 days; HRT = 12–24 h; HLR = 3–4 L day^{-1}	P-removal efficiency is close to 100%; adsorbed P amount = 2.2 mg P g^{-1}	[43]
Skin split waste loaded with iron. Particle size: 0.5–1 mm; SA = 5.23 m^2/g	Column	Industrial wastewater: C = 1.7 mg L^{-1}; HRT = 0.5 h	Adsorbed P amount = 7.28 mg g^{-1}	[40]
Skin split waste loaded with aluminum. Particle size: 0.5–1 mm; SA = 4.68 m^2/g	Column	Industrial wastewater: C = 1.7 mg L^{-1}; HRT = 0.5 h	Adsorbed P amount = 0.17 mg g^{-1}	[40]

tolerate PMW dosage and aqueous phosphorus concentrations fluctuations than influent flow rates or contact times between the low-cost material and dissolved phosphorus.

3.3. Comparison of PMW efficiency with other materials and their prospect of using to remove and recover phosphorus using CSTR system

Table 2 gives a comparison between the efficiency of PMW and other natural or industrial by-products on the removal of phosphorus from aqueous solutions under dynamic conditions (column or CSTR). It shows clearly that PMW could be considered as promising materials to remove and recover phosphorus. Indeed, for an aqueous phosphorus concentration of 100 mg L^{-1}, a PMW dosage of 12 g L^{-1} and HRT of 8 h (two CSTRs disposed in serial mode), the found removal efficiency in this study is several 10 times more than some Danish sands [36]; shellsand from Norway [15]; coal ash [39]; skin split waste loaded with aluminum [40]; and several times higher than other type of Norwegian shellsand [37]; oyster shell from Korea [41]; Mediterranean Posidonia oceanica fibers [42]; Tunisian phosphate mines slimes [32]; crushed Norwegian marble [10] and is comparable to and apatite [12]. Other industrial by-products, which have higher specific area than PMW and are relatively rich in Ca, Mg, Al, and Fe, such as blast furnace slag have demonstrated significant capability to remove phosphorus from aqueous solutions [43,44]. However, at the contrary of PMW, these enriched phosphorus products could not be easily valorized as fertilizer due to their possible of harmful side-effects on soils [45].

4. Conclusions

This study shows that powdered marble wastes can be considered as attractive materials for phosphorus removal and recovery from aqueous solutions compared to various other materials. In CSTR mode, the main parameter influencing the phosphorus removal efficiency by PMW is the hydraulic residence time. For PMW dosage of 12 g L^{-1}, a sufficient HRT of 8.8 h, the phosphorus removal efficiency from synthetic solutions exceeds 88%. The CSTR system could be integrated in existing urban or industrial wastewaters treatment plants with the added benefits of reducing derogatory environmental impacts of wastewaters discharge in water bodies, PMW discharge in landfills and reusing nutrients-saturated PMW as fertilizer. Large-scale pilot studies are recommended with raw and thermally treated PMW in order to corroborate the encouraging results obtained at laboratory scale.

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References

[1] World Resources Institute [WRI], Agriculture and ''DeadZones'', 2008. Available from http://www.wri.org/publication/content/7780.

[2] B. Nowack, A.T. Stone, Competitive adsorption of phosphate and Phosphonates onto goethite, Water Res. 40 (2006) 2201–2209.

[3] D. Cordell, A. Rosemarin, J.J. Schröder, A.L. Smit, Towards global phosphorus security: A systems framework for phosphorus recovery and reuse options, Chemosphere 84 (2011) 747–758.

[4] B.K. Biswas, K. Inoue, K.N. Ghimire, S. Ohta, H. Harada, K. Ohto, H. Kawakita, The adsorption of phosphate from an aquatic environment using metal-loaded orange waste, J. Colloid Interf. Sci. 312 (2007) 214–223.

[5] K. Ashley, D. Cordell, D. Mavinic, A brief history of phosphorus: From the philosopher's stone to nutrient recovery and reuse, Chemosphere 84 (2011) 737–746.

[6] L.E. De Bashan, Y. Bashana, Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003), Water Res. 38 (2004) 4222–4246.

[7] L. Pastor, D. Mangin, R. Barat, A. Seco, A pilot-scale study of struvite precipitation in a stirred tank reactor: Conditions influencing the process, Bioresour. Technol. 99 (2008) 6285–6291.

[8] K. Riahi, B. Ben Thayer, K. Ben Mammou, A. Ben ammar, M. H. Jaafoura, Biosorption characteristics of phosphate from aqueous solution onto Phoenix dactylifera L. Date palm fibers, J. Hazard. Mater. 161 (2009) 608–613.

[9] M.A. Wahab, R. Ben Hassine, S. Jellali, Posidonia oceanica (L.) fibers as a potential low-cost adsorbent for the removal and the recovery of phosphate, J. Hazard. Mater. 191 (2011) 333–341.

[10] H. Brix, C.A. Arias, D.M. Bubba, Media selection for sustainable phosphorus removal in subsurface flow constructed wetlands, Water Sci. Technol. 44 (2001) 47–54.

[11] N. Bellier, F. Chazarenc, Y. Comeau, Phosphorus removal from wastewater by mineral apatite, Water Res. 40 (2006) 2965–2971.

[12] P. Molle, A. Lienard, A. Grasmick, A. Iwema, A. Kabbabi, Apatite as an interesting seed to remove phosphorus from wastewater in constructed wetlands, Water Sci. Technol. 51(9) (2005) 193–193.

[13] S. Karaca, A. Gürses, M. Ejder, M. Açikyildiz, Adsorptive removal of phosphate from aqueous solutions using raw and calcinated dolomite, J. Hazard. Mater. B128 (2006) 273–279.

[14] L. Johansson, Industrial by-products and natural substrata as phosphorus sorbents, Environ. Technol. 20 (1999) 309–316.

[15] K. Adam, T. Krogstad, L. Vrale, A.K. Sovik, P.D. Jenssen, Phosphorus retention in the filter materials shellsand and Filtralite P (R) - batch and column experiment with synthetic P solution and secondary wastewater, Ecol. Eng. 29 (2007) 200–208.

[16] K. Sakadevan, H.J. Bavor, Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems, Water Res. 32 (1998) 393–393.

[17] X. Wei, R.C. Viadero, S. Bhojappa, Phosphorus removal by acid mine drainage sludge from secondary effluents of municipal wastewater treatment plants, Water Res. 32 (2008) 3275–3284.

[18] S. Jellali, M.A. Wahab, R. Ben Hassine, A.H. Hamzaoui, L. Bousselmi, Adsorption characteristics of phosphorus from aqueous solutions onto phosphate mine wastes, Chem. Eng. J. 16 (2011) 157–165.

[19] C. Vohla, M. Koiv, H.J. Bavor, F. Chazarenc, U. Mander, Filter materials for phosphorus removal from wastewater in treatment wetlands-A review, Ecol. Eng. 37 (2011) 70–89.

[20] Industry promotion agency [API]. Round table: Marble in Tunisia, 2005. Available from http://www.tunisieindustrie.nat.tn.

[21] F.J. Aukour, M.I. Al-Qinna, Marble production and environmental constrains: Case study from Zarqa governorate, Jordan, Jordan J. Earth Environ. Sci. 1 (2008) 11–21.

[22] L. Gervin, H. Brix, Removal of nutrients from combined sewer overflows and lake water in a vertical-flow constructed wetland system, Water Sci. Technol. 44 (2001) 171–176.

[23] International Fertilizer Industry Association [IFA], Production and International Trade Statistics, Paris, 2006. Available from http://www.fertilizer.org/ifa.

[24] D.N.H. Beach, J.E. McCray, K.S. Lowe, R.L. Siegrist, Temporal changes in hydraulic conductivity of sand porous media biofilters during waste water infiltration due to biomat formation, J. Hydrol. 311 (2005) 1–14.

[25] S. Jellali, E. Diamantopoulos, H. Kallali, S. Bennaceur, M. Anane, N. Jedidi, Dynamic sorption of ammonium by sandy soil in fixed bed columns: Evaluation of equilibrium and non-equilibrium transport processes, J. Environ. Manage. 91 (2010) 897–905.

[26] W.S.W. Ngah, M.A.K.M. Hanafiah, Adsorption of copper on rubber (Heveabrasiliensis) leaf powder: Kinetic, equilibrium and thermodynamic studies, Biochem. Eng. J. 39 (2008) 521–530.

[27] APHA, Standard Methods for the Examination of Water and Wastewater, 18th ed., APHA/AWWA/WPCF, Washington, DC, 1992.

[28] H.U. So, D. Postma, R. Jakobsen, F. Larsen, Sorption of phosphate onto calcite; results from batch experiments and surface complexation modeling, Geochimica et Cosmochimica Acta 75 (2011) 2911–2923.

[29] K. Karageorgiou, M. Paschalis, G.N. Anastassakis, Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent, J. Hazard. Mater. A139 (2007) 447–452.

[30] G. Gong, S. Yea, Y. Tiana, Q. Wang, J. Ni, Y. Chen, Preparation of a new sorbent with hydrated lime and blast furnace slag for phosphorus removal from aqueous solution, J. Hazard. Mater. 166 (2008) 714–719.

[31] C. Liu, Y. Li, Z. Luan, Z. Chen, Z. Zhang, Z. Jia, Adsorption removal of phosphate from aqueous solution by active red mud, J. Environ. Sci. 19 (2007) 1166–1170.

[32] S. Jellali, M.A. Wahab, M. Anane, K. Riahi, L. Bousselmi, Phosphate mine wastes reuse for phosphorus removal from aqueous solutions under dynamic conditions, J. Hazard. Mater. 184 (2010) 226–233.

[33] J. Lin, Y. Zhan, Z. Zhu, Evaluation of sediment capping with active barriers systems (ABS) using calcite/zeolite mixtures to simultaneously manage phosphorus and ammonium release, Sci. Total Environ. 409 (2011) 638–646.

[34] W. Stumm, J.J. Morgan, Aquatic Chemistry, 2nd ed., Wiley, New York, NY, 2001.

[35] A.S. Brooks, M.N. Rozenwald, L.D. Geohring, L.W. Lion, T.S. Steenhuis, Phosphorus removal by wollastonite: A constructed wetland substrate, Ecol. Eng. 15 (2000) 121–132.

[36] C.A. Arias, M.D. Bubba, H. Brix, Phosphorus removal by sands for use as media in subsurface flow constructed reed beds, Water Res. 35 (2001) 1159–1168.

[37] R. Roseth, Shell sand a new filter medium for constructed wetlands and wastewater treatment, J. Environ. Sci. Health A35 (2000) 1335–1355.

[38] T.J. Strang, D.G. Wareham, Phosphorus removal in awaste-stabilization pond containing limestone rock filters, J. Environ. Eng. Sci. 5 (2006) 447–457.

[39] A. Drizo, C.A. Frost, J. Grace, K.A. Smith, Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems, Water Res. 33(17) (1999) 3595–3602.

[40] X. Huang, X. Liao, B. Shi, Adsorption removal of phosphate in industrial wastewater by using metal-loaded skin split waste, J. Hazard. Mater. 166 (2009) 1261–1265.

[41] D.C. Seo, J.S. Cho, H.J. Lee, J.S. Heo, Phosphorus retention capacity of filter media for estimating the longevity of constructed wetland, Water Res. 39 (2005) 2445–2457.

[42] M.A. Wahab, R. Ben Hassine, S. Jellali, Removal of phosphorus from aqueous solution by Posidonia oceanica fibers using continuous stirring tank reactor, J. Hazard. Mater. 189 (2011) 577–585.

[43] A. Drizo, C. Forget, R.P. Chapuis, Y. Comeau, Phosphorus removal by electric arc furnace steel slag and serpentinite, Water Res. 40 (2006) 1547–1554.

[44] K. Cameron, C. Madramootoo, A. Crolla, C. Kinsley, Pollutant removal from municipal sewage lagoon effluents with a free-surface wetland, Water Res. 37 (2003) 2803–2812.

[45] T. Krogstad, T.A. Sogn, A. Asdal, A. Saebo, Influence of chemically and biologically stabilized sewage sludge on plant-available phosphorous in soil, Ecol. Eng. 25 (2005) 51–60.

[46] J.P. Gustafsson, A. Renman, G. Renman, K. Poll, Phosphate removal by mineral-based sorbents used in filters for small-scale wastewater treatment, Water Res. 42 (2008) 189–197.

[47] E.H. Kim, S.B. Yim, H.C. Jung, E.J. Lee, Hydroxyapatite crystallization from a highly concentrated phosphate solution using powdered converter slag as a seed material, J. Hazard. Mater. 136 (2006) 690–697.