



“Gheorghe Asachi” Technical University of Iasi, Romania



POWDERED MARBLE WASTES REUSE FOR CADMIUM REMOVAL FROM AQUEOUS SOLUTIONS UNDER DYNAMIC CONDITIONS

Ammar Mlayah^{1*}, Salah Jellali²

¹Water Research and Technologies Centre (CERTe), Georesources Laboratory, Tunisia

²Water Research and Technologies Centre (CERTe), Wastewaters and Environment Laboratory, Tunisia

Abstract

A factorial design analysis was performed in order to determine the significant factors influencing cadmium removal from aqueous solutions by powdered marble wastes (PMW), using a continuous stirring tank reactor (CSTR) system. Investigated factors were initial cadmium aqueous concentration (5-30 mg L⁻¹), PMW dosage (5-15 g L⁻¹) and flow rate (20-40 mL min⁻¹). Results showed that the cadmium aqueous concentration and PMW dosage were the most influencing factors on metal removal from synthetic aqueous solutions. Furthermore, interactions between cadmium concentration-PMW dosage and cadmium concentration-flow rate have also significant effects. The optimal conditions for highest cadmium removal rate by PMW (96.04%) were established at initial cadmium concentration of 5 mg L⁻¹, adsorbent dosage of 15 g L⁻¹ and flow rate of 20 mL min⁻¹. According to SEM, EDS and especially XRD analyses, cadmium removal is likely to be controlled by adsorption onto particle surface through cation exchange and complexation. On the other hand, the competition between four metals showed that the selectivity sequence of the metals was: Pb > Cu > Zn > Cd. The proposed low cost material efficiently removes metals present in synthetic solutions and can be applied for industrial effluents treatment.

Key words: cadmium, CSTR, factorial design, marble wastes, removal

Received: March, 2014; *Revised final:* July, 2014; *Accepted:* July, 2014; *Published in final edited form:* May, 2018

1. Introduction

Wastewater discharge from metal plating, textile, tanneries, batteries and fertilizers industries often contain relatively high concentrations of cadmium (Cd) and could present a serious environmental problem due to Cd toxicity, non biodegradability and bioaccumulation in living tissues and food chain (Volesky, 1990). The presence of Cd above critical levels may cause several diseases to human such as anemia, hepatitis, nephrite syndrome etc. (Volesky, 1990). In the last decades, various technologies have been tested and developed to remove heavy metals from wastewater, such as chemical precipitation (Sadeghi et al., 2017; Zaki et al., 2007), ion exchange (Chaudhari and Murthya,

2010), membrane filtration (Guo et al., 2008) and electrochemical processes (Babel and Kurniawan, 2003; Mahitti and Fuangfa, 2008). However some of these technologies have the drawback of high costs due to chemical reagent consumption, energy requirements as well as the production of large amounts of sludges (Volesky, 1990). Hence, it has become necessary to develop new environmentally friendly and low cost technologies for heavy metal removal from industrial effluents. One of the promising alternatives that has been intensively tested and applied over the last two decades is the use of low cost materials and natural wastes for cadmium removal from wastewaters through adsorption processes. Various materials have been tested under static mode (batch tests) including activated carbon

*Author to whom all correspondence should be addressed: e-mail: ammarmlayah@yahoo.fr; salah.jallali@certe.rnrt.tn; Phone: +21679325199; Fax: +21679325802

(Depci et al., 2012; Qu et al., 2013), limestone (Aziz et al., 2008), clays (Turan and Ergun, 2009), silt (Oudjenia-Marouf et al., 2013), lignite (Uçurum, 2009), bentonite (Mohammed-Azizi et al., 2013), hydroxyapatite (Mateiuc et al., 2017) and zeolite (Javadian et al., 2013). Due to their small dimensions and non-continuous renewal of effluent, the extrapolation of batch results to real applications is generally very difficult. Only a few experiments have been carried out using laboratory columns but confronted to the clogging phenomenon caused by suspended solid filtration (Jellali et al., 2010a, 2016; Oliva et al., 2011). Continuous stirring tank reactors are other techniques used to tackle these problems by treating an important amount of wastewaters and ensuring continuous renewal of both the aqueous solutions and the adsorbents. The need of using this technique at laboratory or field scale has been pointed out by several authors (Jellali et al., 2010b; Mlayah and Jellali, 2015; Wei et al., 2008). On the other hand, laboratory assays addressing heavy metals removal efficiency through adsorption process showed dependence on several factors such as pH, adsorbent dosage, initial aqueous concentration, contact time, and particle size distribution. In conventional methods used to evaluate the impact of each of these factors, experiments have been conducted by varying one factor and keeping others as constants (Jellali et al., 2010b; Krika et al., 2016; Tang et al., 2013). The factorial design technique has been successfully employed in order to reduce the number of experiments and to determine not only the importance of each factor but also the possible interactions between two or more factors. Recently, this method has been used for a number of investigations dealing with the adsorption of heavy metals (Başak, 2013; Calero et al., 2013; Saadat and Karimi-Jashni, 2011, Srivastava et al., 2017). However, there are limited investigations concerning such applications for Cd ion adsorption using CSTR technique.

Powdered marble wastes are generated by marble processing during large stone polishing. This phase is accompanied with the discharge of huge amounts of PMW into the environment and landfills (Aukour and Al-Qinna, 2008). However, these wastes could be interesting materials for heavy metal removal from aqueous media due to their unique mineralogical composition and their confirmed effects onto aqueous pH (Jaouadi et al., 2014). To date, only very few studies have investigated PMW reuse for urban wastewater treatment especially for phosphorus removal and recovery (Gervin and Brix, 2001; Jaouadi et al., 2014).

The main purposes of the present study are i) to investigate the initial aqueous solution pH, ii) to determine the individual effects and the double interactions between flow rate, initial aqueous concentration and adsorbent dosage on Cd removal efficiency from aqueous solutions under dynamic conditions. Accordingly, a 2³ factorial design is applied with abundant, renewable and eco-friendly

calcitic materials: Bianco Gioia marble wastes in CSTR system, iii) to study the influence of other cations in the medium, and finally iv) to explore the involved mechanisms through specific assays and analyses.

2. Material and methods

2.1. PMW preparation and characterization

In this study, the solid matrix is constituted by powdered marble wastes (PMW) resulting from the manufacturing of large stones of “BIANCO GIOIA” marble. PMW were collected as a dry pure powder at the vicinity of cutting and polishing devices from a marble processing company located in the southern suburb of Tunis, the capital city of Tunisia. Collected PMW were first sieved mechanically in order to remove bulk materials and debris, then washed with distilled water and dried 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 (Philips PW 1710). Scans were conducted from 0° to 60° at a rate of 2°min⁻¹. The elemental composition of 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 pH of zero point charge (pH_{ZPC}) of PMW was performed according to the solid addition method described by Ngah and Hanafiah (2008), using 0.01 M KNO₃ solutions, 1g of PMW for initial pH values of 2, 4, 6, 8, 10, and 12.

2.2. Synthetic cadmium solution preparation and analysis

Cadmium nitrate (Cd(NO₃)₂) was used in CSTR tests as the source of cadmium ions. The working solutions were prepared through dilutions with distilled water of a stock cadmium solution of 1 g L⁻¹. Cd concentration analysis was performed by AAS (Perkin Elmer AAnalyst). pH measurements were performed by a pH meter (692 pH/Ion Meter, Metrohm).

2.3. CSTR cadmium removal studies

2.3.1. Laboratory CSTR presentation and experimental protocol

Continuous flow tests were carried out using a CSTR system for Cd removal from synthetic solutions (Fig. 1). A 1.2 L glass reactor was used to ensure the contact between PMW and cadmium in aqueous solutions. At the start of the assays, the desired PMW dosage was put in the reactor, which is then rapidly filled with aqueous cadmium solution at the desired concentration. Afterwards, the cadmium-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 pre-defined 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 had been reached. This state is characterized by a quasi-stability of cadmium concentrations at the entrance of the settling set up (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 Cd removal. 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 dissolved cadmium concentration. All assays presented hereafter were conducted in duplicate and only mean values are reported.

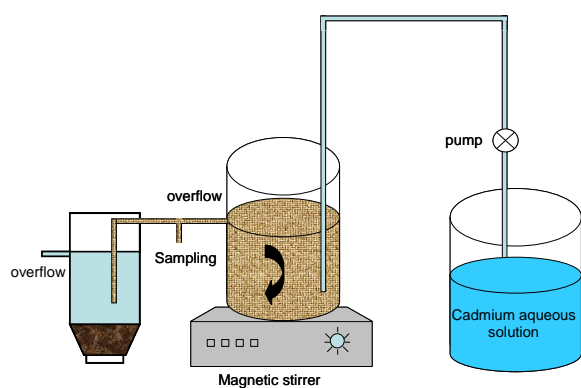


Fig. 1. Schematic representation of the experimental design for cadmium removal studies

2.3.2. Studied factors in the factorial design

In order to determine individual and double interactions of various parameters on Cd removal from aqueous solution by PMW using CSTR technique, a factorial design of experimental series was applied. For this purpose, three factors, namely initial aqueous concentration, adsorbent dosage and flow rate were varied at two levels as described in Table 1. During these experiments, the initial aqueous pH was fixed to 3.6.

Table 1. Experimental ranges and levels of studied factors in the factorial design

Factor	Coded symbol	Range and level	
		-1	+1
Initial cadmium concentration (mg L^{-1})	A	5	30
PMW dosage (g L^{-1})	B	5	15
Flow rate (mL min^{-1})	C	20	40

The cadmium removal efficiency ($R\%$) is given by (Eq. 1):

$$R(\%) = \frac{(C_0 - C_f)}{C_0} \cdot 100 \quad (1)$$

where: C_0 and C_f are the influent and the equilibrium aqueous cadmium concentration measured at the outlet of the reactor, respectively.

2.3.3. Effect of ion competition

In order to assess the competing effect of other cations on cadmium removal by PMW, a CSTR removal test of cadmium (10 mg L^{-1}) was performed in the presence of lead, zinc and copper at aqueous concentration of 50, 10 and 10 mg L^{-1} respectively. The PMW dosage, aqueous pH and feeding flow rate were fixed at 5 g L^{-1} , 3.6 and 20 mL min^{-1} respectively.

3. Results and discussion

3.1. PMW characterization

The PMW used in this study can be considered as a very fine solid porous media (Table 2). In fact, particle mean diameter is relatively low ($22.6 \mu\text{m}$). The BET specific area of PMW was estimated to $0.14 \text{ m}^2 \text{ g}^{-1}$ which is comparable to commercial calcium carbonate (So et al., 2011) and dolomite (Karaca et al., 2006). X-ray and EDS analyses indicate that PMW is exclusively formed by calcite with relatively high contents of Ca. The pH_{ZPC} value was 8.11 which is very close to the value found for calcite with a purity of 98% in CaCO_3 (Karageorgiou et al., 2007). As a consequence, under the chosen experimental conditions (initial $\text{pH} = 3.6$), PMW particles surface should be positively charged.

Table 2. Main physico-chemical characteristics of the used powdered marble 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})

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

3.2. Effect of initial aqueous pH

The pH is an important factor for determining the form of cadmium species in aqueous solutions. It influences the strength of Cd adsorption mechanism as it determines the degree and sign of the charge on these ions (Rangel-Porras et al., 2010). For aqueous pH lower than 4, the dominant species is free Cd^{2+} . For pH higher than 6, cadmium is mainly present as CdHO_3^+ , $\text{CdCO}_3(\text{aq})$ and $\text{Cd}(\text{CO}_3)_3^{4+}$. The results, depicted in Fig. 2, showed that aqueous pH has a significant effect on cadmium removal. Therefore, it appears that cadmium removal was inhibited at low pH values. For the lowest tested aqueous pH ($\text{pH}=2$), maximal removal efficiency was evaluated to about 88% during only 15 min. However, for initial

aqueous pH values of 3.6 and 5, the measured cadmium concentrations at the outlet of the reactor were lower than detection limits for a relatively long period. Removed cadmium amounts were estimated according to mass balance method to 1.069, 2.782 and 2.973 mg g⁻¹ for initial pH of 2, 3.6 and 5 respectively. At an initial pH of 3.6, the removed cadmium amount was about 8.6 times higher than silt (Oujadjenia-Marouf et al., 2013), 4.3 times than perlite (Mathialagan and Viraraghavan, 2002) and 2.1 times than calcitic limestone materials (Rangel-Porras et al. 2010).

These findings are mainly caused by the fact that at lower pH, the concentration of positive charge (protons) increased on the sites of solid particles surface, which limited the adsorption of Cd ions because of charge repulsion phenomenon. As the aqueous pH values increase, the charge density on PMW surface becomes more negative and proton concentrations decrease. This behavior favors the removal of positively charged cadmium ions onto particle surface. On the other hand, due to the dissolution of PMW into the distilled water (Jaouadi et al., 2014), the aqueous pH values of the solution in the reactor during equilibrium phase become more important when increasing the initial pH solutions. Indeed, these equilibrium pH values were evaluated to 5.73, 6.64 and 6.68 for initial pH of 2; 3.6 and 5 respectively. These outcomes indicate that Cd precipitation should be negligible. This trend has been also pointed out by Rangel-Porras et al. (2010) when they studied cadmium removal using calcitic materials. Consequently, the experiments carried out hereafter were conducted at an initial aqueous pH of 3.6.

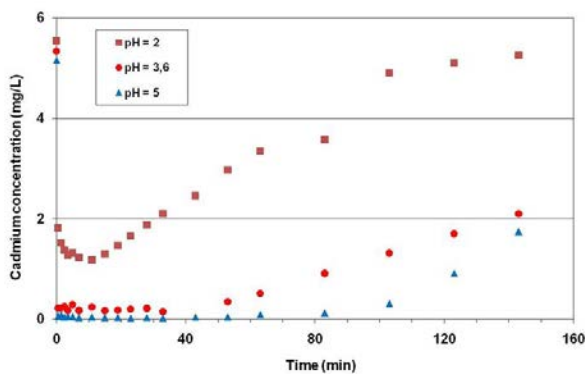


Fig. 2. Effect of initial aqueous solution pH on Cd adsorption by PMW

3.3. Factorial design adsorption experiments

The design matrix of uncoded values for the studied factors and the response in term of average cadmium removal efficiency are shown in Table 3. Results were analyzed using Minitab 15 program and the main effects and interactions between studied factors were determined. The coded model employed for the 2³ factorial designs is given by (Eq. 2):

$$R(\%) = a_0 + a_1A + a_2B + a_3C + a_{12}AB + a_{13}AC + a_{23}BC + a_{123}ABC \tag{2}$$

where: *R*(%) is the percentage removal of cadmium, *a*₀ is global mean, *a*₁, *a*₂ and *a*₃ are the individual effect of the concentration, dose and flow rate respectively. Coefficients *a*₁₂, *a*₁₃ and *a*₂₃ describe the interacting effects of cadmium concentration- PMW dosage, cadmium concentration- flow rate and PMW dosage- flow rate respectively. *a*₁₂₃ shows the interacting effect of cadmium concentration- PMW dosage- flow rate.

Table 3. Uncoded design table for the factors and responses

Run order	Concentration (mg L ⁻¹)	Dose (g L ⁻¹)	Flow rate (mL min ⁻¹)	Removal (R (%))
1	5	5	20	94.14
2	30	5	20	45.94
3	5	15	20	96.04
4	30	15	20	90.90
5	5	5	40	92.13
6	30	5	40	38.5
7	5	15	40	95.92
8	30	15	40	78.43

Effects, regression coefficients, standard errors and “t” values (standardized effects) are illustrated in Table 4. By substituting the coefficients “a_i” in Eq. (2), we obtain a model equation relating to the level of parameters and cadmium removal efficiency:

$$R(\%) = 79.00 - 15.56A + 11.32B - 2.76C + 9.90AB - 2.22AC - 0.39BC - 0.86ABC \tag{3}$$

A positive sign of a given parameter indicates that the response increases with the increase in the value of this parameter (Turan et al., 2011).

Table 4. Statistical parameters for the used 2³ factorial designs for cadmium removal by PMW using CSTR technique

Term	Effect	Coefficient	Standard error	t-value	P-value
Constant		79.00	0.388	203.62	0.000
a ₁	-31.11	-15.56	0.388	-40.10	0.001
a ₂	22.65	11.32	0.388	29.18	0.001
a ₃	-5.51	-2.76	0.388	-7.10	0.019
a ₁₂	19.80	9.90	0.388	25.52	0.002
a ₁₃	-4.45	-2.22	0.388	-5.73	0.029
a ₂₃	-0.79	-0.39	0.388	-1.01	0.418
a ₁₂₃	-1.73	-0.86	0.388	-2.23	0.156
R-Sq		0.9994			
R-Sq (adj)		0.9969			

The coefficient of determination (*R*²) value for the regression model is 0.9994 (Table 4). This indicates that 99.94% of the total variation in cadmium removal response is attributed to the studied experimental variables; the obtained coefficient is satisfying comparing to some other

studies dealing with lead removal from aqueous solutions (Berrama et al., 2013; Martín-Lara et al., 2011). The closer the R^2 value to unity, the better the model will be; it will provide a predicted value which is closer to the actual values for the response (Berrama et al., 2013). R^2 value of 0.9994 is considered highly significant, indicating that there is a good agreement between the experimental and the predicted value of cadmium removal.

3.3.1. Student's test

Student's t-test was performed in order to determine whether calculated main and interaction effects were significantly different from zero. Absolute values of individual and combined effects of the studied parameters are presented in the Pareto chart as horizontal columns (Fig. 3). The vertical line in the chart gives the minimum statistically significant effect magnitude with a 95% confidence level. Since the effects extending this line are considered to be significant factors, the main effects of cadmium concentration, PMW dosage and flow rate and also interactions between cadmium concentration-PMW dosage, and cadmium concentration are important parameters for cadmium removal from aqueous solutions by PMW using the CSTR technique. However, interactions between flow rate-PMW dosage and also cadmium concentration- PMW dosage- flow rate are considered to have relatively insignificant effects on cadmium removal.

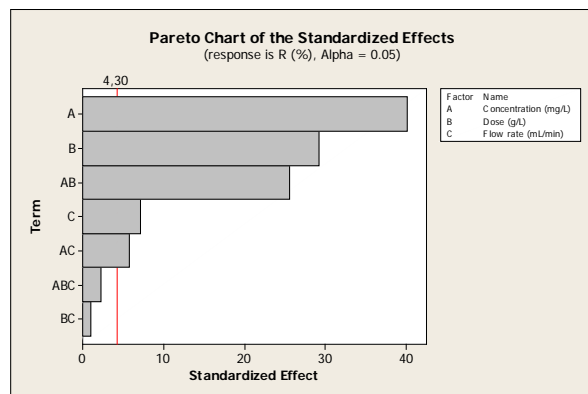


Fig. 3. Pareto chart of the standardized effects for cadmium removal by PMW

3.3.2. Analyses of variance (ANOVA)

Table 5 illustrates the sum of squares (SS) and the mean of squares (MS) of each studied factor, P-value, and F-ratio, which is defined as the ratio of respective mean square effect and mean square error. P-values are probabilities that could be used to determine the statistically significant parameters in the model. For a 95% confidence level, P-values for significant parameters should be lower than 0.05 (Saadat and Karimi-Jashni 2011; Srinivasan and Viraraghavan, 2010). According to the obtained F-values and p-values (Table 4) and as determined by the Pareto chart, the effect of cadmium concentration,

PMW dosage, flow rate and interactions between cadmium concentration- PMW dosage and cadmium concentration and flow rate are statistically significant.

Thus, according to Student's t-test and F-test, and taking into account only the significant parameters, Eq. (3) becomes Eq. (4):

$$R(\%) = 79.00 - 15.56A + 11.32B - 2.76C + 9.90AB - 2.22AC \quad (4)$$

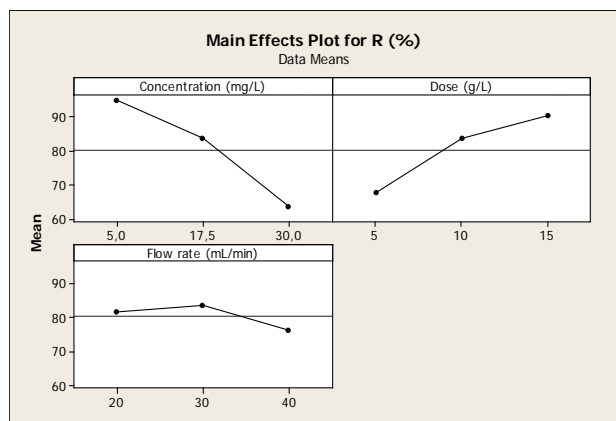
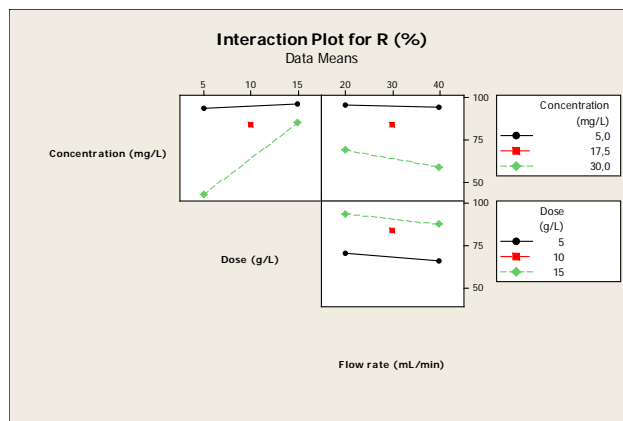
3.3.3. Main and interaction effects

The main effect plot of Cd removal from aqueous solutions by PMW using CSTR technique is shown in Fig. 4. A main effect is present when the mean response changes significantly across the level of a given factor. It can be concluded from Fig. 3 that cadmium aqueous concentration was the most important factor regarding cadmium removal efficiency since the corresponding coefficient was the largest (-15.56). The negative sign of this coefficient reveals that cadmium removal was favoured at low aqueous concentrations. Decreasing cadmium concentration from 30 mg L⁻¹ to 5 mg L⁻¹ increased the adsorption efficiency by 31.12%. This is mainly due to the fact that for low aqueous concentrations, the ratio of active adsorption sites to the initial cadmium ions is larger, resulting in higher removal efficiency. However, at higher initial cadmium aqueous concentrations, the amount of metal ions is relatively higher as compared to the available sorption sites, which induces lower cadmium percentage removal. On the other hand, PMW dosage effect seems to be also relatively important since its coefficient was significant (11.32). The positive sign of this coefficient proves that cadmium removal was favored when PMW dosage increased. Consequently, increasing PMW dosage from 5 to 15 g L⁻¹ increases cadmium removal efficiency by 22.64%. This finding is due to the greater availability of exchangeable sites or active adsorption sites at higher dosages of PMW. The same trend has been reported by Turan et al. (2011) for the adsorption of copper and zinc ions using illite. Flow rate impact is relatively weaker than cadmium concentration and PMW dosage. Nevertheless, it has a non-negligible effect on cadmium removal especially when it was increased from 30 to 40 mL min⁻¹. In fact, increasing the flow rate from 20 to 40 mL min⁻¹ decreases cadmium removal efficiency by 5.51%. This trend can be explained by the fact that higher is the flow rate, lower is the contact time between cadmium ions and PMW particles.

Interaction effect plots are presented in Fig. 5. The non-parallel lines in this figure indicate that there is a significant interaction between these two factors. Trends in Fig. 5 and coefficients of Eq. (3) showed positive interactions between cadmium concentration and PMW dosage. Increasing PMW dosage from 5 to 15 g L⁻¹ increased cadmium removal efficiency by 2.85% at 5 mg L⁻¹ cadmium concentration and by 42.44% at 30 mg L⁻¹.

Table 5. Analysis of variance for cadmium removal by PMW using CSTR technique

Source	Degrees of freedom	Sum of squares	Adj. Sum of squares	Adj. Mean of squares	F-ratio	P-value
Main effects	3	3022.60	3022.60	1007.53	836.66	0.001
2-way interactions	3	824.83	824.83	274.94	228.31	0.004
3-way interactions	1	5.99	5.99	5.99	4.97	0.156
Residual error	2	2.41	2.41	1.20		
Pure error	2	2.41	2.41	1.20		
Total	9	3855.83				

**Fig. 4.** Main effects plot for the removal of cadmium from aqueous solutions by PMW using CSTR technique**Fig. 5.** Interaction effect plot for Cd removal from aqueous solutions by PMW using CSTR technique

This indicates that at higher cadmium concentrations, changes in PMW dosages have a greater effect. However, a negative interaction between cadmium concentration and flow rate was registered. In fact, at lower flow rate (20 mL min⁻¹), cadmium removal efficiency was 95.09% and 68.42% at cadmium concentrations of 5 and 30 mg L⁻¹, respectively. However, at higher flow rate (40 mL min⁻¹), increasing cadmium concentration from 5 to 30 mg L⁻¹ decreased cadmium removal efficiency from 94.02% to 58.46%. Interactions between PMW dosage and flow rate and also between all the studied factors are, however, non-significant.

3.3.4. Normal probability plot of residuals

For statistical analysis of experimental data, it is necessary to check that the data of cadmium removal from aqueous solutions using the CSTR technique follow a normal distribution pattern (Antony, 2003). The normality of data can be checked by plotting a normal probability plot of the residuals (Fig. 6). If the points of the plot fall close enough to the straight line, then corresponding data are normally distributed (Antony, 2003; Abdel-Ghani et al., 2009). It is obvious from Fig. 6 that the experimental points follow a straight line suggesting normal distribution of data.

3.4. Effect of ion competition

Generally, several metal ions are ubiquitous in natural waters and industrial effluents, so it is important to study the sorption selectivity of PMW

towards target metal ions when assessing its technical applicability. In this regard, the impact of the presence of other heavy metals (Cu, Pb, Zn) on cadmium removal from synthetic aqueous solutions was carried out accordingly. Experimental results indicated that maximal cadmium removal efficiency by PMW (at equilibrium) has decreased due to the presence of other (Cu, Pb, Zn) from 100% to 4.9% (Fig. 7). This observed decrease could be explained by competition between metal ions over the same sorption sites. Removal efficiencies of Pb, Cu and Zn were estimated to 82.5%, 41.8% and 15.1% respectively (Fig. 7). These were relatively higher than the one relative to Cd, which proves that for real wastewater rich in various heavy metals, cadmium ions will not be selectively removed. The same trend has been observed by Ouadjenia-Marouf et al. (2013) when they studied the removal of Cu, Cd and Cr by dam silt under batch mode. Furthermore, Rangel-Porras et al. (2010) found that Cd removal efficiency by three calcitic limestone materials from Mexico had been so much lower than Pb. This low selectivity to cadmium in comparison to other metals could be attributed to their physicochemical characteristics (size and electronegativity), their low availability, and the difficulty of the formation of corresponding metal hydroxide complexes (Abdel-Aty et al., 2013). Furthermore, this sorption preference to Pb may be also imputed to the fact that its hydration energy is lower than those of the other mentioned heavy metal ions (Deng et al., 2013; Rangel-Porras, 2010). In fact, cations with highest (absolute value) free energy of hydration should therefore prefer to remain in the

solution phase where their hydration requirements may be better satisfied.

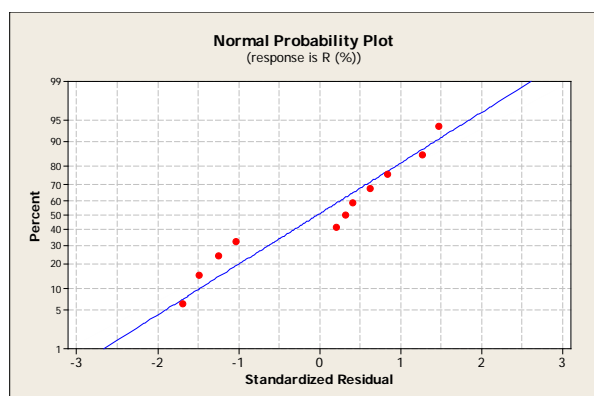


Fig. 6. Normal probability plot of residuals for Cd removal from aqueous solutions by PMW using CSTR technique

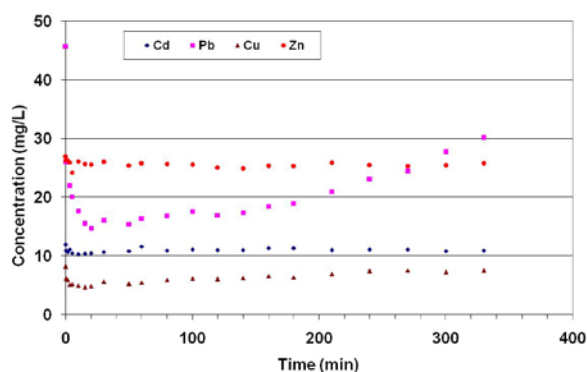


Fig. 7. Effect of the presence of other cations on Cd removal from aqueous solutions by PMW

3.5. Cadmium removal mechanism exploration

Cadmium removal from aqueous solutions might occur by precipitation as cadmium carbonate or cadmium hydroxide complexes and also by adsorption onto the active sites of PMW particle surface. The precipitation of Cd is instantaneous and very dependent on the aqueous pH values and solutions contents of OH^- , HCO_3^- and Cd^{2+} . However, the adsorption phenomenon can be speculated to occur in three steps: (1) transfer of cadmium from the aqueous solution to the sites of the adsorbent (boundary layer diffusion); (2) chemical complexation/ion exchange at the active sites of the adsorbent surface; and (3) intra-particle diffusion of cadmium into the interior pores of PMW particles (Weber and Morris, 1963). In order to differentiate between these two mechanisms cited above, specific batch assays have been carried out. In the first set of assays, aqueous cadmium at an initial concentration of 5 mg L^{-1} and initial pH of 3.6 was put in contact for one hour with 5 g L^{-1} of PMW. Thus, Cd removal was imputed to both adsorption and precipitation mechanisms. In the second set of experiments, the same cadmium concentration was put in contact for 1 h with a filtrate aqueous solution (using a $0.45 \mu\text{m}$

paper filter). This filtrate solution results from the shaking of 5 g L^{-1} PMW in distilled water at the same initial pH (3.6). In this case, Cd concentration decrease is exclusively due to precipitation. The experimental results showed that in the first set of assays, adsorption and precipitation mechanisms achieved about 97.7% of Cd removal from the aqueous solution. However, for the second type of assays, where only cadmium precipitation mechanism is present, cadmium concentration did not show a decrease which testifies to the absence of cadmium precipitation phenomenon. Therefore, under the experimental conditions cited above, cadmium removal from synthetic aqueous solutions occurs exclusively by adsorption.

On the other hand, EDS spectra of PMW samples before and after cadmium removal are shown in Figs. 8a-b respectively. The EDS spectra of PMW before Cd removal exhibit peaks of Ca, C, O and Mg, which are their main basic constituents of PMW (Fig. 8a). The EDS analysis of PMW after cadmium removal showed the appearance of new peaks relative to this metal (Fig. 8b).

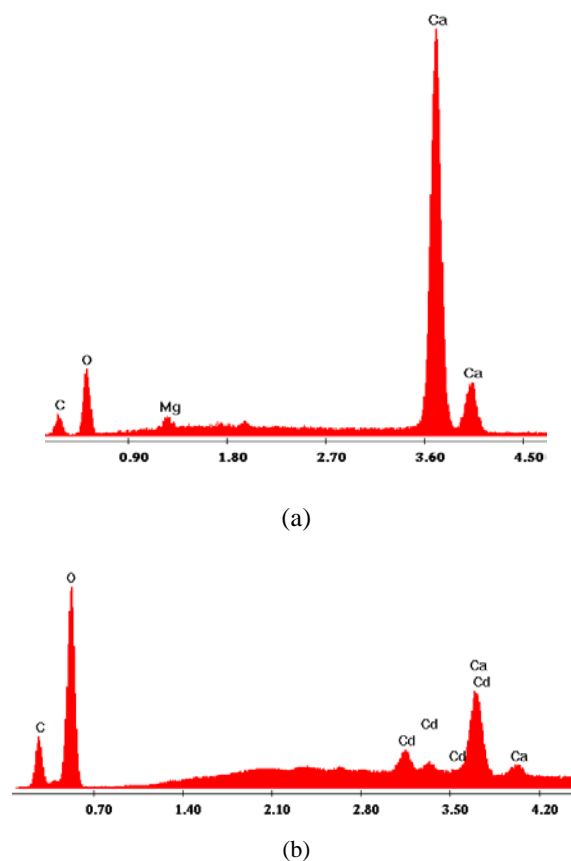


Fig. 8. EDS analysis results of PMW before (a) and after cadmium removal (b)

On the other hand, the XRD spectra of PMW before cadmium adsorption exhibit peaks relative to calcite and dolomite, which are the main basic constituents of the used adsorbent (Fig. 9-C1). The XRD analysis of PMW after cadmium removal (Fig.

9-C2) confirms that the precipitation of CdCO_3 (otavite) is absent since no new mineralogical species were registered. It is important to underline that cadmium removal from aqueous solutions could be attributed also to a cation exchange phenomenon with calcium cations.

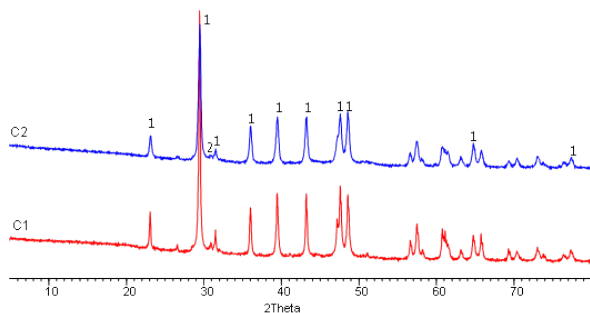


Fig. 9. XRD analysis of raw PMW (C1), Cd-loaded PMW (C2) (1: Limestone (calcite), 2: dolomite)

4. Conclusions

The study of cadmium removal efficiency from aqueous solutions by PMW under dynamic conditions has been performed through a 2^3 factorial design. Outcomes showed that cadmium concentration (A), PMW dosage (B) and influent flow rate (C) as well as interactions of AxB and AxC were statistically significant. The most significant effects were ascribed to cadmium concentration and PMW dosage, and also to the interaction between these two factors. Furthermore, results indicated that the use of PMW which is a low cost material and locally available could be considered as an attractive adsorbent for cadmium and other metal removal from aqueous solutions. Further investigation will address i) the removal of other metals under different experimental conditions, especially Pb and ii) the test of up scaled dynamic set-ups for metals removal from real wastewaters.

References

- Abdel-Aty A.M., Ammar N.S., Abdel-Ghafar H.H., Ali R.K., (2013), Biosorption of cadmium and lead from aqueous solution by fresh water alga *Anabaena sphaerica* biomass, *Journal of Advanced Research*, **4**, 367-374.
- Abdel-Ghani N.T., Hegazy Ahmad K., El-Chaghaby G.A., Lima Eder C., (2009), Factorial experimental design for biosorption of iron and zinc using *Typha domingensis* phytomass, *Desalination*, **249**, 343-347.
- Antony J., (2003), *Design of Experiments for Engineers and Scientists*, Elsevier Science & Technology Books, Amsterdam.
- Aukour F.J., Al-Qinna M.I., (2008), Marble production and environmental constrains: case study from Zarqa Governorate, *Jordan. Jordan Journal of Earth and Environment Sciences*, **1**, 11-21.
- Aziz H.A., Adlan M.N., Ariffin K.S., (2008), Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr (III)) removal from water in Malaysia: Post treatment by high quality limestone, *Bioresource Technology*, **99**, 1578-1583.
- Babel S., Kurniawan T.A., (2003), Low-cost adsorbents for heavy metals uptake from contaminated water: a review, *Journal of Hazardous Materials*, **97**, 219-243.
- Berrama T., Benaouag N., Kaouah F., Bendjama Z., (2013), Application of full factorial design to study the simultaneous removal of copper and zinc from aqueous solution by liquid-liquid extraction, *Desalination and Water Treatment*, **51**, 2135-2145.
- Başak M., (2013), A novel approach for modeling Cu^{2+} and Zn^{2+} adsorption from industrial leachate by peanut shells, *Environmental Engineering and Management Journal*, **12**, 2289-2298.
- Calero M., Ronda A., Martín-Lara M.A., Perez A., Blázquez G., (2013), Chemical activation of olive tree pruning to remove lead(II) in batch system: Factorial design for process optimization, *Biomass and Bioenergy*, **58**, 322-332.
- Chaudhari L.B., Murthya Z.V.P., (2010), Separation of Cd and Ni from multicomponent aqueous solutions by nanofiltration and characterization of membrane using IT model, *Journal of Hazardous Materials*, **180**, 309-315.
- Deng Y., Gao Z., Liu B., Hu X., Wei Z., Sun C., (2013), Selective removal of lead from aqueous solutions by ethylenediamine-modified attapulgite, *Chemical Engineering Journal*, **223**, 91-98.
- Depci T., Kul A.R., Onal Y., (2012), Competitive adsorption of lead and zinc from aqueous solution on activated carbon prepared from Van apple pulp: Study in single- and multi-solute systems, *Chemical Engineering Journal*, **200-202**, 224-236.
- Gervin L., Brix H., (2001), Removal of nutrients from combined sewer overflows and lake water in a vertical-flow constructed wetland system, *Water Sciences and Technology*, **44**, 171-176.
- Guo X., Zhang S., Shan X.Q., (2008), Adsorption of metal ions on lignin, *Journal of Hazardous Materials*, **151**, 134-142.
- Jaouadi S., Mlayah A., Jellali S., (2014), Phosphates removal from aqueous solutions by marble wastes under static conditions, *Desalination and Water Treatment*, **52**, 1716-1724.
- Javadian H., Ghorbani F., Tayebi H., Hosseini Asl S.M., (2013), Study of the adsorption of Cd (II) from aqueous solution using zeolite-based geopolymer, synthesized from coal fly ash; kinetic, isotherm and thermodynamic studies, *Arabian Journal of Chemistry*, **8**, 837-849.
- Jellali S., Diamantopoulos E., Haddad K., Anane M., Durner W., Mlayah A., (2016), Lead removal from aqueous solutions by raw sawdust and magnesium pretreated biochar: experimental investigations and numerical modelling, *Journal of Environmental Management*, **180**, 439-449.
- Jellali S., Diamantopoulos E., Kallali H., Bennaceur S., Anane M., Jedidi N., (2010a), Dynamic sorption of ammonium by sandy soil in fixed bed columns: Evaluation of equilibrium and non-equilibrium transport processes, *Journal of Environment and Management*, **91**, 897-905.
- Jellali S., Wahab M.A., Anane M., Riahi K., Bousselmi L., (2010b), Phosphate mine wastes reuse for phosphorus removal from aqueous solutions under dynamic conditions, *Journal of Hazardous Materials*, **184**, 226-233.
- Karaca S., Gürses A., Ejder M., Açıkyıldız M., (2006), Adsorptive removal of phosphate from aqueous solutions using raw and calcinated dolomite, *Journal of Hazardous Materials*, **B128**, 273-279.

- Karageorgiou K., Paschalis M., Anastassakis G.N., (2007), Removal of phosphate species from solution by adsorption onto calcite used as natural adsorbent, *Journal of Hazardous Materials*, **A139**, 447-452.
- Krika F., Azzouz N., Ncibi M.C., (2016), Adsorptive removal of cadmium from aqueous solution by cork biomass: Equilibrium, dynamic and thermodynamic studies, *Arabian Journal of Chemistry*, **9**, S1077-S1083.
- Mahitti P., Fuangfa U., (2008), Preparation and use of chemically modified MCM-41 and silica gel as selective adsorbents for Hg(II) ions, *Journal of Hazardous Materials*, **154**, 578-587.
- Martín-Lara M.A., Rodríguez I.L., Blázquez G., Calero M., (2011), Factorial experimental design for optimizing the removal conditions of lead ions from aqueous solutions by three wastes of the olive-oil production, *Desalination*, **278**, 132-140.
- Mateiuc A.M., Ciobanu G., Luca C., Luca F.A., (2017), Copper(II) adsorption onto hydroxyapatite, *Environmental Engineering and Management Journal*, **16**, 2353-2359.
- Mathialagan T., Viraraghavan T., (2002), Adsorption of cadmium from aqueous solutions by perlite, *Journal of Hazardous Materials*, **B94**, 291-303.
- Mlayah A., Jellali S., (2015), Study of continuous lead removal from aqueous solutions by marble wastes: efficiencies and mechanisms, *International Journal of Environmental Science and Technology*, **12**, 2965-2978.
- Mohammed-Azizi F., Dib S., Boufatit M., (2013), Removal of heavy metals from aqueous solutions by Algerian bentonite, *Desalination and Water Treatment*, **51**, 4447-4458.
- Ngah W.S.W., Hanafiah M.A.K.M., (2008), Adsorption of copper on rubber (*Hevea brasiliensis*) leaf powder: Kinetic, equilibrium and thermodynamic studies, *Biochemical Engineering Journal*, **39**, 521-530.
- Oliva J., De Pablo J., Cortina J.L., Cama J., Ayora C., (2011), Removal of cadmium, copper, nickel, cobalt and mercury from water by apatite IITM: Column experiments, *Journal of Hazardous Materials*, **194**, 312-323.
- Oudjenia-Marouf F., Marouf R., Schott J., Yahiaoui A., (2013), Removal of Cu(II), Cd(II) and Cr(III) ions from aqueous solution by dam silt, *Arabian Journal of Chemistry*, **6**, 401-406.
- Qu G., Liang D., Qu D., Huang Y., Liu T., Mao H., Ji P., Huang D., (2013), Simultaneous removal of cadmium ions and phenol from water solution by pulsed corona discharge plasma combined with activated carbon, *Chemical Engineering Journal*, **228**, 28-35.
- Rangel-Porras G., Garcia-Magno J.B., Gonzalez-Munoz M.P., (2010), Lead and cadmium immobilization on calcitic limestone materials, *Desalination*, **262**, 1-10.
- Saadat S., Karimi-Jashni A., (2011), Optimization of Pb(II) adsorption onto modified walnut shells using factorial design and simplex methodologies, *Chemical Engineering Journal*, **173**, 743-749.
- Sadeghi M., Karimi H., Alijanvand M.H., (2017), Removal of lead ions from industrial wastewater using precipitation process, *Environmental Engineering and Management Journal*, **16**, 1563-1568.
- Srinivasan A., Viraraghavan T., (2010), Oil removal from water by fungal biomass: a factorial design analysis, *Journal of Hazardous Materials*, **175**, 695-702.
- Srivastava V., Gusain D., Bux F., Chandra G.C., Sharma Sharma Y.C., (2017), Optimization of important process parameters for the removal of Cr(VI) by a modified waste material, *Environmental Engineering and Management Journal*, **16**, 2719-2730.
- Tang Y., Chen L., Wei X., Yao Q., Li T., (2013), Removal of lead ions from aqueous solution by the dried aquatic plant, *Lemma perpusilla* Torr, *Journal of Hazardous Materials*, **244-245**, 603-612.
- Turan N.G., Ergun O.N., (2009), Removal of Cu (II) from leachate using natural zeolite as a landfill liner material, *Journal of Hazardous Materials*, **167**, 687-700.
- Turan N.G., Eleveli S., Mesci B., (2011), Adsorption of copper and zinc ions on illite: Determination of the optimal conditions by the statistical design of experiments, *Applied Clay Science*, **52**, 392-399.
- Uçurum M., (2009), A study of removal of Pb heavy metal ions from aqueous solution using lignite and a new cheap adsorbent (lignite washing plant tailings), *Fuel*, **88**, 1460-1465.
- Volesky B., (1990), *Biosorption by Fungal Biomass*, In: *Biosorption of Heavy Metals*, CRC Press: Boca Raton, FL, 139-172.
- Weber W.J., Morris J.C., (1963), Kinetics of adsorption on carbon from solution, *Journal of Sanitary Engineering Division*, **89**, 31-60.
- Wei X., Viadero R.C., Bhojappa S., (2008), Phosphorus removal by acid mine drainage sludge from secondary effluents of municipal wastewater treatment plants, *Water Research*, **32**, 3275-3284.
- Zaki N.G., Khattab I.A., Abd el-Monem N.M., (2007), Removal of some heavy metals by CKD leachate, *Journal of Hazardous Materials*, **147**, 21-27.