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## ORIGINAL ARTICLE

# Lead separation by sorption onto powdered marble waste



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## KEYWORDS

Lead;  
Sorption;  
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**Abstract** Batch adsorption experiments were carried out, aiming to remove lead ions from aqueous solutions and water samples using powdered marble wastes (PMW) as an effective inorganic sorbent, which is cheap, widespread, and may represent an environmental problem. The main parameters (i.e., solution pH, sorbent and lead concentration, shaking time, and temperature) influencing the sorption process, were investigated. The results obtained showed that the sorption of  $Pb^{2+}$  ions onto PMW was fitted well with the linear Freundlich and Langmuir models over the concentration range studied. From the Dubinin–Radushkevick (D–R) isotherm model it was found that the adsorption was chemical in nature. Thermodynamic parameters *viz.* the change in Gibbs free energy change ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were also calculated. These parameters indicated that the adsorption process of  $Pb^{2+}$  ions on PMW was spontaneous and endothermic in nature. Under the optimum experimental conditions employed, the removal of about 100% of  $Pb^{2+}$  ions was attained. The procedure was successfully applied to remove lead ions from aqueous and different natural water samples. Moreover, the adsorption mechanism is suggested.

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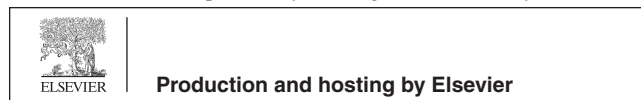
## 1. Introduction

The current pattern of industrial activity alters the natural flow of materials and introduces novel chemicals into the environment (Fasal and Hasnain, 2004; Igwe and Abia, 2006). The rate at which effluents are discharged into the environment

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especially water bodies has been increased as a result of urbanization. Toxic metal ions (among them is lead) are dangerous contaminants that are accumulated by the living organisms and, up to now, there are no widely accepted methods to have them removed. Therefore, the best solution is preventing the entrance of toxic metals in the ecosystem (Chubar et al., 2003). Furthermore, the removal of toxic metal ions and recovery of valuable metal ions from mine wastewaters, soils and waters have been important in economic and environmental viewpoints (Monteagudo and Ortiz, 2000; Capponi et al., 2006).

Lead is accumulated in the human system through a number of processes like breathing air from industrial environment (lead smelting, refining and manufacturing industries), ingesting plants or food grown on contaminated soils and breathing

in fumes from hobbies that use lead (leaded-glass, ceramics). The health hazards resulting from the presence of lead in domestic and industrial wastewaters are of extreme concern to the public, government and industries for over the past decades up to now (Ho et al., 2001). Because of the great mobility, the heavy metal may reach the main source of drinking water such as surface and underground water (Ghazy and Ragab, 2007a). The deleterious effects of lead on neurobehavioral development (Dietrich et al., 1990) and brain cell function (Goldstein, 1990) have been investigated. The maximum allowable  $Pb^{2+}$  concentration in drinking water was restricted to be  $20 \text{ ng ml}^{-1}$  (Senkal et al., 2007) and by international regulations on water quality, by World Health Organization (WHO, 2000) and European Commission Directive (EUD, 1998). Hence, easy, effective, economic and eco-friendly techniques are required for fine tuning of effluent wastewater treatment. The search for a low cost and easily available adsorbent has led to the investigation of materials applicable to most treatment systems.

A number of technologies have been developed over the years to remove heavy metals from industrial wastewaters. The most important technology includes coagulation/flocculation (Amuda et al., 2006). Other conventional chemical methods include precipitation, ion-exchange, electrochemical processes, solvent extraction, and membrane technology. All the chemical methods have proved to be much costlier and less efficient (Preetha and Viruthagiri, 2005). Adsorption is one of the most interesting methods for the removal of heavy metals from various effluents. The main properties of adsorbents for heavy metal removal are strong affinity and high loading capacity (Sari et al., 2007). Natural organic or inorganic sorbents, which are particularly abundant and inexpensive, have generally these properties (Sari et al., 2007; Ghazy et al., 2005; Kumar et al., 2000). Therefore, the study of the adsorption process is of utmost importance for the understanding of how heavy metals are transferred from a liquid mobile phase to the surface of a solid phase (Bradl, 2004). Finally, researchers strive-themselves to find a low cost and easily available adsorbent.

Large amounts of marble are produced in some countries, such as the United States, Italy, Greece, Egypt and others. The by-product generated from marble processing is a powdered dust and may represent an environmental problem. Hence, the objective of this work was to study the possibility of utilizing PMW (naturally occurring and cheap) as a sorbent for removing lead ions from aqueous solutions and natural waters. The different parameters influencing the adsorption of lead ions onto powdered marble wastes were optimized and the results are presented in this paper.

## 2. Experimental

### 2.1. Materials and solutions

The powdered marble waste (PMW) samples used in this study were obtained, free of charge, from the dust of some private marble processing workshops located in Bilqas city, Egypt. The samples were sieved and those with size (25–63  $\mu\text{m}$ ) were used in the experiments. The samples contained 60% calcite,  $\text{CaCO}_3$ , and 6% dolomite,  $\text{MgCO}_3$ , (as found by chemical analysis), with the remainder being composed of common constituents such as quartz, feldspar, clays, pyrite and siderite

(Bates and Jackson, 1980). The samples were dried for 2 h in large trays in an oven maintained at  $125^\circ\text{C}$ , allowed to cool to room temperature and then packed into stoppered bottles and stored in a desiccator for future use.

Functional groups of PMW were characterized through infrared analysis. The observable peaks at about 710, 875, 1420, 1807 and  $2520 \text{ cm}^{-1}$  coincided with pure  $\text{CaCO}_3$ . The surface area and porosity of PMW was measured using Brunauer, Emmett, Teller (BET) method. PMW samples have 18.9  $\text{\AA}$  pore diameter, 31.2  $\text{\AA}$  pore size, 0.98  $\text{cc/g}$  pore volume and its measured surface area was  $21.8 \text{ m}^2/\text{g}$ . The pH values of points of zero charge (pHPZC) were 9.1 (not aged), 6.2 (aged 60 min) and 8.3 (aged several days) and this agreed with the previously reported data (Somasundran and Agar, 1967). Stirring or soaking of 1 g PMW sorbent in 100 ml distilled water (pH 6.9) for 1 h or more increased the suspension pH to 9.3, confirming the negative charge of the PMW surface.

Lead(II) stock solution (4 g/l) was prepared from  $\text{Pb}(\text{NO}_3)_2$  (BDH Ltd., Poole, England) by dissolving 1 g in 250 ml doubly distilled water. The working solutions were made by diluting with doubly distilled water. Xylenol orange (XO) indicator (1%) was freshly prepared daily before use. Aqueous solutions of  $\text{HNO}_3$  and  $\text{NaOH}$  were used for pH adjustment. Any other chemicals were prepared from certified reagent grade chemicals.

### 2.2. Apparatus

A Buck Scientific Accusys 211 Atomic Absorption Spectrophotometer (AAS), provided with micro-burettes 5 and 10 ml, was used for the determination of lead concentration at 217 nm. The infrared analyses were undertaken via a Mattson 5000 FT-IR spectrophotometer using KBr disc method. The pH was measured using a Jeanway 3311 pH meter, provided with a glass electrode. The shaking of solutions was carried out with a shaker Model (Heidolph promax 2020, Germany).

### 2.3. Procedure

Unless stated otherwise, all batch sorption experiments were done at room temperature ( $\sim 25^\circ\text{C}$ ). Known volumes of lead solutions were pipetted into quick-fit glass bottles containing 0.05 g of PMW sorbent in 50 ml aqueous solution to give concentrations ranging from 500 to 1500  $\text{mg/l}$ . Since the pH of any resulting solution was  $\sim 7.0$ , further controlling of pH was not necessary since pH 7 was suitable for most adsorption experiments. The resulting solution was then shaken at 270 rpm and the samples were taken at fixed time periods (1, 5, 10, 15, 20 and 25–135 min) in order to study the kinetics of the adsorption process. Preliminary experiments showed that this time length was sufficient for adsorption of  $\text{Pb}^{2+}$  ions onto PMW. The samples were subsequently filtered off and the residual  $\text{Pb}^{2+}$  ions concentration in the filtrate were analyzed using AAS at a wavelength of 217 nm, or with EDTA titration for high concentrations of lead using xylenol orange (XO) indicator.

The percentage adsorption of  $\text{Pb}^{2+}$  ions from the solution was calculated from the relationship:

$$\% \text{ Adsorption} = (C_i - C_r)/C_i \times 100 \quad (1)$$

where  $C_i$  corresponds to the initial concentration of  $Pb^{2+}$  ions and  $C_r$  is the residual concentration after equilibration. The metal uptake  $q$  (mg/g) was calculated as:

$$q = [(C_i - C_r)/m]V \quad (2)$$

where  $m$  is the quantity of sorbent (mg) and  $V$  the volume of the suspension (ml).

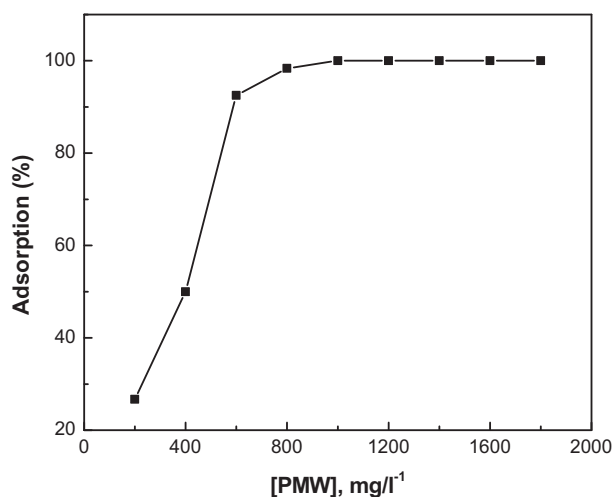
To assess the applicability of the procedure, another series of experiments was conducted on 50 ml of clear and pre-filtered natural water samples with an initial pH adjusted to 7.0. These suspensions contained 500 mg/l of  $Pb^{2+}$  ions, 1000 mg/l of PMW at 25 °C and were shaken for optimum time at 270 rpm.

### 3. Results and discussion

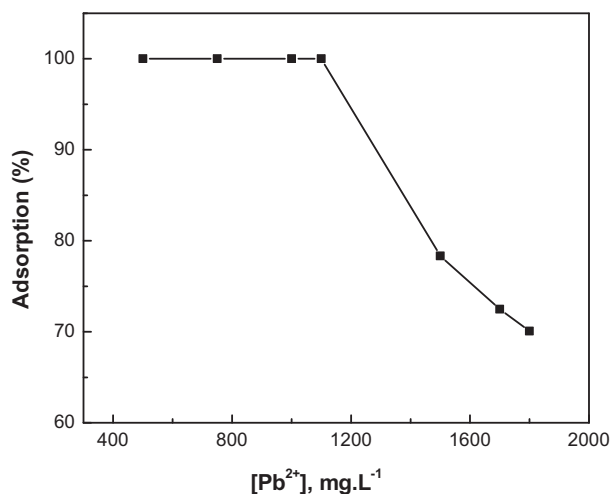
#### 3.1. Effect of sorbent and metal ion concentrations

Sorbent amount is an important parameter because this determines the capacity of a sorbent for a given initial concentration of adsorbate at the operating conditions. The effect of varying the amount of PMW as adsorbent on the adsorption of  $Pb^{2+}$  ions (500 mg/l) from aqueous solutions of pH 7 was depicted in Fig. 1. The data show that the adsorption efficiency increases as the amount of PMW increases and reaches a maximum value (~100%) at  $\geq 1000$  mg/l of PMW. This may be attributed to an increase in the surface area of the sorbent and hence the number of binding sites available to the metal ions. Therefore, 1000 mg/l PMW was fixed for further experiments.

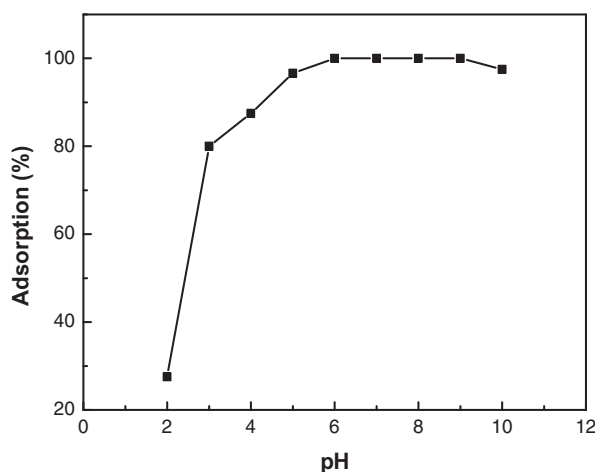
In contrast, varying  $Pb^{2+}$  ion concentrations show that the adsorption efficiency decreases with increasing metal ion concentration in the solution (Fig. 2). This may be explained in terms of relatively smaller number of active sites available at higher concentration of lead and to a desorption phenomena of Pb ions from PMW to the solution. However, it was found that with the increase of initial Pb(II) concentration,  $q$  [metal uptake (mg/g)] increased. Increase of  $q$  with the increase of  $C_0$  [initial metal ion concentration (mg/l)] was expected due to the increase of the sorbed Pb(II) ions quantity per unit weight of sorbent.



**Figure 1** Effect of PMW concentration on the adsorption of  $Pb^{2+}$  ions (500 mg/l) from aqueous solutions of pH 7.



**Figure 2** Adsorption of different concentrations of  $Pb^{2+}$  ions (500 mg) from aqueous solutions of pH 7 using 1000 mg/l PMW.



**Figure 3** Adsorption (%) of  $Pb^{2+}$  ions (500 mg/l) by PMW (1000 mg/l) vs. pH.

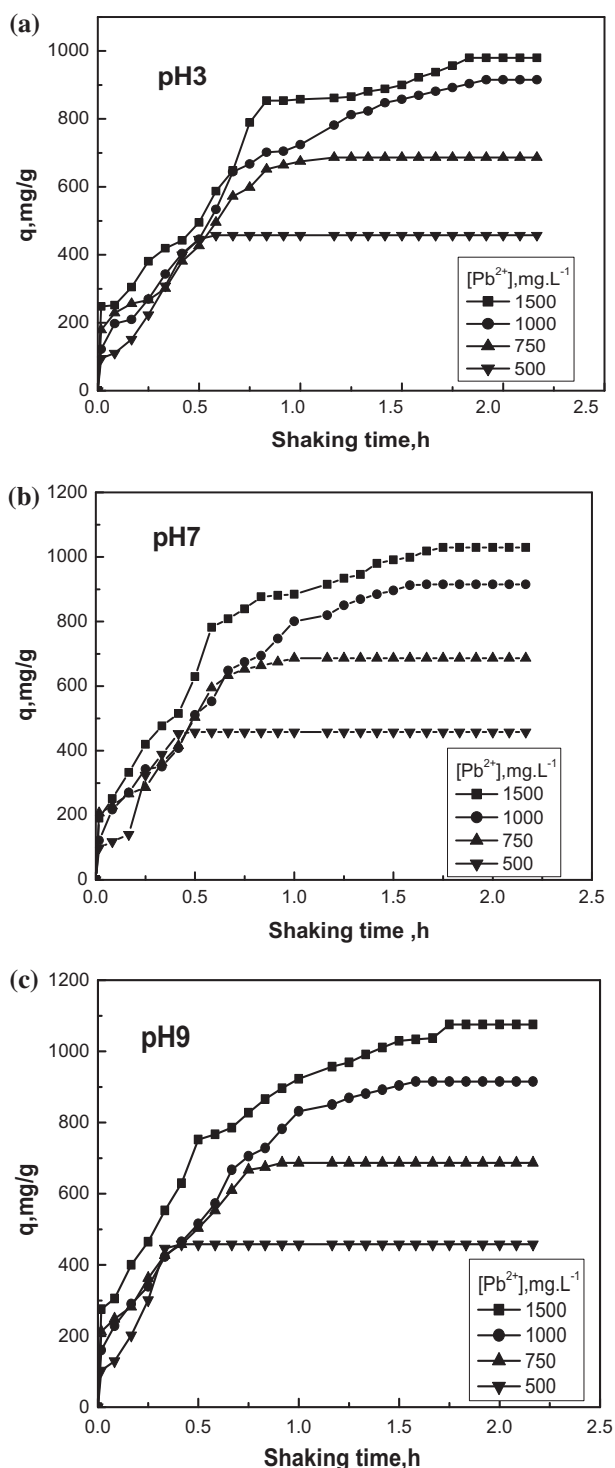
#### 3.2. Effect of pH value

The pH seems to be the most important parameter for controlling the sorption process (Friis and Keith, 1998). It affects the solution chemistry of the metal and the network of charges on the surface of the sorbent, as well as physico-chemistry and hydrolysis of the metal (Collins and Stotzky, 1996; Lopez et al., 2000).

It was reported that at acidic pH (< 5)  $Pb^{2+}$  ions were the dominant species. At higher pH (> 5) solubility of  $Pb^{2+}$  ions was lowered (Chang et al., 1997; Bradl, 2004). Between pH 6 and 10, Pb undergoes hydrolysis to  $Pb(OH)^+$ . Above pH 9, solid lead hydroxide  $Pb(OH)_2$  is thermodynamically the most stable phase, while  $Pb(OH)_3^-$  and  $Pb(OH)_4^{2-}$  are the predominant species at pH above 11.

A series of experiments was conducted in the pH range 2–10 to investigate the effect of pH on the adsorption of 500 mg/l  $Pb^{2+}$  ions by 1000 mg/l PMW as sorbent and the data were depicted in Fig. 3. It should be noted that below pH 2, the

removal of  $\text{Pb}^{2+}$  ions reaches zero because of almost solubility of the sorbent (consists mainly of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ ) thereby hindering the sorption process. Above pH 2, the adsorption of  $\text{Pb}^{2+}$  ions increases as the pH increases, reaching a maximum value ( $\sim 100\%$ ) followed by a decrease.



**Figure 4** Influence of shaking time on adsorption of various concentrations of  $\text{Pb}^{2+}$  ions by PMW (1000 mg/l) in acidic (pH 3), neutral (pH 7) and alkaline (pH 9) media.

The sorption of lead ions under pH 5 may be attributed to a possible ion-exchange mechanism between  $\text{Pb}^{2+}$  ions and calcium containing PMW in similar manner to that reported (Mandjiny et al., 1995; Ghazy and Ragab, 2007a). Also, this was confirmed by measuring the concentration of calcium ion in the solution before and after the adsorption where its value was increased. Adsorbed lead ions generally occupy calcium site within the calcite lattice (Chermiak, 1997). The enhanced removal of metal ion as the solution pH increased (more than 5) can be attributed to adsorption of hydrolytic species  $\text{Pb}(\text{OH})^+$  (Ghazy et al., 2005) and/or surface precipitation of the metal as the insoluble carbonates,  $\text{PbCO}_3$ , forming successive layers on the sorbent surface (Apak et al., 1998). The decrease in the removal efficiency at high pH value (more than 9) may be attributed to the fact that the negative species of lead,  $\text{Pb}(\text{OH})_3^-$  and  $\text{Pb}(\text{OH})_4^{2-}$ , are not capable of a combination with the negative surface of PMW. Therefore, pH 7 was selected for all further studies.

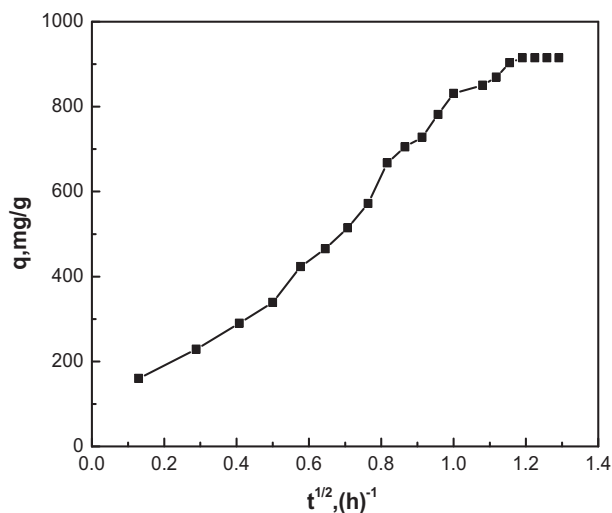
### 3.3. Kinetics of the adsorption process

Fig. 4 shows the variation in the  $\text{Pb}^{2+}$  uptake by PMW with shaking time at different initial metal ion concentrations in acidic (pH 3), neutral (pH 7) and alkaline (pH 9) media. The data depicted in this figure indicate that: (i) A similar trend in adsorption process was attained in acidic, neutral and alkaline medium. Moreover, the sorption capacity of  $\text{Pb}^{2+}$  ions by PMW is nearly the same in pHs 7 and 9 and higher than that at pH 3. This agrees with the data obtained in Fig. 3 and hence pH 7 was recommended for further experiments. (ii) The adsorption of lead ions was quite rapid at the first stage which may suggest that adsorption occurred mainly at the surface of the solid sorbent and to some extent by the internal macropores, transitional pores and micro-pores (Al-Asheh and Banat, 2001; Ghazy and Ragab, 2007a). However, with the passage of time, the rate of adsorption decreased owing to the decrease of diffusion of lead ions through the pores (Akhtar and Qadeer, 1997; Ghazy and Ragab, 2007a) and ultimately reached a constant value (equilibrium time). On the basis of the results, a 2 h of shaking time was found suitable for maximum adsorption and used in all subsequent measurements. (iii) The uptake capacities increased with increasing initial  $\text{Pb}^{2+}$  ion concentrations which may be attributed to higher collision between  $\text{Pb}^{2+}$  ions and sorbent. However, it was found that there is a decrease in adsorption percentage at higher initial  $\text{Pb}^{2+}$  concentrations which may be due to rapid saturation of the metal binding sites of the sorbent (Ghazy and Ragab, 2007a).

When the data depicted in Fig. 4 were re-plotted against the square root of the shaking time, the obtained linear correlations (Fig. 5) may verify the Morris–Weber equation (Weber and Morris, 1963):

$$q = K_d(t)^{1/2} \quad (3)$$

where  $q$  is the amount of  $\text{Pb}^{2+}$  ions adsorbed (mg/g). This indicates that an intra-pore diffusion mechanism was involved in adsorption of  $\text{Pb}^{2+}$  ions by PMW (Fig. 4). Fig. 5 shows that two distinct regions were observed: an initial linear portion which may be due to the boundary layer effect (Crank, 1965; Unuabonah et al., 2007) and a second portion which may be due to the intra-particle diffusion effect (McKay et al.,



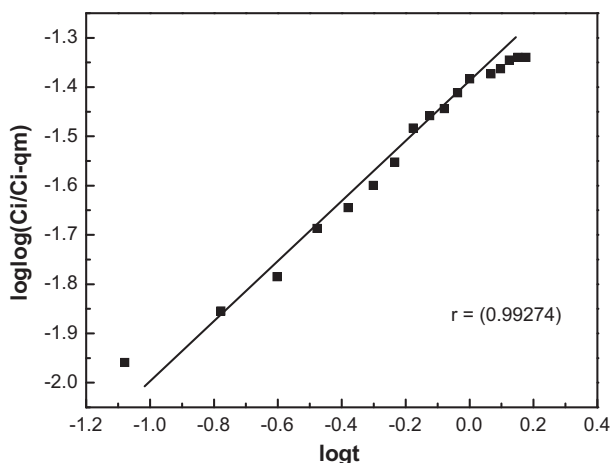
**Figure 5** Plot of amount of  $\text{Pb}^{2+}$  ions adsorbed onto PMW (1000 mg/l) vs. square root of time at pH 7.

1980). However, the fact that the line depicted in Fig. 5 does not pass through the origin indicates that intra-pore diffusion is not the controlling step in sorption of  $\text{Pb}^{2+}$  ions by PMW (Al-Asheh and Banat, 2001; Weber and Morris, 1963). These data agree with those of Juang et al. (2000) who proposed that the first sharp portion of the curve should be attributed to adsorption on the external surface of the sorbent while the second gradual portion should be attributed to intra-pore diffusion. The larger the intercept, the greater the contribution of the surface adsorption in the rate-limiting step. The value of the rate constant  $K_d$  was evaluated as  $749.37 \text{ (mg/g min}^{-1}\text{)}$  which give indication about the mobility of the  $\text{Pb}^{2+}$  ions toward the PMW surface.

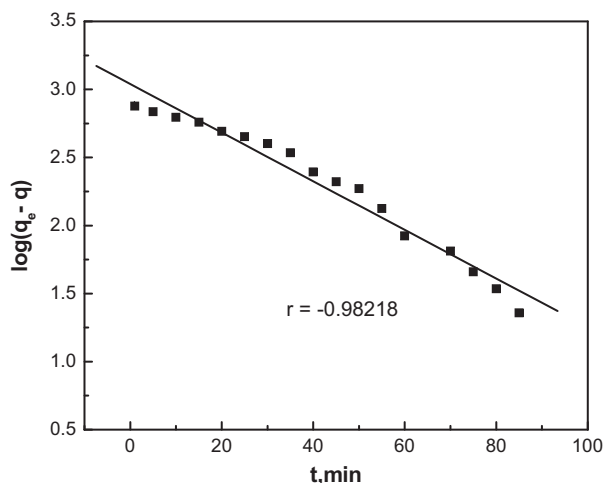
The kinetic data (Fig. 4) of the adsorption of  $\text{Pb}^{2+}$  ions by PMW was examined by Bangham equation (Ghazy and Ragab, 2007a):

$$\log \log [C_i / (C_i - qm)] = \log (K_o m / 2.303V) + \alpha \log t \quad (4)$$

where  $q$ ,  $m$ ,  $V$  and  $C_i$  have been defined above,  $t$  is the time (h),  $K_o$  is the proportionality constant, and  $\alpha$  is Bangham equation



**Figure 6** Plot of  $\log \log (C_i / C_i - qm)$  vs.  $\log t$  for the adsorption of  $\text{Pb}^{2+}$  ions (500 mg/l) by PMW (1000 mg/l) at pH 7.



**Figure 7** Plot of  $\log(q_e - q)$  vs. shaking time  $t$  for the adsorption  $\text{Pb}^{2+}$  ions (500 mg/l) by PMW (1000 mg/l) at pH 7.

constant. Plot of  $\log \log [C_i / (C_i - qm)]$  vs.  $\log t$  gives a straight line (Fig. 6). These results show that the diffusion of  $\text{Pb}^{2+}$  ions into PMW pores played a role in the adsorption process and were similar to those described elsewhere (Akhtar and Qadeer, 1997; Qadeer and Hanif, 1994). The value of  $K_o$  and  $\alpha$  constants deduced were 3.02 and 0.55, respectively.

Again the kinetic data obtained in Fig. 4 for  $\text{Pb}^{2+}$  ion adsorption by PMW were tested by Lagergren equation, as cited by Gupta and Shukla (1996):

$$\log(q_e - q) - \log q_e = -K_{\text{ads}} t / 2.303 \quad (5)$$

where  $q_e$  is the amount of  $\text{Pb}^{2+}$  ions adsorbed at equilibrium (mg/g),  $K_{\text{ads}}$  is the first order rate constant for  $\text{Pb}^{2+}$  ions adsorption onto PMW ( $\text{min}^{-1}$ ), while  $q$  and  $t$  have been defined previously. The linear plot of  $\log(q_e - q)$  vs.  $t$  (Fig. 7) shows the appropriateness of the above equation and consequently the first-order nature of the process involved. The value of  $K_{\text{ads}}$  was calculated to be  $0.04 \text{ min}^{-1}$ .

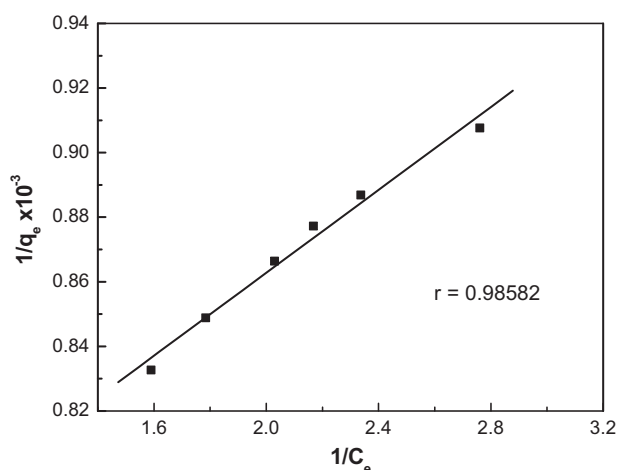
### 3.4. Adsorption isotherms

Since adsorption isotherms can be generated based on numerous theoretical models and to determine the capacity of PMW as sorbent for  $\text{Pb}^{2+}$  ions, Langmuir and Freundlich models are the most commonly used.

The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The linear form of the Langmuir equation applied to the  $\text{Pb}^{2+}$  ions adsorption data was:

$$1/q_e = 1/K_L + (1/K_L b) \cdot 1/C_e \quad (6)$$

where  $q_e$  is the amount of  $\text{Pb}^{2+}$  ions adsorbed at equilibrium (mg/g),  $C_e$  is the final equilibrium concentration (mg/l),  $K_L$  (mg/g) is the monolayer adsorption capacity and  $b$  (ml/mg) is the Langmuir constant. Fig. 8 shows that the plot of  $1/q_e$  vs.  $1/C_e$  gave a straight line with a correlation coefficient of 0.9858 suggesting the applicability of the Langmuir model. The values of  $K_L$  and  $b$  obtained from the intercept and slope of the linear plot were  $0.136 \text{ mg/g}$  and  $0.05209 \text{ l/g}$ , respectively.



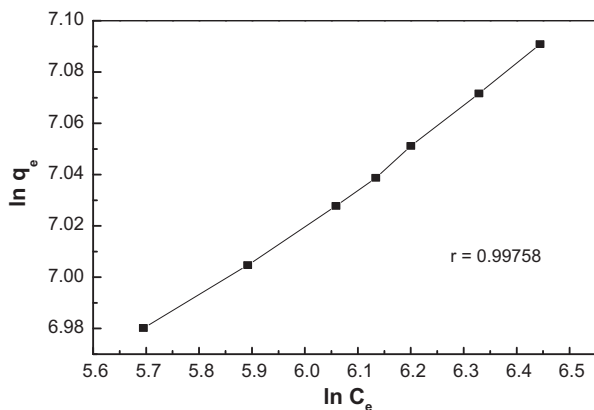
**Figure 8** Langmuir plot for  $Pb^{2+}$  ions adsorption by PMW (1000 mg/l).

The Freundlich adsorption isotherm can be used successfully for modeling the equilibrium data in metal-surface systems. It is an empirical equation based on adsorption on a heterogeneous surface. The linearized form of the Freundlich equation may be written as:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (7)$$

where  $K_F$  (mg/g) and  $n$  are the Freundlich equation parameters related to adsorption capacity and adsorption intensity, respectively. Fig. 9 shows that the plot of  $\ln q_e$  vs.  $\ln C_e$  gave a straight line with a correlation coefficient of 0.99758 suggesting the applicability of the Freundlich model to lead adsorption onto PMW. The parameters  $K_F$  and  $1/n$  for adsorption of  $Pb^{2+}$  ions onto PMW were calculated from the intercept and slope of the figure giving values of 5.54 l/g and 0.149, respectively. Favorable adsorption of  $Pb^{2+}$  ions by PMW was demonstrated by the fact that the value of  $n$  is greater than unity (Akhtar and Qadeer, 1997; Nassar et al., 1996; Erdem et al., 2004).

The Dubinin–Radushkevich (D–R) isotherm equation was also tested to determine the adsorption type (physical or chemical). The linear form of this model (Ghazy and Ragab, 2007b; Sari et al., 2007) is expressed by:



**Figure 9** Freundlich plot for  $Pb^{2+}$  ions adsorption by PMW (1000 mg/l).

$$\ln q = \ln q_e - \beta \varepsilon^2 \quad (8)$$

where  $q_e$  (monolayer capacity) is the amount of  $Pb^{2+}$  ions adsorbed at equilibrium per unit of PMW (mol/l),  $q$  is the liquid-phase concentration of  $Pb^{2+}$  ions (mol/l),  $\varepsilon$  is Polanyi potential and  $\beta$  is the parameter of (D–R) isotherm related to mean sorption energy.  $\varepsilon$  is the Polanyi potential described as:

$$\varepsilon = RT \ln(1 + 1/C) \quad (9)$$

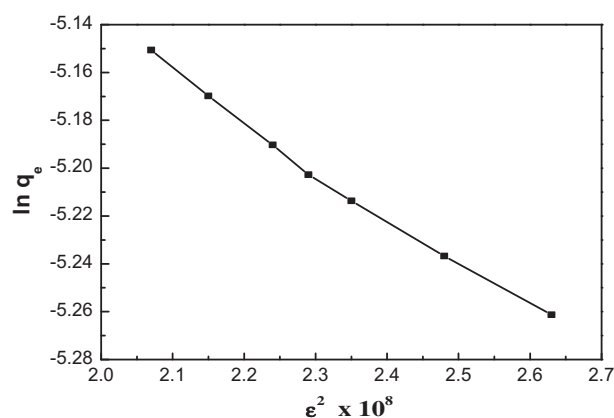
where  $T$  is the absolute temperature (K) and  $R$  is gas constant [8.3143 J/K mol].

Plotting of  $\ln q_e$  vs.  $\varepsilon^2$  gave a straight line (Fig. 10), so indicating the applicability of the (D–R) equation for the  $Pb^{2+}$  ions adsorption onto PMW. From the slope of this plot, the value of  $\beta = -1.96 \times 10^{-9}$  mol/kJ was obtained for  $Pb^{2+}$  ions adsorption.

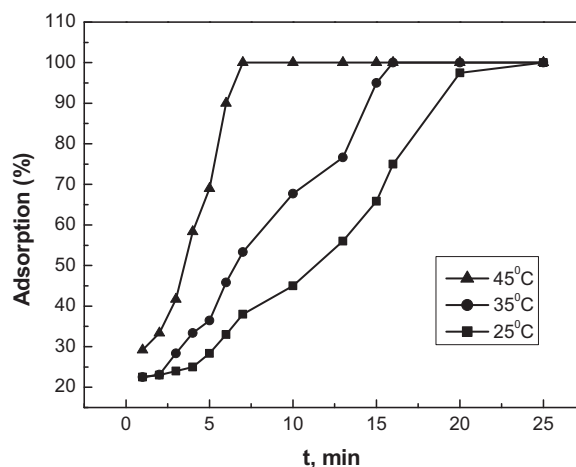
The value of the mean adsorption energy  $E$  (kJ/mol) was obtained from the relationship (Ghazy and Ragab, 2007b; Sari et al., 2007; Tahir and Nassem, 2003):

$$E = (-2\beta)^{-1/2} \quad (10)$$

and it was found to be 20.4 kJ/mol. The  $E$  value ranges from 1.0 to 8.0 kJ/mol is for physical adsorption and from 9.0 to



**Figure 10** Plot of D–R isotherm of  $Pb^{2+}$  adsorption onto PMW (1000 mg/l).



**Figure 11** Effect of temperature on the sorption (%) of  $Pb^{2+}$  ions (500 mg/l) by PMW (1000 mg/l) at different shaking times.

16.0 kJ/mol is for chemical adsorption (Sari et al., 2007; Donat et al., 2005). Therefore, the  $E$  value calculated for the adsorption of  $Pb^{2+}$  ions may be chemically in nature.

### 3.5. Effect of temperature and thermodynamic parameters

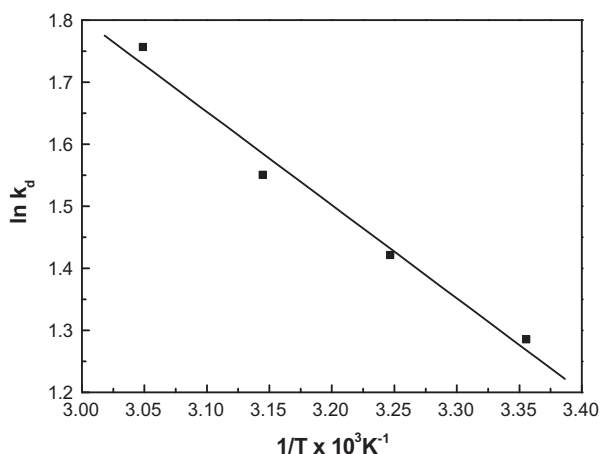
A series of experiments was conducted to study the effect of temperature on the adsorption of 500 mg  $Pb^{2+}$  ions onto 1000 mg/l of PMW at different times. The adsorption results are shown in Fig. 11. Close inspection of the figure shows that the adsorption efficiency increased as the temperature of the system increased. Such results may either be attributed to the creation of some new active sites on the adsorbent or to the acceleration of some originally slow adsorption steps. The enhancement of mobility of  $Pb^{2+}$  ions from the bulk solution toward the adsorbent surface should also be taken into consideration. This agrees well with the literature data (Al-Asheh and Banat, 2001; Nassar et al., 1996). Moreover, there was a decrease in the equilibration time to reach to a  $\sim 100\%$  for lead adsorption.

Such results could suggest that the adsorption of  $Pb^{2+}$  ions involves chemical bond formation and ion exchange (Al-Asheh and Banat, 2001). Accordingly, chelate formation may occur between  $Pb^{2+}$  ions and oxygen atoms on the limestone surface together with ion exchange between  $Pb^{2+}$  ions and  $Ca^{2+}$  ions present in  $CaCO_3$  (one of the major constituents of marble waste). Since most industrial effluents are usually hot, the simple adsorption procedure presented here may find application in industrial wastewater treatment for the removal of  $Pb^{2+}$  ions.

In order to investigate the thermodynamic parameters for the adsorption of  $Pb^{2+}$  ions by PMW, the distribution coefficient  $K_d$  (l/g) was calculated at the temperatures 298, 308, 318 and 328 K according to the following equation (Sari et al., 2007; Donat et al., 2005; Gupta and Bhattacharyya, 2005):

$$K_d = q_e / C_e \quad (11)$$

The  $K_d$  values calculated for the sorption of  $Pb^{2+}$  ions by PMW are 3615, 4143, 4714 and 5792 l/g. These results show that the  $K_d$  increased as the temperature increased from 298 to 328 K and revealing that the sorption of  $Pb^{2+}$  ions by PMW may be endothermic in nature.



**Figure 12** Thermodynamic distribution coefficient calculated for the sorption of  $Pb^{2+}$  ions (500 mg/l) by PMW (1000 mg/l) at pH 7.

The enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated from the slope and intercept of the plot of  $\ln K_d$  against  $1/T$ , respectively as depicted in Fig. 12 and according to the following equation (Sari et al., 2007; Donat et al., 2005; Gupta and Bhattacharyya, 2005):

$$\ln K_d = \Delta S^\circ / R - \Delta H^\circ / RT \quad (12)$$

The Gibbs free energy change ( $\Delta G^\circ$ ) was calculated by:

$$\Delta G^\circ = RT \ln K_d \quad (13)$$

The calculated enthalpy change  $\Delta H^\circ$  was 12.49 kJ/mol for the sorption of  $Pb^{2+}$  ions by PMW. The positive value of  $\Delta H^\circ$  clarified that the sorption process was endothermic. The entropy change ( $\Delta S^\circ$ ) was found to be 52.48 J/mol K. According to Sari et al. (2007), this result showed that  $Pb^{2+}$  ions in bulk phase (aqueous solution) is in a much chaotic distribution compared with the relatively ordered state of solid phase (sorbent surface). Moreover, the Gibbs free energy change ( $\Delta G^\circ$ ) was between  $-3.18$ ,  $-3.64$ ,  $-4.09$  and  $-4.79$  kJ/mol at the temperatures 298, 308, 318 and 328 K, respectively. The negative values of  $\Delta G^\circ$  indicated that the sorption of  $Pb^{2+}$  ions by PMW was feasible and spontaneous thermodynamically.

### 3.6. Comparison of lead uptake capacity by PMW and other inorganic sorbents

Comparison of lead uptake capacity by powdered marble waste with other inorganic sorbents is summarized in Table 1. The lead uptake by PMW was relatively higher than those obtained by other sorbents. In conclusion PMW may have a

**Table 1** Comparison of lead uptake capacity by various inorganic sorbents.

Sorbent	Sorption capacity (mg/g)	Reference
Powdered marble waste (PMW)	101.6	Our study
Celtex clay	40.0	Sari et al. (2007)
Kaolinite clay		Unuabonah et al. (2007)
Native clay	16.0	
Phosphate modified clay	18.0	
$\gamma$ - $Al_2O_3$	20.3	Yoshida et al. (2003)
Red mud		Apak et al. (1998)
Washed with water	165.8	
Acid treated	117.3	
Acid treated (heated to 600 °C)	138.8	
Zeolite		Babel and Kurniawan (2003)
Clinonoptilolite	62.0	
Chbaazite	175.0	
Bentonite	20.0	Nassem and Tahir (2001)
Natural oxides		Babel and Kurniawan (2003)
Aluminum oxide	33.0	
Ferric oxide	230.0	
Waste slurry	1030	Srivastava et al. (1989)
Palestinian soils		Abdel Aziz (2005)
Biet Lahya	4.8	
Biet Hanoun	6.8	

**Table 2** Recovery of Pb<sup>2+</sup> ions added to some water samples using 1000 mg/l of PMW sorbent at pH 7.

Sample (location)	Pb <sup>2+</sup> added (mg/l)	Pb <sup>2+</sup> found (mg/l)	Recovery (%)
Distilled water	500	499.85	99.97
Tap water (Our laboratory)	500	430.00	86.00
Nile water (Mansoura city)	500	428.50	85.70
Sea water (Gamasah)	500	97.90	99.58
Sea water (Ras El-Barr)	500	488.30	97.66
Underground water (Mansoura)	500	499.76	99.95

potential in treating the wastewater contained lead from industrial effluent.

### 3.7. Application

To investigate the applicability of the recommended procedure, a series of experiments were performed to recover 500 mg/l of Pb<sup>2+</sup> ions added to aqueous and some natural water samples. The adsorption experiments were carried out using 50 ml clear, filtered, uncontaminated sample solutions adjusted to pH ~ 7. The results obtained are listed in Table 2 and show that the recovery was satisfactory. However, the low recovery in some samples could be enhanced by increasing the sorbent (PMW) dose.

### 3.8. Adsorption mechanism

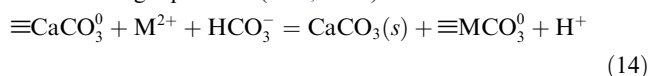
Although adsorption from solution by solids is of great practical importance and a vast number of papers have been published, it has been only over the last three decades a fundamental understanding has been developed. However, sharp limits between the different adsorption mechanisms are not clear. Before discussing the adsorption mechanism involved, the following points need to be taken into consideration:

- (1) Most metal cations are removed by:
  - (i) adsorption on solid phases via precipitation of their insoluble hydroxides;
  - (ii) ion exchange;
  - (iii) flocculation by adsorption of hydrolytic species; or
  - (iv) complexation with specific surface sites, provided the appropriate conditions prevailing (Apak et al., 1998; Zouboulis et al., 1995).
- (2) As a function of solution pH (Sheng et al., 2004; Bradl, 2004), lead species may exist as soluble Pb<sup>2+</sup> and hydroxo-species [Pb(OH)<sup>+</sup>, Pb(OH)<sub>3</sub><sup>-</sup> and Pb(OH)<sub>4</sub><sup>2-</sup>] in addition to the insoluble lead hydroxide Pb(OH)<sub>2</sub>.
- (3) The powdered marble waste (PMW) consists mainly of calcite (CaCO<sub>3</sub>) and to some extent of quartz (SiO<sub>2</sub>). When calcite (as sparingly soluble salt-type mineral) is

suspended with water, HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, CaHCO<sub>3</sub><sup>+</sup> and CaHO<sup>+</sup> are formed as surface-charged species and their presence is a function of solution pH. Moreover, OH<sup>-</sup>, H<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> are considered as potential determining ions in addition to Ca<sup>2+</sup> and CaCO<sub>3</sub>. Chemisorptions of water molecules on silica (as one of the minor constituents of marble wastes) surface induces a formation of surface OH groups with an amorphous character; the dissociation of these groups leads to an acidic or alkaline surface (positive or negative surface charge). These findings were confirmed practically by stirring the PMW sorbent with distilled water for 1 h after which the suspension pH increases from 6.7 to 9.3. This may be attributed to sorption of H<sup>+</sup> ions from the solution or desorption of OH<sup>-</sup> ions from sorbent surface which agree with the literature data that marble as a naturally occurring material has a negatively charged surface (Rosen, 1989).

Therefore, the proposed mechanism may occur as follows:

At pH < 5, the adsorption is less than 100% which may be due to the partial dissolution of PMW and to repulsion between Pb<sup>2+</sup> ions and positive surface charge, as determined from ZPC (pH<sub>ZPC</sub> = 6.2). The removal of the Pb<sup>2+</sup> ions may be attributed to a possible ion-exchange mechanism between Pb<sup>2+</sup> ions and calcium containing PMW in a similar manner to that reported (Mandjiny et al., 1995). This was confirmed by measuring the concentration of calcium ion in the solution before and after adsorption where its value was increased. Adsorbed lead ions generally occupy calcium sites within the calcite lattice (Chermiak, 1997). Also, adsorption may take place through precipitation of lead carbonate on PMW surface according to the following equations (Zhu, 2002):



In the pH range 6–9, where the maximal removal of Pb<sup>2+</sup> ions occurred, adsorption may be electrostatically in nature and take place between Pb(OH)<sup>+</sup>, the predominant species in this pH range, and the negatively charged surface of powdered marble waste and precipitation of lead carbonate on PMW surface. In alkaline medium, at pH > 9, the removal of Pb<sup>2+</sup> ions decreases, which may be attributed to the incapability of adsorption of the negative species Pb(OH)<sub>3</sub><sup>-</sup> and Pb(OH)<sub>4</sub><sup>2-</sup> onto the negative surface of PMW sorbent.

## 4. Conclusion

The powdered marble has been investigated as a cheap and effective inorganic sorbent for the removal of Pb<sup>2+</sup> ions from aqueous solutions. The experimental results revealed the following:

- (i) The adsorption occurred mainly at the surface of the solid marble waste and slightly by the internal pores.
- (ii) The adsorption data were well described by Freundlich and Langmuir models over the concentration range studied. It could occur through ion-exchange, adsorption of



hydrolytic species,  $\text{Pb}(\text{OH})^+$ , and precipitation of lead carbonate onto LS sorbent depending on the solution pH.

- (iii) The procedure was successfully applied for the removal of  $\text{Pb}^{2+}$  ions from aqueous solutions and natural water samples.
- (iv) Moreover, the lead ions were essentially held by PMW sorbent and would not leach out by acids owing to the solubility of the sorbent. Therefore, the metal-loaded solid waste could be solidified to an environmentally safe form thereby serving the double-fold aim of water treatment and solid waste disposal.

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