

Separation of Zn(II) by sorption onto powdered marble wastes

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Batch adsorption experiments were carried out to remove Zn(II) ions from aqueous solutions and water samples using powdered marble wastes (PMW) as an effective sorbent which is inexpensive, widespread, and considered as an environmental problem. The parameters such as solution pH, sorbent and Zn(II) concentrations, stirring times, foreign ions and temperature were investigated. The sorption of Zn(II) ions onto (PMW) is described by Langmuir model. Dubinin-Radushkevich (D-R) isotherm model was also applied to describe the nature of the adsorption of the metal. Thermodynamic parameters, viz. the Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also calculated. These parameters indicated that the adsorption process of Zn(II) ions on PMW was spontaneous and endothermic in nature. Under the optimum experimental conditions employed, the removal of ~100% of Zn(II) ions was attained. The procedure was successfully applied to remove Zn(II) ions from aqueous and different natural water samples. The adsorption mechanism is also suggested.

Keywords: Zinc(II) sorption, Langmuir, Dubinin-Radushkevich isotherm, Marble waste, Natural water

Rapid industrialization has led to increased disposal of heavy metals into the environment. The tremendous increase in the use of the heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment. The metals are special because of their persistency in the environment¹. At least 20 metals are classified as toxic, and half of these are emitted into the environment in quantities that pose risks to human health².

The ability of a water body to support aquatic life as well as its suitability for other uses, however, depends on many trace elements. Trace concentrations of zinc are important for the physiological functions of living tissue and regulate many biochemical processes. In humans, Zn(II) is found in over 20 metallo-enzymes, including several that are involved in nucleic acid metabolism³. However, just like other heavy metals, when zinc is discharged into natural waters at increased concentrations, can have severe toxicological effects on humans and aquatic ecosystems^{4,5}. Zn(II) ions being in the list of priority pollutants proposed by Environmental Protection Agency (EPA) give rise to serious poisoning cases. The main symptoms of zinc poisoning are dehydration, electrolyte imbalance, stomachache, nausea, dizziness and in coordination in muscles⁶. Instances of acute toxicity have occurred from ingestion of fruit juices that were stored in

galvanized (zinc plated) steel containers³. Hence, it is essential to remove zinc from industrial wastewaters before transport and cycling into the natural environment and threshold values have been set for this metal for waste water discharged into natural recipients and for drinking water. The maximum allowable Zn(II) ions concentration in drinking water was restricted to be not more than 3 mg.L⁻¹ by international regulations on water quality, ca. World Health Organization⁷ and European Commission Directive⁸.

A number of technologies have been developed in the last years to remove heavy metals from industrial wastewater. The most important technology includes coagulation/flocculation^{9,10}. Other conventional chemical methods include precipitation, ion-exchange, electrochemical processes and membrane technology. Adsorption receives considerable interest with the high efficiency in heavy metal removal. Although there are many adsorbents used in adsorption methods, active carbon is the most common one used in wastewater treatment all over the world¹¹. However, its high cost causes restrictions in use¹². For this reason, many studies have been carried out in order to find out effective and low cost organic and inorganic adsorbents. Different adsorbents are used in zinc removal such as chitosan¹³, eutrophic and oligotrophic marsh peat¹⁴, agricultural wastes like wheat shell¹⁵ and cacao shell¹⁶

clays, zeolites, red mud, fly ash and agricultural siliceous wastes, etc^{12,17}.

Powdered marble waste is considered as an appropriate adsorbent due to its negligible cost and high metal ion removal efficiency. The sorption capability of PMW comes from its ion exchange capacity¹⁸. 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 the present work was to study the possibility of utilizing powdered marble wastes (PMW) as sorbent for removing Zn(II) ions from aqueous solutions and natural waters. The different parameters influencing the adsorption of Zn(II) ions onto PMW were optimized and the results are presented in this paper.

Experimental Procedure

Samples and solutions

PMW samples used in this study were obtained, free of charge, from some private marble processing workshops located in Bilqas City (Egypt). The samples were sieved and particles with size 25-63 μm were used in the experiments. The samples contained 60% calcite, CaCO_3 , and 6% dolomite, MgCO_3 , (as found by chemical analysis), with the remainder being composed of common constituents such as quartz, feldspar, clays, pyrite and siderite¹⁹. The samples were dried for 2 h in large trays in an oven maintained at 125°C then cooled to room temperature, packed into stoppered bottles and stored in a desiccator for future use.

Functional groups of PMW were characterized through IR analysis. The observed peaks at about 710, 875, 1420, 1807 and 2520 cm^{-1} coincided with pure CaCO_3 ^{20,21}. The surface area and porosity of PMW was measured using Brunauer, Emmett, Teller (BET) method. PMW samples have 18.9 Å pore diameter, 31.2 Å pore size, 0.98 cc/g pore volume and its measured surface area was 21.8 m^2/g . Stirring or soaking of 1 g PMW in 100 mL distilled water ($\text{pH} = 6.9$) for 12 h or more increased the suspension pH to 9.3, confirming the negative charge of the PMW surface.

Zinc(II) stock solution was prepared by dissolving 7 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (BDH Ltd, Poole, England) in 250 mL doubly distilled water. The working solutions were prepared by appropriate

dilution of the stock solution with doubly distilled water. Xylenol orange (XO) indicator (1%) was freshly prepared daily before use. Aqueous solutions of HNO_3 and NaOH were used for pH adjustment. All other solutions were prepared from certified reagent grade chemicals.

Apparatus

A Buck Scientific Accusys 211 Atomic Absorption Spectrophotometer (AAS), provided with micro burettes of 5 and 10 mL, was used for the determination of zinc concentration at 213.9 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. Stirring of solutions was carried out with a magnetic stirrer Model VEHP, Sientifica, Italy.

Recommended method

Unless stated otherwise, all batch sorption experiments were done at room temperature ($\sim 25^\circ\text{C}$). Known volumes of zinc solutions were pipetted into quick-fit glass bottles containing 0.1 g of PMW to give concentrations ranging from 100 to 300 $\text{mg}\cdot\text{L}^{-1}$ in 50 mL aqueous solution. Since the pH of any resulting solution was ~ 7.0 , no further control was necessary as it was suitable for most adsorption experiments. The resulting solution was then stirred with a magnetic stirrer at 650 rpm and the samples were taken at fixed time periods (1, 2, 3, 5, 10, 15, 30, to 240 min) in order to study the kinetics of the adsorption process. Preliminary experiments showed that this time length was sufficient for complete adsorption of Zn(II) ions onto PMW. The samples were subsequently filtered off and the residual Zn(II) ions concentrations in the filtrate were analyzed using Atomic Absorption Spectrometry or EDTA titration for determining zinc using XO indicator (for high concentrations). The percentage adsorption of Zn(II) ions from the solution was calculated using the relationship:

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

where C_i corresponds to the initial concentration of Zn(II) ions and C_r is the residual concentration after stirring time. The metal uptake q (mg/g) was calculated as:

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

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

Results and Discussion

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 on the adsorption of Zn(II) ions (100 mg.L^{-1}) from aqueous solutions of pH 7 is depicted in Fig. 1. The data show that the adsorption efficiency increases as the amount of PMW increases and reaches a maximum value ($\sim 100\%$) at $\text{PMW} \geq 2000 \text{ mg.L}^{-1}$. 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, 2000 mg.L^{-1} PMW was selected for further experiments.

On contrast, varying Zn(II) ions concentrations shows that the efficiency decreases (Fig. 2). This may be explained in terms of relatively smaller number of active sites available at higher concentration of zinc.

Effect of pH

The pH seems to be the most important parameter for controlling the sorption process²². 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^{23,24}.

From the speciation diagram reported by Carrott *et al.*²⁵, using the reactions and equilibrium constants given by Baes and Messmer²⁶, it was concluded that at acidic $pH < 7$, the predominant ionic species are Zn^{2+} ions, whereas, zinc is present mainly as Zn^{2+} , Zn(OH)^+ and Zn(OH)_2 near pH 9. By increasing the pH more than 9, the negative species Zn(OH)_3^- and Zn(OH)_4^{2-} appear.

Adsorption of zinc on PMW was studied at varying pH values from 1.0 to 10.0 to optimize the metal removal and the data are shown in Fig. 3. It is apparent that the uptake is quite low at low pH values. However, with increasing the pH , a significant enhancement in adsorption is recorded reaching a maximum value ($\sim 100\%$), at $pH \geq 6$.

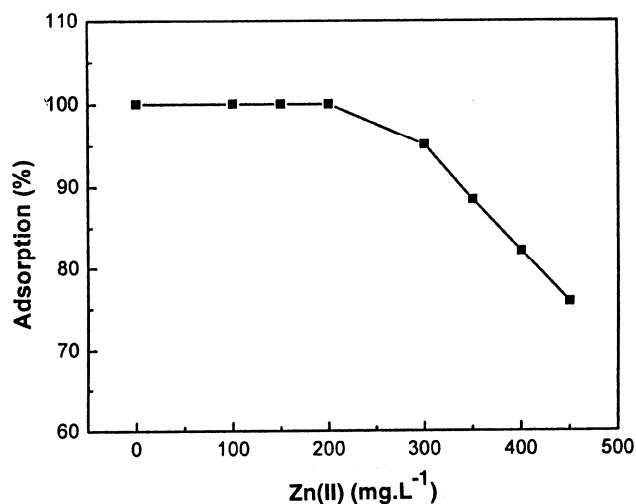


Fig. 2 — Adsorption of different concentrations of Zn(II) ions from aqueous solutions of pH 7 using 2000 mg.L^{-1} PMW.

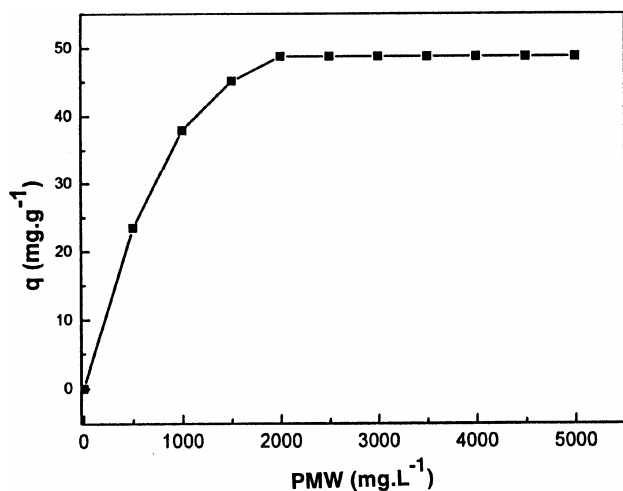


Fig. 1 — Effect of PMW concentration on the adsorption of Zn(II) ions (100 mg.L^{-1}) from aqueous solutions of pH 7.

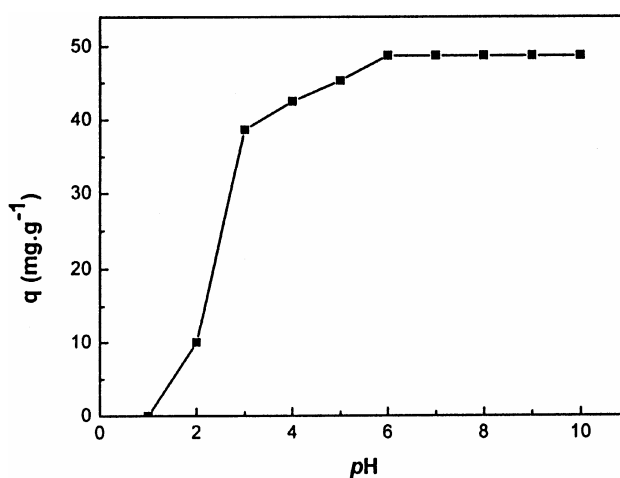


Fig. 3 — Adsorption (%) of Zn(II) ions (100 mg.L^{-1}) by PMW (2000 mg.L^{-1}) versus pH .

At pH values below 2.0, the removal of Zn^{2+} reaches zero because of almost solubility of the sorbent (consists mainly of $CaCO_3$ and $MgCO_3$) thereby hindering the sorption process. Between pH 3 and 5, the percentage removal increases sharply which may be attributed to a possible ion-exchange mechanism between Zn^{2+} ions and calcium containing PMW^{27,28}. This was confirmed by measuring the concentration of calcium ion in the solution before and after the adsorption where its value increased. At $pH \geq 6$, there is a possibility of zinc precipitation on the surface of the adsorbent as $ZnCO_3$ and/or $Zn(OH)_2$ forming successive layers on the sorbent surface. The decrease in the removal efficiency at high pH values more than 10 (data not included) may be attributed to the fact that the negative species $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ are not attracted to the negative surface of PMW, since the pH of its suspension was always increased from 6.9 to 9.3 after shaking the PMW for 1 h or more. Therefore, pH 7 was selected for all further studies.

Kinetics of adsorption process

Figure 4 shows the variation in the $Zn(II)$ ions uptake by PMW with stirring 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) similar trend in adsorption process was attained in all the three media. Moreover, the sorption of $Zn(II)$ ions by PMW is nearly the same at pH s 7 and 9 and higher than that at pH 3. This agrees with the data depicted in Fig. 3 and hence pH 7 was recommended for further experiments. (ii) The adsorption of $Zn(II)$ 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^{28,29}. However, with the passage of time, the rate of adsorption decreased owing to the decrease of diffusion of $Zn(II)$ ions through the pores^{28,30} and ultimately reached a constant value (equilibrium state). On the basis of the results, 4 h of stirring time was found suitable for maximum adsorption and was used in all subsequent measurements. (iii) The uptake capacities increased with increasing initial $Zn(II)$ ions concentrations which may be attributed to higher collision between $Zn(II)$ ions and sorbent. However, it was found that there is a decrease in adsorption percentage at higher initial $Zn(II)$ ions concentrations which may be due to rapid saturation of the metal binding sites of the sorbent²⁸.

When the data depicted in Fig. 4 were re-plotted against the square root of the stirring time, the obtained linear correlations (Fig. 5) verify the Morris-Weber equation³¹:

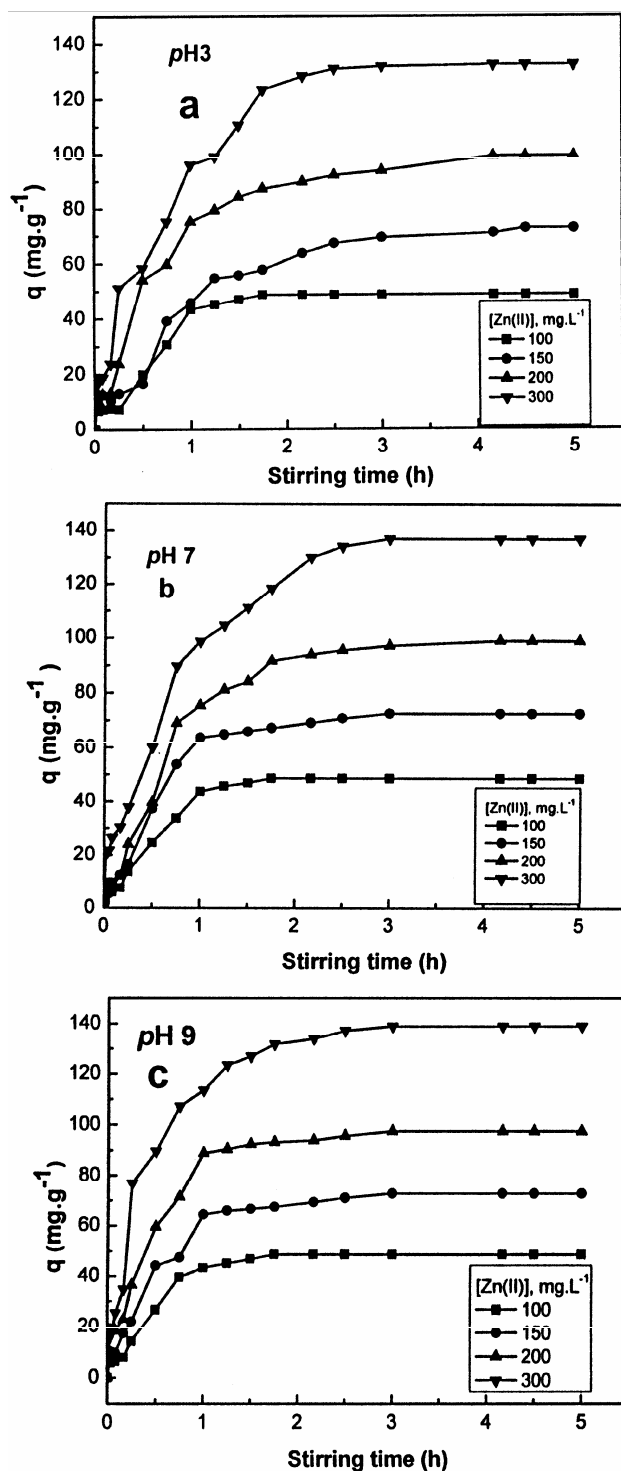


Fig. 4 — Influence of stirring time on the adsorption of various concentrations of $Zn(II)$ ions by PMW (2000 mg.L^{-1}) in acidic (pH 3), neutral (pH 7) and alkaline (pH 9) media.

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

where q is the amount of Zn(II) ions adsorbed (mg.g^{-1}). This indicates that an intrapore diffusion mechanism was involved in adsorption of Zn(II) ions by PMW. Figure 5 shows two distinct regions: an initial linear portion which may be due to the boundary layer effect³² and a second portion which may be due to the intra-particle diffusion effect³³. 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 Zn(II) ions by PMW^{29,31}. These data agree with those of Juang *et al.*³⁴ 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 value of the rate constant K_d was evaluated as $42.09 \text{ mg/g min}^{-1}$ which gives indication about the mobility of the Zn(II) ions towards the PMW surface.

The kinetic data depicted in Fig. 4 for the adsorption of Zn(II) ions by PMW was examined by using Bangham equation²⁸

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

where q , m , V , and C_i have the usual meaning, t is the time (h), K_o is the proportionality constant and α is Bangham equation constant. Plot of $\log \log [C_i / (C_i - qm)]$ versus $\log t$ gives a straight line (Fig. 6). These results show that the diffusion of Zn(II) ions into PMW pores played a role in the adsorption process and were similar to those described elsewhere^{30,35}. The value of K_o and α constants deduced were 2.82 and 0.653, respectively.

Again the kinetic data obtained in Fig. 4 for Zn(II) ions adsorption by PMW were tested by Lagergren equation, as cited by Gupta and Shukla³⁶

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

where q_e is the amount of Zn(II) ions adsorbed at equilibrium (mg.g^{-1}), k_{ads} is the first order rate constant for Zn(II) ions adsorption onto PMW ($\text{mg.g}^{-1}.\text{h}^{-1}$), while q and t have usual meaning. The data obtained from the adsorption of 100 mg.L^{-1} Zn(II) ions onto 2000 mg.L^{-1} of PMW at pH 7, stirred at 650 rpm showed the appropriateness of the above equation and consequently the first-order nature of the process involved. The value of k_{ads} was calculated to be 0.038 min^{-1} .

Adsorption isotherms

Adsorption isotherms can be generated based on numerous theoretical models where Langmuir models are the most commonly used. The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface of adsorbent by monolayer adsorption without any interaction. The linear form of the Langmuir equation applied to the Zn(II) ions adsorption data in Fig. 4 was:

$$1/q_e = 1/k_L + (1/k_L b).1/C_e \quad \dots(6)$$

where q_e is the amount of Zn(II) ions adsorbed at equilibrium (mg/g), C_e is the final equilibrium concentration (mg.L^{-1}), k_L (mg.g^{-1}) is the monolayer

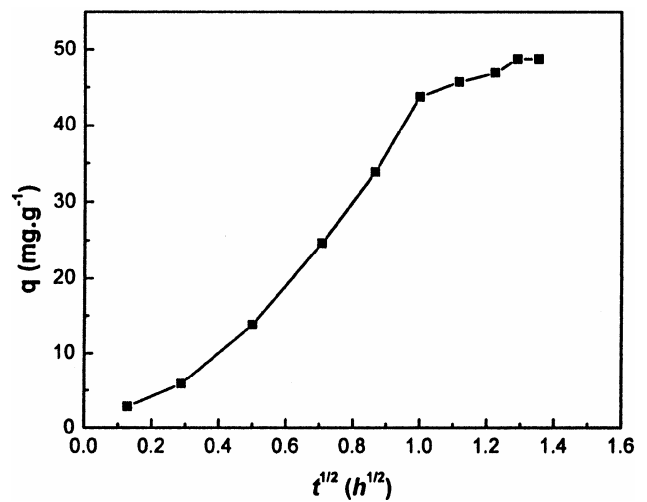


Fig. 5 — Plot of the amount of Zn(II) ions adsorbed onto PMW (2000 mg.L^{-1}) versus square root of time at pH 7.

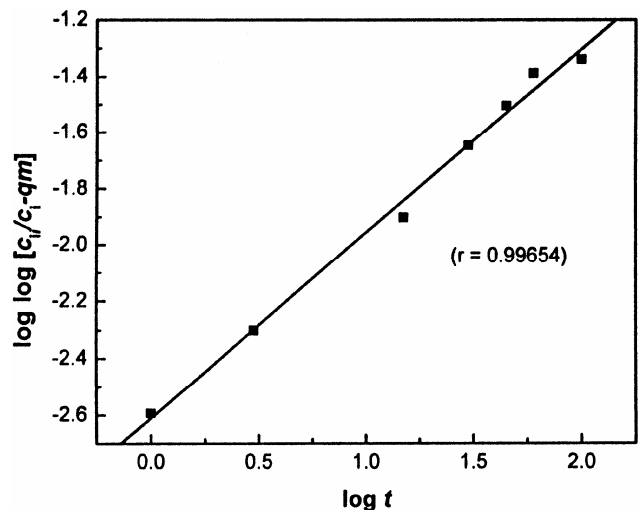


Fig. 6 — Plot of $\log \log [C_i / (C_i - qm)]$ versus $\log t$ for the adsorption of Zn(II) ions (100 mg.L^{-1}) by PMW(2000 mg.L^{-1}) at pH 7.

adsorption capacity and b ($\text{mL}\cdot\text{mg}^{-1}$) is the Langmuir constant. Figure 7 shows that the plot of $1/q_e$ versus $1/C_e$ gave a straight line suggesting the applicability of the Langmuir model. The values of k_L , b and the correlation coefficient (r) were $175.13 \text{ mg}\cdot\text{g}^{-1}$, $0.518 \text{ mL}\cdot\text{mg}^{-1}$ and 0.994 , respectively.

The sorption data was modeled by D-R isotherm (Fig. 8) to determine the adsorption type (physical or chemical). The linear form of this model^{37,38} is expressed by:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad \dots(7)$$

where q_e is the amount of the metal adsorbed per unit dosage of the PMW ($\text{mol}\cdot\text{L}^{-1}$), q_m the monolayer capacity ($\text{mol}\cdot\text{g}^{-1}$), and β is the activity coefficient related to mean sorption energy ($\text{mol}^2\cdot\text{J}^{-2}$) and ε is the Polanyi potential described as:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad \dots(8)$$

The mean sorption energy, E ($\text{kJ}\cdot\text{mol}^{-1}$), can be calculated by Eq. (9)^{37,38}

$$E = (-2\beta)^{-1/2} \quad \dots(9)$$

As seen in Fig. 8, the slopes of the D-R plots give the value of β which was evaluated as -1.05×10^{-9} . The mean sorption energy (E) was found to be $21.85 \text{ kJ}\cdot\text{mol}^{-1}$. The E value ranges from 1.0 to $8.0 \text{ kJ}\cdot\text{mol}^{-1}$ is for physical adsorption and from 9.0 to 16.0 or more $\text{kJ}\cdot\text{mol}^{-1}$ for chemical adsorption^{38,39}. Therefore, the E value calculated for the adsorption of Zn(II) onto PMW showed that the sorption may be chemical in nature.

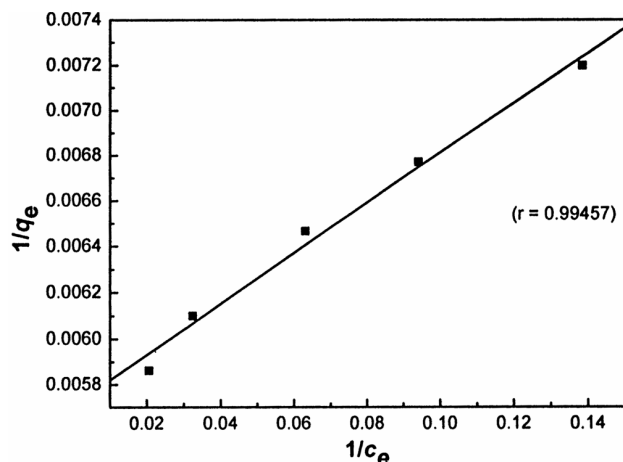


Fig. 7 — Langmuir plot for Zn(II) ions adsorption onto PMW ($2000 \text{ mg}\cdot\text{L}^{-1}$).

Effect of temperature and thermodynamic parameters

The temperature has two major effects on the sorption process. Increase in the temperature is known to increase the rate of diffusion of the sorbate while changing the temperature will change the equilibrium capacity of the sorbent for a particular sorbate. In this study, experiments were conducted on the adsorption of $100 \text{ mg}\cdot\text{L}^{-1}$ Zn(II) ions onto $2000 \text{ mg}\cdot\text{L}^{-1}$ of PMW at 298, 308 and 318 K to investigate the effect of temperature on the sorption dynamics at different stirring times. The results depicted in Fig. 9 show that the sorption increases as the temperature increases confirming that the process is endothermic in nature. Such results may either be attributed to the creation of some new active sites on the sorbent or to the acceleration of some originally slow adsorption steps. Moreover, the enhancement of mobility of Zn(II) ions from the bulk of solution towards the adsorbent surface should also be taken into consideration. This agrees well with the literature data^{29,40}. However, there was a decrease in the equilibration time to reach to a 100% for Zn(II) ions adsorption.

Such results could suggest that the adsorption of Zn(II) ions involves chemical bond formation and ion exchange²⁹. Accordingly, chelate formation may occur between Zn(II) ions and oxygen atoms on the marble surface together with ion exchange between Zn(II) 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 Zn(II) ions.

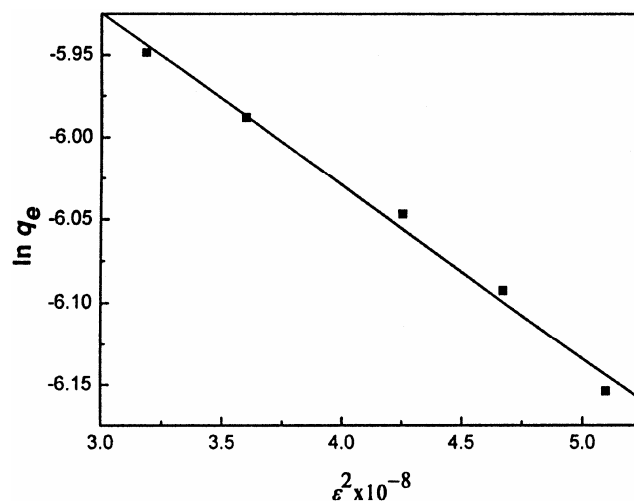


Fig. 8 — D-R isotherm for Zn(II) ions adsorption onto PMW.

In order to investigate the thermodynamic parameters for the adsorption of Zn(II) by PMW, the distribution coefficient K_d ($L \cdot g^{-1}$) was calculated at the temperatures 298, 308, 318 and 328 K according to the following equation^{38,39,41}

$$K_d = q_e / C_e \quad \dots (10)$$

The K_d values calculated for the sorption of Zn(II) ions by PMW are 9.62, 13.18, 15.96 and 17.15 $L \cdot g^{-1}$. These results show that the K_d increased as the temperature increased from 298 to 328 K and revealing that the sorption of Zn(II) ions by PMW may be endothermic in nature.

The enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the slope and intercept of the plot of $\ln K_d$ against $1/T$, respectively as depicted in Fig. 10 and according to the following equation^{38,39,41}

$$\ln K_d = \Delta S^\circ / R - \Delta H^\circ / RT \quad \dots (11)$$

The Gibbs free energy change (ΔG°) was calculated by:

$$\Delta G^\circ = -RT \ln K_d \quad \dots (12)$$

where R is the universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and T is the temperature (K).

The calculated enthalpy change ΔH° was $15.76 \text{ kJ} \cdot \text{mol}^{-1}$ for the sorption of Zn(II) ions by PMW. The positive value of ΔH° confirmed that the sorption process was endothermic. The entropy change (ΔS°) was found to be $72.15 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. According to Sari *et al.*³⁸, this result showed that Zn(II) 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 (ΔG°) was between -5.60 , -6.60 , -7.32 , and $-7.75 \text{ kJ} \cdot \text{mol}^{-1}$ for the adsorption of Zn(II) ions at the temperatures 298, 308, 318 and 328 K respectively. The negative ΔG° values indicated that the adsorption of Zn(II) ions on PMW was spontaneous thermodynamically.

Comparison of zinc uptake capacity using inorganic sorbents

Comparison of zinc uptake capacity by powdered marble waste (present investigation) with other inorganic sorbents is summarized in (Table 1). The

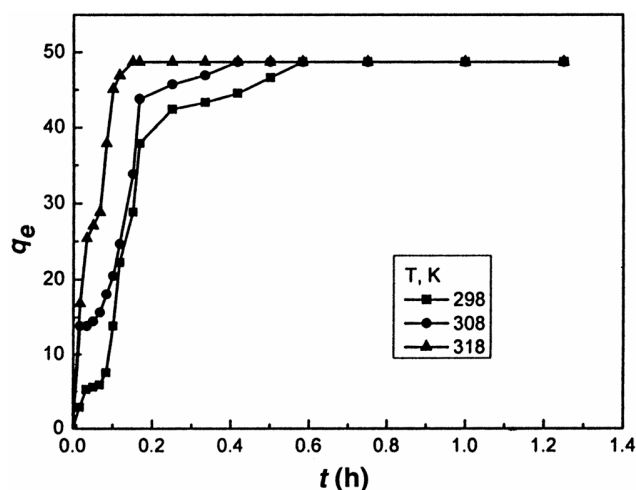


Fig. 9 — Effect of temperature on the sorption (%) of Zn(II) ions onto PMW at different stirring times.

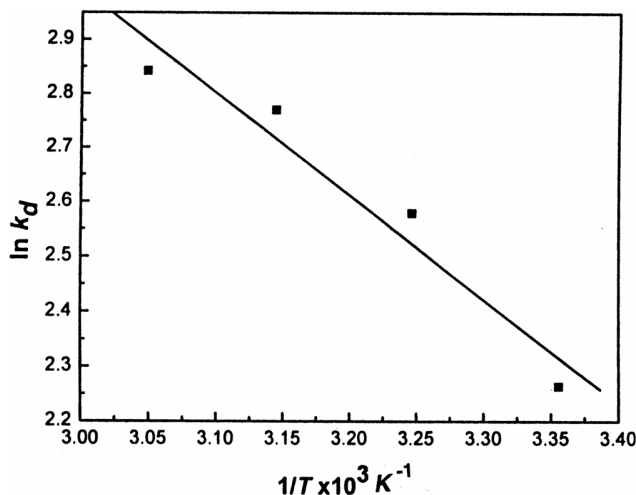


Fig. 10 — Thermodynamic distribution coefficient (K_d) calculated for the adsorption of Zn(II) ions on PMW as a function of temperature.

zinc uptake by PMW was relatively higher than those obtained by other sorbents. Thus, PMW may have a potential in treating wastewater, which contained zinc from industrial effluents.

Effect of various ions

Under the optimized conditions determined in this investigation, the percentage removal of $100 \text{ mg} \cdot \text{L}^{-1}$ Zn(II) ions from a solution of pH 7 containing $2000 \text{ mg} \cdot \text{L}^{-1}$ PMW was studied in the presence of high concentrations of various cations and anions, usually present in some water samples. All the cations were used as their chlorides whereas the anions were used as the corresponding sodium or potassium salts. The tolerable amounts of each ion, giving an error of

$\pm 2\%$ in the removal efficiency of Zn(II) ions, are listed in Table 2. Inspection of the data indicates that the removal of Zn(II) ions is quantitative in all cases. However, it should be noted that higher concentrations of Cu(II), Cd(II), Hg(II) and or Zn(II) ions could have deterrent effect on the Zn(II) removal process. This may be due to a competition between these cations and Zn(II) ions for adsorption on the active sites of PMW. This problem could be overcome by increasing the amount of PMW. Moreover, higher concentrations of some anions have no adverse effect on the removal of Zn(II) ions instead they may accelerate the process. This may be attributed to the precipitation of zinc with most of the investigated anions on the surface of marble.

Application

To investigate the applicability of the recommended procedure, experiments were performed to recover 100 mg.L^{-1} of Zn(II) ions added to aqueous and some natural water samples. The adsorption experiments were carried out using 50 mL clear, filtered, uncontaminated sample solutions with their natural pH values. The results listed in Table 3 show that the recovery was satisfactory. However, the lower values of adsorption with some samples were enhanced to reach about 100% by increasing the PMW dose.

Adsorption mechanism

The adsorption from solution by solids is of great practical importance but only in the last three decades a fundamental understanding has been developed. However, sharp limits between the different adsorption mechanisms are not clear. Before discussing the possible adsorption mechanisms involved, the following points need to be taken into consideration:

(a) Most metal cations are removed by: (i) Adsorption on solid phases via precipitation of their insoluble hydroxides; (ii) Flocculation by adsorption of hydrolytic products; (iii) Ion exchange and (iv) Complexation with specific surface sites, provided the appropriate conditions prevail^{35,52}.

(b) As a function of solution pH^{26} , zinc species may exist as soluble Zn^{2+} and hydroxo-species $[Zn(OH)^+]$, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ in addition to the insoluble zinc hydroxide $Zn(OH)_2$.

(c) The powdered marble waste (PMW) consists mainly of calcite ($CaCO_3$) and to some extent of quartz (SiO_2). When calcite as a sparingly soluble salt-

Table 1 — Comparison of zinc uptake capacity by various inorganic sorbents

Sorbent	Sorption capacity (mg/g)	Reference
Marble waste (PMW)	138.90	Present study
Clinoptilolite	0.50	42
Clinoptilolite	2.70	43
Chabazite	5.50	43
Chabazite-phillipsite	0.04	44
Montmorillonite	4.98	45
Bentonite	52.91	46
Ca-bentonite	5.75	47
Na-bentonite	23.10	47
Red mud	12.59	48
Blast furnace slag	17.65	49
Natural zeolite	13.40	50
Bigadic zeolite	2.11	51
Gordes zeolite	4.41	51

Table 2 — Effect of some selected foreign ions on the percentage removal, Re (%), of 100 mg.L^{-1} Zn(II) ions from aqueous solutions using 2000 mg.L^{-1} of PMW at pH 7

Foreign ions added	Tolerance limit mg.L^{-1}	Zn(II) found mg.L^{-1}	Re, %
Ca^{2+}	25	96.3	96.3
Na^+	10000	100.0	100.0
NH_4^+	396	97.5	97.5
K^+	10000	100.0	100.0
Mg^{2+}	30	96.3	96.3
Hg^{2+}	45	97.5	97.5
Mn^{2+}	25	96.3	96.3
Cu^{2+}	5	96.3	96.3
Al^{3+}	20	96.3	96.3
Co^{2+}	20	96.3	96.3
Fe^{3+}	15	96.3	96.3
$S_2O_3^{2-}$	34975	98.7	98.7
CO_3^{2-}	50	100.0	100.0
SO_4^{2-}	961	100.0	100.0
CH_3COO^-	9971	98.7	98.7
$HCOO^-$	4995	97.5	97.5
$C_2O_4^{2-}$	59	96.3	96.3
Cl^-	15439	100.0	100.0

Table 3 — Recovery of Zn(II) ions added to some water samples using 2000 mg.L^{-1} of PMW Sorbent at pH 7

Sample (location)	Added Zn(II) ions (mg.L^{-1})	Found Zn(II) ions (mg.L^{-1})	Re, %
Distilled water (Double distilled)	100	99.85	99.85
Tap water (laboratory)	100	92.4	92.4
Nile water (Mansoura city)	100	89	89.0
Sea water (Gamasah)	100	97.8	97.8
Sea water (Ras elbar)	100	98.1	98.1
Underground water (Mansoura)	100	92.5	92.5

type mineral dissolves in water, HCO_3^- , Ca^{2+} , CaHCO_3^+ and CaHO^+ exist as surface charged species, their presence being a function of solution pH ^{28,53}. Moreover OH^- , H^+ and HCO_3^- are considered as potential determining ions in addition to Ca^{2+} and CaCO_3 . Chemisorptions of water molecules on silica (as one of the minor constituents of marble wastes) surface induces 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 by stirring or soaking PMW in distilled water for about 12 h after which the suspension pH increases. This may be attributed to adsorption of H^+ ions from solution or desorption of OH^- ions from the sorbent surface which agree well with the literature data that most natural surfaces are negatively charged⁵³.

Therefore, the proposed mechanism may occur as follows:

At $\text{pH} < 6$, the removal of Zn^{2+} ions may be attributed to a possible ion exchange mechanism between Zn^{2+} and calcium containing PMW in manner similar to that reported earlier²⁷. This was confirmed by determining the concentration of calcium ions in the solution before and after adsorption where its value was found to increase. Adsorbed Zn(II) ions generally occupy calcium sites within the calcite lattice²⁷.

In the pH range 6-10, where the maximal removal of Zn(II) ions occurred, adsorption may be electrostatic in nature and takes place between $\text{Zn}(\text{OH})^+$, the predominate species in this pH range, and negatively charged surface of PMW. Adsorption may also take place through precipitation of the insoluble zinc hydroxide $\text{Zn}(\text{OH})_2$ and/or zinc carbonate on PMW surface according to the following equations⁵⁴:



In alkaline medium, at pH value (>10) the removal of zinc decreased (data not included) which may be attributed to the fact that the negative species of zinc, $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$ are not able to associate with the negative surface of PMW.

Conclusions

The powdered marble waste has been investigated as a cheap and effective inorganic sorbent for the

removal of Zn(II) ions from aqueous solutions. The experimental results revealed the following:

- (i) The removal of Zn (II) could occur through ion exchange, adsorption of hydrolytic species, $\text{Zn}(\text{OH})^+$, and the precipitation of zinc hydroxide and carbonate onto PMW sorbent depending on solution pH .
- (ii) The procedure is successfully applied for the removal of Zn(II) ions from aqueous and natural water samples.
- (iii) The adsorption of Zn(II) ions onto PMW was chemical in nature.
- (iv) The calculated thermodynamic parameters i.e. the change in Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) confirm that the adsorption is spontaneous and endothermic in nature.

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