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Kinetic Investigation of the Removal of Aluminum from Water Samples by Adsorption Onto Powdered Marble Wastes

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Abstract: Batch adsorption experiments were conducted in the laboratory, aiming to the removal of aluminum from aqueous solutions onto powdered marble wastes (PMW) as an effective inorganic sorbent, which is inexpensive, widespread, and may represent an environmental problem. The main parameters (i.e., initial solution pH, sorbent and Al^{3+} ions concentrations, stirring times and temperature) influencing the sorption process in addition to the effect of some foreign ions was examined. The results obtained revealed that the sorption of Al^{3+} ions onto PMW is endothermic in nature and followed first-order kinetics. The adsorption data were well described by the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption models over the concentration range studied. Under the optimum experimental conditions employed, the removal of ca. 100% of Al^{3+}ions was attained. The procedure was successfully applied to the removal of aluminum from aqueous and different natural water samples with an RSD (%), does not exceed 2.12%. Moreover, the adsorption mechanism is suggested.

Keywords: Aluminum, sorption, powdered marble wastes, natural waters

INTRODUCTION

Rapid industrialization has led to an increased disposal of toxic metals and radio-nuclides into the environment. The concentrations of toxic metals in wastewater are normally much higher than standards set by environmental

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agencies and therefore might endanger public health and the ecosystem if they are discharged without proper treatment (1–3).

Aluminum is an abundant metal in the earth's crust; in the industrialized world the metal is second only to iron in its usage, and its compounds can justifiably be said to touch our lives daily (4). Because aluminum salts are still used as flocculating agents in potable water treatment units (5), there is a strong need for aluminum monitoring in treated and raw waters (6). It is now well known that this metal is harmful to several organisms, such as fish (7, 8), zoo-plankton (9, 10), algae (11), and plants (12). Moreover, there are potential health risks associated with the intake of dissolved aluminum which play an active role in the development and advancement of senile dementia of Alzheimer type (13–15), renal insufficiency, pulmonary fibrosis, microcytic anemia, and disturbances of sleeping (16). Owing to these potential risks, European Community legislation on the quality of water for human consumption sets a MAC (maximum admissible concentration) level of $200\,\mu g \cdot L^{-1}$ and guideline level, around which Member States should set their quality standards, of $50\,\mu g \cdot L^{-1}$ (17). Therefore, the removal of this metal from natural and wastewater is a vital process.

Different physicochemical methods used for the removal of metal ions from wastewater include precipitation, coagulation, reduction, ion exchange, membrane processes (such as ultrafiltration, electrodialysis, and reverse osmosis) and adsorption (18). Of these, adsorption onto activated carbon has proved to be a very effective technique in this concern owing to its high efficiency and removal capacity (19–22). However, the high capital and regeneration costs of activated carbon limit its use in adsorption. Therefore, a search for a low-cost and easily available adsorbent has led to the investigation of materials of agricultural and biological origin, along with industrial by-products, as potential metal sorbents.

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 PMW (which is naturally occurring or readily available and cheap) as a sorbent for removing aluminum ions from aqueous solutions and natural waters. The different parameters influencing the adsorption of aluminum ions onto powdered marble wastes were optimized and the results are presented in this paper.

EXPERIMENTAL

Samples

The PMW samples used in this study were obtained, free of charge, from the dust of some private marble processing workshops located in Mansoura City.

The samples were sieved and those with a mean size of ca. 12 μm were used in the experiments. Chemical analysis showed that the samples contained 60% calcite ($CaCO_3$) and 6% dolomite ($MgCO_3$), with the remainder being composed of common constituents such as quartz, feldspar, clays, pyrite, and siderite (23). The samples were dried for 2 h in large trays in an oven maintained at 125°C, allowed to cool to room temperature, and then packed into stoppered bottles and stored in a desiccator for future use.

Reagents

All the solutions were prepared from certified reagent grade chemicals. Aluminum stock solution (1 mg/mL) was prepared from $(AlK(SO_4)_2) \cdot 12H_2O$ (BDH Ltd, Poole, England) by dissolving 17.59 g in doubly distilled water containing 5 mL of concentrated H_2SO_4, and diluting to 1 L. Further dilutions were prepared daily as required. Chrome Azurol S (CAS) and 1% ascorbic acid were freshly prepared. Aqueous solutions of HCl and NaOH were used for pH adjustments.

Apparatus

Spectrophotometric measurements were carried out using a Unicam UV2-100 UV/Visible Spectrophotometer v3.32 with 1 cm glass cells. Sometimes the data were recorded using a Griffin Model 40 Colorimeter. The infrared analyses were undertaken via a Mattson 5000 FT-IR spectrophotometer using the KBr disc method. The stirring of solutions was performed with a magnetic stirrer Model VEHP, Sientifica, Italy. The pH was measured using Jeanway 3310 pH meter.

Procedure

Unless stated otherwise, all batch sorption experiments were conducted at room temperature (ca. 25°C). Known volumes of aluminum solutions with concentrations ranging from 1.35 to 11.0 mg/l were pipetted into quick-fit glass bottles containing 0.1 g of PMW sorbent in 100 mL aqueous solution. Since the pH of any of the resulting solutions was ca. 7.0, no further control was necessary since it was suitable for most adsorption experiments. The resulting solutions were then stirred with a magnetic stirrer at 200 rpm and the samples were taken at fixed time periods (1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, . . . , and 90 min) in order to study the kinetics of the adsorption process. In other studies, equilibrium was attained after stirring for known time (ca. 25 min). Preliminary experiments showed that this time length was sufficient for adsorption of Al(III) onto PMW. The samples were subsequently filtered and the residual Al^{3+} ion content in the filtrate was analyzed using CAS at 545 nm.

The percentage adsorption of Al^{3+} ions from the solution was calculated from the relationship

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

where C_i corresponds to the initial concentration of Al^{3+} ions and C_r is the residual concentration after equilibration. The metal uptake q (mg/g) was calculated as

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

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

To asses the applicability of the procedure, another series of experiments was conducted on 1 L suspensions of clear and prefiltered natural water samples with an initial pH adjusted to 7. These suspensions were placed in a 2 L glass beaker containing 1.575 or 2.985 mg Al^{3+} ions and $100\,\text{mg} \cdot L^{-1}$ of PMW at 25°**C** and stirred magnetically for 10 min at 200 rpm.

RESULTS AND DISCUSSION

Kinetics of the Adsorption Process

Figure 1 shows the variation in the percentage adsorption (removal) of aluminum ions onto PMW sorbent with stirring time, at various initial metal ion concentrations. The data depicted in this figure indicate that the adsorption of aluminum ions was quite rapid in the first stage, which may suggest that

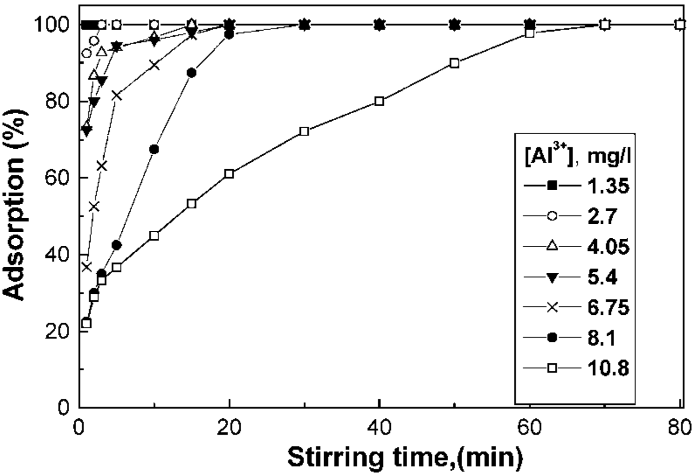

Figure 1. Influence of stirring time on the adsorption of various concentrations of Al^{3+} ions by PMW ($100\,\text{mg} \cdot L^{-1}$) at pH 7.

adsorption occurred mainly at the surface of the solid waste and to some extent by the internal pores (24, 25). However, with the passage of time, the rate of adsorption decreased and ultimately reached a constant value (equilibrium time). The slow adsorption may be due to the diffusion of aluminum ions into the pores of solid waste (25, 26). The time necessary to reach such adsorption equilibrium was found to be 5 min for initial concentrations of 1 and 3 mg $\cdot$ L^{-1} Al^{3+} ions, 25 min for those of 4 and 8 mg $\cdot$ L^{-1} Al^{3+} ions and 70 min for those having more than 10 mg $\cdot$ L^{-1} of aluminum ions. Hence, to ensure that adsorption had reached equilibrium in all cases, a stirring time of 70 min was chosen for all samples studied. The results also indicate that the percentage removal of metal ion from the solution decreases with increasing initial metal ion concentration. This can be explained by a decrease in the number of adsorption sites having an affinity toward Al^{3+} ions.

An interesting series of experiments was carried out to evaluate the effect of soaking time (i.e., without stirring) on the removal rate of 2.7, 5.4, 6.75, and 8.1 mg $\cdot$ L^{-1} of Al^{3+} ions using 100 mg $\cdot$ L^{-1} of PMW sorbent. The results obtained revealed that a maximum removal rate of Al^{3+} ions (ca. 100%) was attained after soaking for $\geq$ 60 min. These results may be useful from economic viewpoints of industrial wastewater treatment.

When the results depicted in Fig. 1 were re-plotted against the square root of the stirring time, linear correlations were obtained (Fig. 2) which may verify the Morris-Weber equation (27):

$$X = K_d(t)^{1/2} \tag{3}$$

where X is the amount of Al^{3+} ions adsorbed (g/g). This indicates that an intra-pore diffusion mechanism was involved in adsorption of Al^{3+} ions by

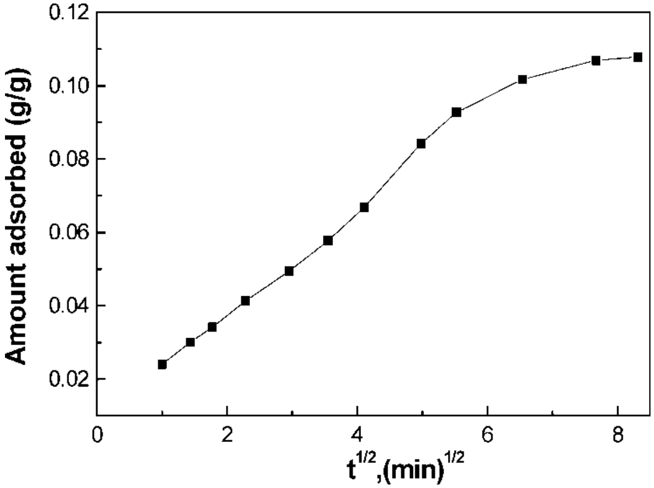

Figure 2. Plot of the amount of Al^{3+} ions adsorbed onto PMW (100 mg $\cdot$ L^{-1}) vs. square root of time at pH 7.

PMW (Fig. 1). Figure 2 shows that two distinct regions were observed: an initial linear portion which is due to the boundary layer diffusion effect (28) and a second portion which is due to the intraparticle diffusion effect (29). The value of the rate constant for intra-pore diffusion K_d was evaluated as 1.03×10^{-2} (g/g min^{-1}).

Again the kinetic data (Fig. 1) of the adsorption of Al^{3+} ions by PMW was checked by the Bangham equation (30):

$$\text{Loglog}[C_o/(C_o - XW)] = \log(K_oW/2.303V) + \alpha \log t \qquad (4)$$

where X and V have been defined above, C_o is the initial concentration of Al^{3+} ions (μg/mL), W is the amount of PMW (g), t is the time (min), α is the Bangham equation constant (its value usually < 1) and K_o is a proportionality constant. Plot of log log $[C_o/(C_o - XW)]$ vs. log t gives a straight line (Fig. 3). These results show that the diffusion of Al^{3+} ions into the pores of PMW played an important role in the adsorption process. These results were similar to those described elsewhere (26, 31). The values of α and K_o deduced were 0.355 and 0.22, respectively.

The kinetic data obtained in Fig. 1 for Al^{3+} ion adsorption onto PMW were tested by lagergren equation, as cited by Gupta and Shukla (32):

$$\text{Log}(X_e - X) - \log X_e = -K_{ads}t/2.303 \qquad (5)$$

where X_e is the amount of Al^{3+} ions adsorbed at equilibrium (g/g), $K_{ads.}$ is the first-order rate constant for Al^{3+} ions adsorption onto PMW (min^{-1}), while X and t have been defined previously. The linear plots of log $(X_e - X)$ vs. t obtained (Fig. 4) show the appropriateness of the above equation and

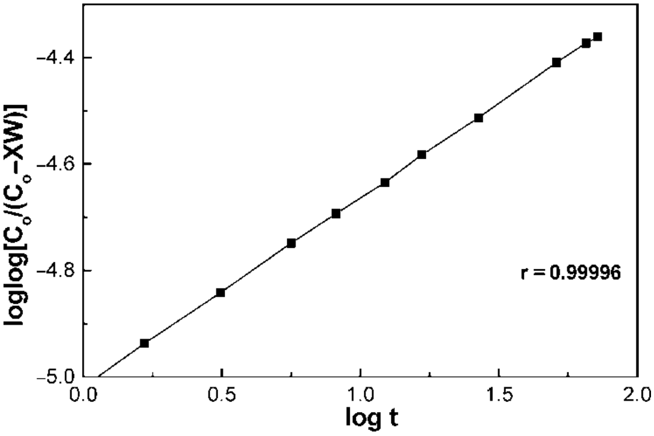

Figure 3. Plot of log log$[C_o/(C_o - XW)]$ vs. log t for the adsorption of Al^{3+} ions (2.7 mg · L^{-1}) by PMW (100 mg · L^{-1}) at pH 7.

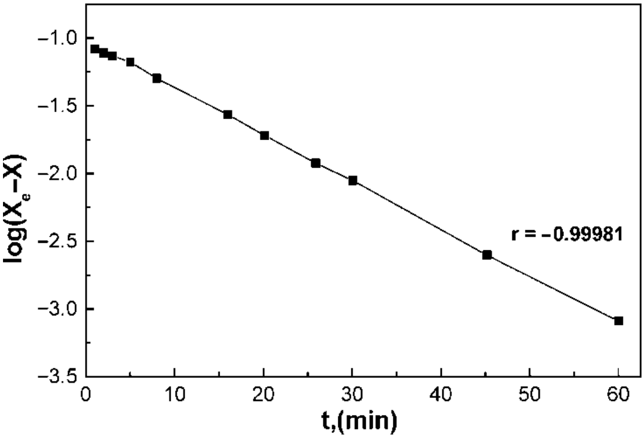

Figure 4. Plot of log ($X_e - X$) vs. stirring time for Al^{3+} ion adsorption onto PMW.

consequently the first-order nature of the process involved. The value calculated of $K_{ads.}$ was 0.0795 min^{-1}.

Effect of Initial pH Value

The influence of the variation of initial suspension pH, which affects significantly the Al^{3+} ions adsorption by PMW, was studied. The sorption of trivalent aluminum by PMW is also influenced by the surface properties of the sorbent and aluminum species present in aqueous solution.

In order to find the optimal pH value for the sorption process, the removal efficiency of Al^{3+} ions in the pH range 3–10 was investigated and the data are depicted in Fig. 5. It should be noted that the removal of Al^{3+} ions was diminished at pH < 3 which may be attributed to the solubility of PMW sorbent used (consists mainly of $CaCO_3$ and $MgCO_3$), thereby hindering the adsorption of Al^{3+} species. Moreover, at pH values > 4, the removal efficiency begins to increase, reaching a maximum value (ca. 100%) over the pH range 5–9 followed by a decrease.

The low removal of Al^{3+} ions at pH values < 5 may be attributed to a possible ion–exchange mechanism between aluminum and the calcium containing PMW in a similar manner to that reported (33) and/or adsorption of the hydrolytic species of Al^{3+} ions such as $Al(OH),^{2+}$ $Al(OH)_2^+$, and polynuclear complexes (7), $Al_n(OH)_m^{(3n-m)+}$. The ion-exchange mechanism was confirmed experimentally where the concentration of Ca^{2+} ions increases in the solution after equilibration. Moreover, IR analysis of PMW sorbent indicated the appearance of a band at 1449–1492 cm^{-1} assigned to carbonate (34), which is shifted to a sharp absorption band at 1425 cm^{-1} upon addition of Al^{3+} ions confirming the formation of aluminum carbonate.

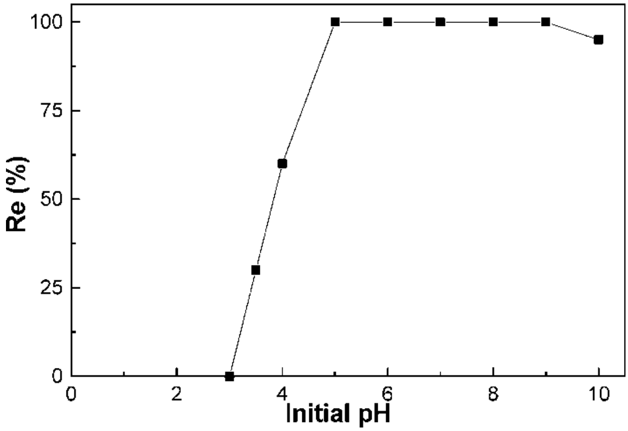

Figure 5. Removal of Al^{3+} ions ($2.7\,mg\cdot L^{-1}$) by PMW ($100\,mg\cdot L^{-1}$) versus pH.

The enhanced removal of metal ions as the solution pH is increased (more than 5) can be attributed to adsorption of hydrolysis products (35–37) and/or surface precipitation of the metal as colloidal insoluble hydroxides, $Al(OH)_3$ (s), forming successive layers on the sorbent surface (38). The precipitation of aluminum hydroxide was also checked by IR analysis of the system Al-PMW, where a broad absorption band appeared at $3426\,cm^{-1}$, which is assigned to the hydroxide of $Al(OH)_3$ (34).

The decrease in the removal rate at high pH values > 9 may be attributed to the fact that the negative species of aluminum, $Al(OH)_4^-$, formed in alkaline pH values (7) are not capable of combination with the negative surface of PMW, since the pH of its suspension was always increased after stirring the PMW powder for some time when the system was not buffered. The initial pH values were taken only into consideration (not final pH values), since they remained constant at the recommended stirring time (less than 25 min). Therefore, pH 7 was recommended throughout all other experiments.

Effect of the Amount of Adsorbent

An extensive series of experiments was conducted to study the effect of the amount of PMW as the adsorbent at different stirring times on the adsorption of Al^{3+} ions from aqueous solutions. The results depicted in Fig. 6, show that the adsorption efficiency increases as the amount of PMW increases and reaches a maximum value (ca. 100%) at $\geq 100\,mg\cdot L^{-1}$ of PMW. Moreover, there is a decrease in stirring time with the increase in the sorbent dose. This may be attributed to an increase in the number of binding sites on the adsorbent available to the metal ions. Therefore, $100\,mg\cdot L^{-1}$ of PMW were fixed for further experiments.

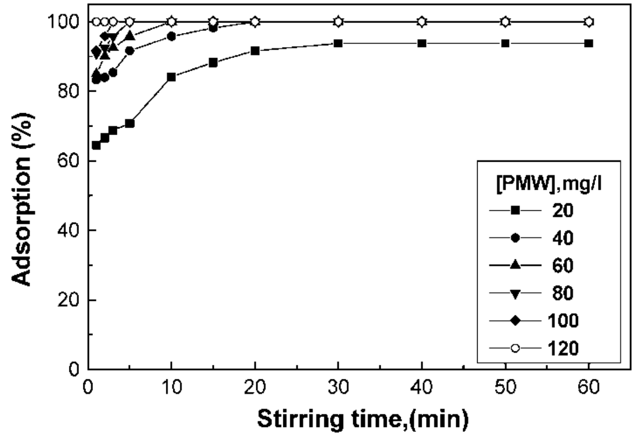

Figure 6. Relationship between adsorption of Al^{3+} ions ($2.7\,mg \cdot L^{-1}$) and PMW concentrations at pH 7 and various stirring times.

Effect of Metal Ion Concentration

Figure 7 shows the effect of varying aluminum ion concentration at different temperatures on the adsorption process. The results obtained indicated that the adsorption of Al^{3+} ions was almost constant (~100%) up to $8\,mg \cdot L^{-1}$ of aluminum, beyond which the adsorption decreases. This may be explained in terms of relatively smaller number of active sites available at higher concentrations of aluminum.

Moreover, the effect of varying the temperature from 5° to 80°C on the adsorption efficiency of various concentrations of aluminum is shown in

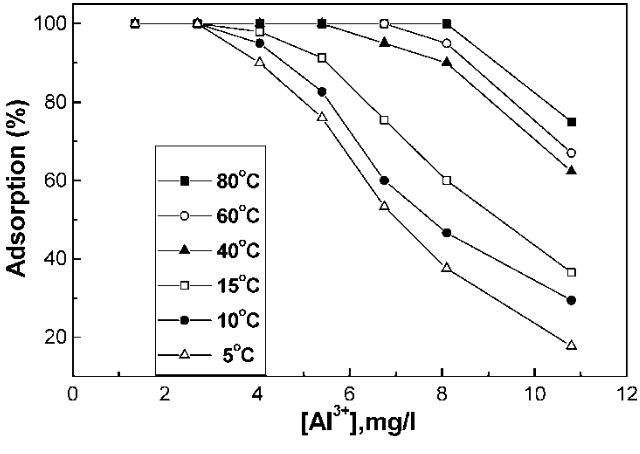

Figure 7. Adsorption of different concentrations of Al^{3+} ion by PMW ($100\,mg \cdot L^{-1}$) at various temperatures.

Fig. 7. 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 Al^{3+} ions from the bulk solution toward the adsorbent surface should also be taken into consideration. This agrees well with the literature data (25, 39).

Such results could suggest that the adsorption of Al^{3+} ions involve chemical bond formation and ion exchange (25). Accordingly, chelate formation may occur between Al^{3+} ions and oxygen atoms on the marble surface together with ion exchange between Al^{3+} ions and Ca^{2+} ions present in $CaCO_3$ (one of the constituents of marble). Since most industrial effluents are usually hot, the simple adsorption procedure presented here may find application in industrial wastewater treatment for the removal of Al^{3+} ions.

Adsorption Isotherms

To determine the capacity of PMW as sorbent for Al^{3+} ions, three isotherm equations, i.e., Freundlich, Langmuir, and Dubinin-Radushkevich equations, were utilized. The linearized form of the Freundlich equation may be written as

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{6}$$

where q_e (mg/g) is the amount of Al^{3+} ion adsorbed, C_e (mg/l) is its final equilibrium concentration, and n and K_F are the Freundlich equation parameters. This equation was applied to the experimental data depicted in Fig. 1 with a linear plot being obtained when ln q_e was plotted against ln C_e (Fig. 8). This demonstrates the applicability of the Freundlich model to aluminum adsorption onto PMW. The parameters K_F and n for the adsorption of Al^{3+} ions were calculated from the intercept and slope of the plot depicted in Fig. 8 giving values of 38.23 and 2.33, respectively, with a correlation coefficient (r) of 0.99987. Favorable adsorption of aluminum ions by PMW was demonstrated by the fact that the value of n is greater than unity (26, 40).

The linear form of the Langmuir equation applied to the aluminum ion adsorption data in Fig. 1 was

$$1/q_e = (1/K_L b) \cdot 1/C_e + 1/K_L \tag{7}$$

where K_L (mg/g) is the Langmuir constant and b (mL/mg) is the monolayer adsorption capacity. Figure 9 showed that a plot of $1/q_e$ vs. $1/C_e$ gave a straight line and thereby suggesting the applicability of the Langmuir model. This also demonstrated that monolayer coverage of aluminum ions occurs on the outer surface of PMW (26, 41). The values of K_L, b and the

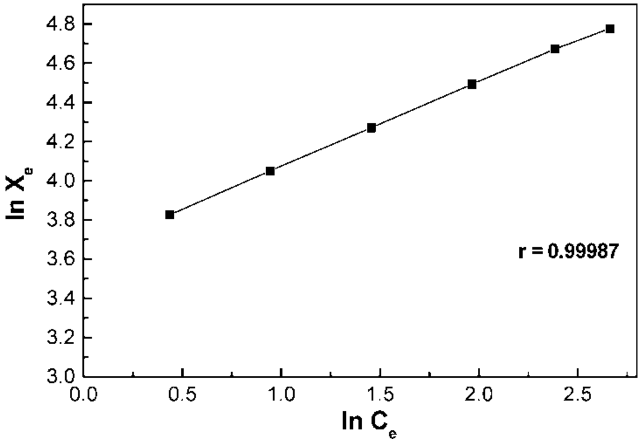

Figure 8. Freundlich plot for Al^{3+} ion adsorption onto PMW ($100\,mg \cdot L^{-1}$).

correlation coefficient (r) were 102.145 mg/g, 0.5326 mL/mg, and 0.9998, respectively.

The Gibbs free energy change, ΔG (kJ/mol), for adsorption of Al^{3+} ions by PMW can be calculated using the following thermodynamic equation (42):

$$\ln(1/b) = -\Delta G/RT \tag{8}$$

where T is the absolute temperature (K) and R is the gas constant [8.3143 J/(K.mol)]. The value of ΔG calculated at 298°K was found to be -1.561 kJ/mol. The negative sign for ΔG indicates the spontaneous nature of Al^{3+} ion adsorption onto PMW.

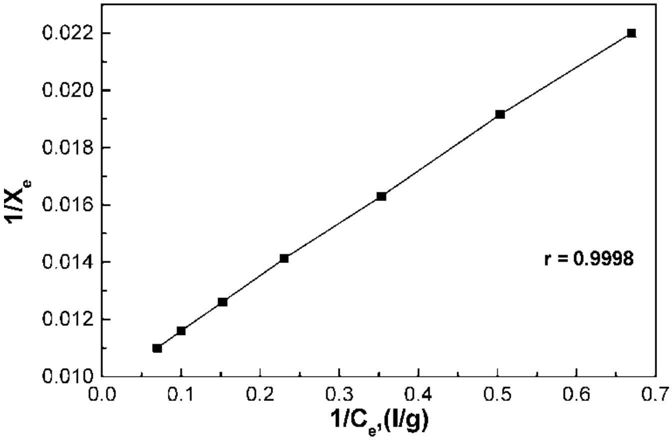

Figure 9. Langmuir plot for Al^{3+} ion adsorption onto PMW ($100\,mg \cdot L^{-1}$).

The Dubinin-Radushkevich (D-R) isotherm equation was also tested in its linearized form:

$$\ln X = \ln X_m - \beta\varepsilon^2 \tag{9}$$

and

$$\varepsilon = RT \ln(1 + 1/C) \tag{10}$$

where C is the liquid-phase concentration of Al^{3+} ions (μg/l), X_m is the monolayer capacity (g/g), ε is the Polanyi potential, and β is the parameter of D-R isotherm with X,T and R have the same meaning as above. The value of X_m [Equation (9)] can be obtained from the slope of the plot (Fig. 10) of another Langmuir equation:

$$C/X = 1/K_L X_m + C/X_m \tag{11}$$

The isotherm expressed in Equation (9) is more general than the Langmuir equation since it does not assume a homogeneous surface or a constant adsorption potential. Plotting of lnX vs. ε^2 gave a straight line (Fig. 11), thereby indicating the applicability of the D-R equation for Al^{3+} ions adsorption onto PMW. From the slope and intercept of this plot, values of $\beta = -6.5 \times 10^{-3}$ mol^2/KJ^2 and $X_m = 0.2\,g/g$ were obtained for aluminum ion adsorption. The corresponding value of the correlation coefficient (r) obtained was 0.9998.

The value of the adsorption energy (E) was obtained from the relationship (26, 43):

$$E = (-2\beta)^{-1/2} \tag{12}$$

and found to be 8.77 kJ/mol, indicating that the adsorption of some of the Al^{3+} ions onto PMW may be physical in nature. This may be attributed to

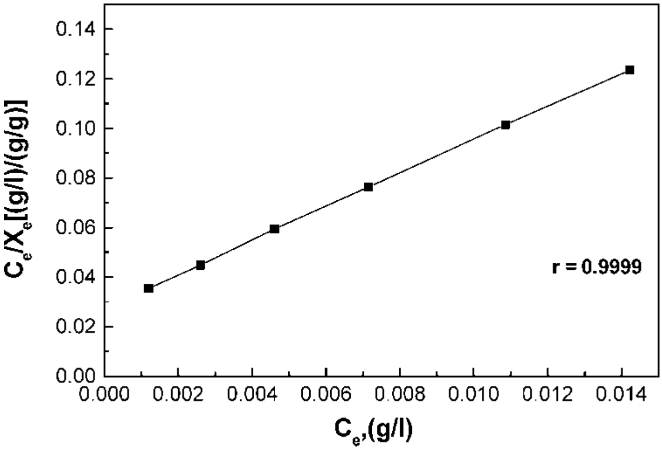

Figure 10. Second Langmuir plot for Al^{3+} ion adsorption onto PMW ($100\,mg \cdot L^{-1}$).

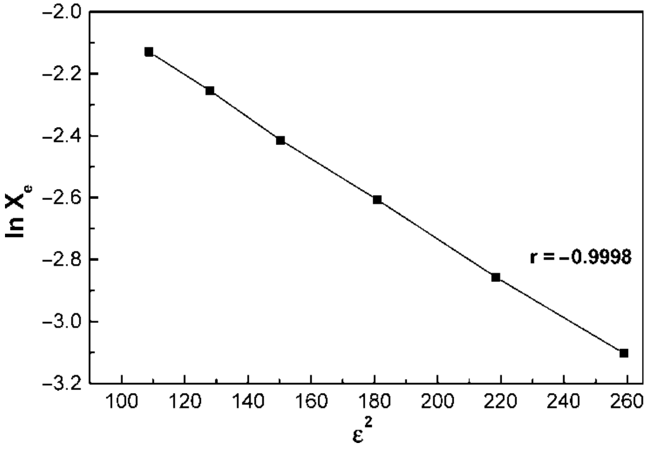

Figure 11. Dubinin-Radushkevich (D-R) plot for Al^{3+} ion adsorption onto PMW ($100\,mg \cdot L^{-1}$).

the formation of weak bonding, such as hydrogen bonding, between aluminum species [$Al(OH)$,$^{2+}$ $Al(OH)_2^+$, $Al(OH)_3$ (s), $Al_n(OH)_m^{(3n-m)+}$] and hydroxyl groups associated with active sites on the surface of marble present as a suspension.

Effect of Various Other Ions

Under the optimized conditions determined for this investigation, the percentage removal of $2.7\,mg \cdot L^{-1}$ Al^{3+} ions from a solution of pH7 containing $100\,mg \cdot L^{-1}$ 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 or sulfates whereas the anions were used as the corresponding sodium salts. The tolerable amounts of each ion giving an error of $\pm$ 2% in the removal efficiency of Al^{3+} ions are listed in Table 1. Inspection of the data indicates that the removal of Al^{3+} ions was quantitative in all cases. However, it should be noted that higher concentrations of Cu^{2+} or Zn^{2+} could have harmful effect on the removal process. This may be due to a competition between these cations and Al^{3+} ions for adsorption onto the active sites of PMW. This problem could be overcome by increasing the dose of PMW sorbent.

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.

Table 1. Effect of various ions on the percentage removal, Re (%), of $2.7\,\mathrm{mg \cdot L^{-1}}$ Al^{3+} ions from aqueous solutions using $100\,\mathrm{mg \cdot L^{-1}}$ PMW at pH 7

Foreign ions added	Tolerance limit, $\times 10^3\,\mathrm{mg \cdot L^{-1}}$	Al(III) found $\mathrm{mg \cdot L^{-1}}$	Re, %
Ca^{2+}	20.1	2.697	99.9
K^+	19.6	2.700	100
Na^+	11.5	2.700	100
NH_4^+	9.0	2.686	99.5
Mg^{2+}	7.1	2.700	100
Mn^{2+}	2.8	2.692	99.7
Co^{2+} or Ni^{2+}	1.2	2.697	99.9
Cd^{2+}	1.1	2.695	99.8
Pb^{2+}	1.04	2.692	99.7
Hg^{2+}	1.0	2.695	99.8
Cu^{2+}	0.2	2.697	99.9
Zn^{2+}	0.004	2.692	99.7
$S_2O_3^{2-}$	56.1	2.700	100
SO_4^{2-}	48	2.700	100
NO_3^-	31	2.700	100
CH_3COO^-	29.5	2.700	100
$HCOO^-$	29.5	2.686	99.5
$C_2O_4^{2-}$	22.0	2.700	100
Cl^-	17.8	2.692	99.7

However, sharp limits between the different adsorption mechanisms are not clear. Before discussing the possible 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) flocculation by adsorption of hydrolytic products; iii) ion exchange or iv) complexation with specific surface sites, provided the appropriate conditions prevail (38, 44).
2. As a function of solution pH (7), aluminum species may exist as soluble hydroxo-complexes ($Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$) and polyhydroxo-complexes ($Al_n(OH)_m^{(3n-m)+}$) in addition to the insoluble colloidal aluminum hydroxide $Al(OH)_3(s)$.
3. 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-type mineral) reacts with water, HCO_3^-, Ca^{2+}, $CaHCO_3^+$, and $CaHO^+$ are formed as surface-charged species and their presence is a function of solution pH (45). Moreover, OH^-, H^+ and HCO_3^- are considered as potential determining ions in addition to Ca^{2+} and $CaCO_3$. Chemisorption 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 by stirring the PMW sorbent with distilled water for 4 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 agrees well with the literature data that most natural surfaces are negatively charged (46).

4. IR analysis of PMW sorbent indicated the appearance of a band at 1449–1492 cm^{-1} assigned to carbonate (34) which is shifted to a sharp absorption band at 1425 cm^{-1} upon addition of Al^{3+} ions confirming the formation of aluminum carbonate. Moreover, the precipitation of aluminum hydroxide was also checked by IR analysis of the system Al-PMW, where a broad absorption band appeared at 3426 cm^{-1} which is assigned to the hydroxide of $Al(OH)_3$ (34).

Therefore, the proposed mechanism may occur as follows. At $pH < 5$, the hydrolytic species of aluminum may be adsorbed or ion exchanged with calcium sites of PMW sorbent. In the pH range 5–9, where the maximal removal of Al^{3+} ions occurred, adsorption may be electrostatically in nature and taking place via precipitation of the colloidal hydroxide precipitates of aluminum. In alkaline medium, at $pH > 9$, the removal of Al^{3+} ions decreases, which may be attributed to the incapability of adsorption of the negative species, $Al(OH)_4^-$ on the negative surface of PMW sorbent.

Application

To investigate the applicability of the recommended procedure, a series of experiments was performed to recover 1.575 and 2.985 mg of Al^{3+} ions added to aqueous and some natural water samples. The adsorption experiments were carried out using 1 L of clear, filtered, uncontaminated sample solutions after adjusting their pH values to 7. The results obtained are listed in Table 2 and show that the recovery was satisfactory, quantitative ($\sim$ 100%). The relative standard deviations (RSD) were calculated for five replicate analyses and the maximum value does not exceed 2.12%. Moreover, the recovery of Al^{3+} ions from brackish water samples is good, in comparison with other fresh water samples, which may be attributed to the presence of Na^+, Mg^{2+}, and Ca^{2+} ions in the former ones acting as activators (47).

CONCLUSIONS

Solid marble wastes have been investigated as cheap and effective inorganic sorbents for the removal of Al^{3+} ions from aqueous solutions. The experimental results revealed the following:

(i) The adsorption process was endothermic and followed first-order kinetics.

Table 2. Recovery of Al^{3+} ions added to 1 L of various water samples using 100 mg of PMW at pH ~7 and stirring for 10 min at 200 rpm

Sample (location)	Al(III) added (mg)	Al(III) found (mg)[a]	Re (%)	RSD (%)[b]
Distilled water	—	ND[c]	—	—
	1.575	1.550	98.41	0.41
	2.985	2.940	98.49	1.20
Tap water	—	ND[c]	—	—
(our laboratory)	1.575	1.571	99.75	0.45
	2.985	2.965	99.33	1.50
Nile water	—	ND[c]	—	—
(Mansoura City)	1.575	1.571	99.75	0.41
	2.985	2.970	99.50	2.12
Sea water (Gamasah)	—	ND[c]	—	—
	1.575	1.575	100.00	0.48
	2.985	2.970	99.50	1.30
(Ras El-Barr)	—	ND[c]	—	—
	1.575	1.570	99.68	0.50
	2.985	2.975	99.66	1.70
(Alexandria)	—	ND[c]	—	—
	1.575	1.570	99.68	0.62
	2.985	2.978	99.77	1.81
Lake water	—	ND[c]	—	—
(Manzalah)	1.575	1.573	99.87	0.41
	2.985	2.980	99.83	1.35
Underground water	—	ND[c]	—	—
(Cinbillaween City)	1.575	1.575	100.00	0.50
	2.985	1.985	100.00	1.50

[a] The mean of five experiments.
[b] Calculated for five experiments.
[c] ND = Not detectable.

(ii) It occurred mainly at the surface of the solid waste and to some extent by the internal pores.
(iii) It was well described by the Langmuir and Freundlich models.
(iv) It could occur through adsorption of hydrolytic species and/or precipitation of aluminum hydroxide onto sorbent.
(v) The procedure was successfully applied for the removal of Al^{3+} ions from drinking and natural waters.
(vi) Moreover, the aluminum 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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