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Removal of Lead from Water Samples by Sorption onto Powdered Limestone

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Abstract: Bench scale batch adsorption experiments were performed, aiming at the removal of the Pb^{2+} ions from aqueous solutions and water samples by fine powdered Limestone (LS) as an effective inorganic sorbent, which is inexpensive, widespread, and cheap. The main parameters (i.e., solution pH, sorbent and lead concentrations, stirring times, and temperature) influencing the sorption process, in addition to the effect of some foreign ions, were investigated. The results obtained stated that the sorption of Pb^{2+} ions onto LS is well described by Freundlich model and deviated from that of Langmuir over the concentration range studied. Under the optimum experimental conditions employed, the removal of ca. 100% of Pb^{2+} ions was attained. The procedure was successfully applied to the removal of lead from aqueous and different natural water samples. Moreover, the adsorption mechanism is suggested.

Keywords: Lead, sorption, powdered limestone, natural waters

INTRODUCTION

Industrialization and urbanization have led to increase in ecological problems. Water is particularly vulnerable to contamination from discharge of wastewaters by various industries. The increasing presence of heavy metals is

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very problematic to surface water and underground water due to their mobility and great toxicity (1, 2). The heavy metal lead is among the most common pollutant found in industrial effluents. Even at low concentration, this metal can be toxic to organisms, including humans as it is extremely toxic and can damage the nervous system, kidneys, and the reproductive system, particularly in children (3). Also, lead is known to have a toxic effect on the neuronal system and the function of the brain cells (4–6). The health hazards of lead in waters have been reported in many journals (7, 8). The U.S. Environmental Protection Agency (EPA) requires lead not to exceed 0.015 mg/L in drinking water (9). Cost-effective treatment technologies, therefore, are needed to meet these requirements.

Many technologies that could eliminate and/or reduce the presence of heavy metals in industrial effluents have been developed. These include precipitation and co-precipitation, Electro-depostion and electro-coagulation, cementation, membrane separation, solvent extraction, ion exchange, adsorption, and bio-sorption (10, 11). However, many technologies are either extremely expensive or too inefficient in reducing metal ion levels in effluent to concentrations which are required by governmental legislation (1). One of the most interesting methods for the removal of heavy metals from various effluents involves the adsorption capacity of natural organic or inorganic materials which are particularly abundant and inexpensive (11, 12). 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 (13).

In recent years there has been considerable interest in the development of new products which are abundant in nature, low in cost, and have minimal environmental impact for restoration or remediation of natural resources (14). Limestone (LS) which is produced in large quantities in many countries (among them is Egypt) is a low-cost reactive medium that can be used for the retaining of heavy metals and the subsequent clean up of industrial effluents, leachates, and contaminated ground water (14–16). Hence, the objective of the present work was to study the possibility of utilizing LS (which is naturally occurring or readily available 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 limestone were optimized and the results are presented in this paper.

EXPEIRMENTAL

Samples

The Limestone (LS), $CaCO_3$, samples used in this study were obtained from the Al-Mokattam area in Cairo (Egypt) where some private and governorate quarries are located. The samples were crushed and pulverized in the laboratory and those with a mean size of ca. 12.5 μm were used in the experiments. The sample contained 92% calcite and 3% dolomite (as found by chemical analysis) as has been described (17), with the remainder being composed of common minor constituents such as silica, clay, feldspar, pyrite, and sedrite (18). The samples were dried for 2 h in an oven at 125°C, packed into stoppered bottles, and stored in a desiccator for future use. Functional groups of LS were characterized through infrared analysis. The LS spectrum coincided with pure $CaCO_3$. The surface area and porosity of LS was measured using Brunauer, Emmett, Teller (BET) method. LS presented no BET porosity and its measured surface area was $0.50\,m^2 \cdot g^{-1}$. The pH values of points of zero charge (pH_{PZC}) were 9.1 (not aged), 6.2 (aged 60 min), and 8.3 (aged several days) and this agree with the previously reported data (19). Stirring the LS sorbent with distilled water (pH = 6.8) for 1 h decreases the suspension pH to 5.8, confirming the positive charge of the LS surface. Also, the concentration of calcium ion in the solution was measured before and after adsorption in order to confirm that cation exchange was involved.

Reagents

All the solutions were prepared from certified reagent grade chemicals. A lead nitrate $Pb(NO_3)_2$ stock solution of $780\,mg \cdot L^{-1}$ concentration was prepared and the working solutions were made by diluting the former with doubly distilled water. Aqueous solutions of HNO_3 and NaOH were used for pH adjustments.

Apparatus

A Pekin-Elmer 2380 Atomic Absorptions Spectrophotometer (AAS) with air-acetylene flame was used for the determination of lead concentration at 217.0 nm. The infrared analyses were undertaken via a Mattson 5000 FT-IR spectrophotometer using KBr disc method. The pH was measured using Jeanway 3311 pH meter. The stirring of the solutions was performed with a magnetic stirrer Model VEHP, Scientifica, Italy.

Procedure

Unless stated otherwise, all batch sorption experiments were conducted at room temperature (ca. 25°C). Known volumes of lead solutions with concentrations ranging from 2 to $80\,mg \cdot L^{-1}$ were pipetted into quick-fit glass bottles containing 0.1 g of LS 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 250 rpm and the samples were taken at fixed time periods (0.0, 0.3, 0.8, 1.0 5.0, 10, 20, 30, and 60 min) in order to study the kinetics of the adsorption process. Preliminary experiments showed that this time length was sufficient for adsorption of Pb^{2+} ions onto LS. The samples were subsequently filtered off and the residual Pb^{2+} ion concentrations in the filtrate were analyzed using AAS at 217.0 nm.

The percentage adsorption of Pb^{2+} 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 Pb^{2+} ions and C_r is the residual concentration after equilibration. The metal uptake q (mg/g) was calculated as

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

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

To asses the applicability of the procedure, another series of experiments was conducted on 1L suspension of clear and pre-filtered natural water samples with an initial pH adjusted to 7.0. These suspensions were placed in 2L glass beakers containing 4.0 or 6.4 mg of Pb^{2+} ions and 800 $mg \cdot L^{-1}$ of LS at 25°C and stirred magnetically for 10 min at 250 rpm.

RESULT AND DISCUSSION

Kinetics of the Adsorption Process

Figure 1 shows the variation in the percentage adsorption (removal) of Pb^{2+} ions onto LS sorbent with stirring time using various initial metal ion concentrations at pH 7. It can be seen that 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 macro-pores, transitional pores and micro-pores (20, 21), However, with the passage of time, the rate of adsorption decreased owing to the decrease of diffusion of lead ions through the pores (21, 22), and ultimately reached a costant value (equilibrium time). The time necessary to reach such adsorption equilibrium was found to be 10 min for 2 $mg \cdot L^{-1}$ Pb^{2+} ions, 20 min for 5.6 $mg \cdot L^{-1}$ Pb^{2+} ions, 30 min for 10 and 40 $mg \cdot L^{-1}$ Pb^{2+} ions, and 60 min for those 80 $mg \cdot L^{-1}$ Pb^{2+} ions. Hence, to ensure that adsorption had reached equilibrium in all cases stirring for 60 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

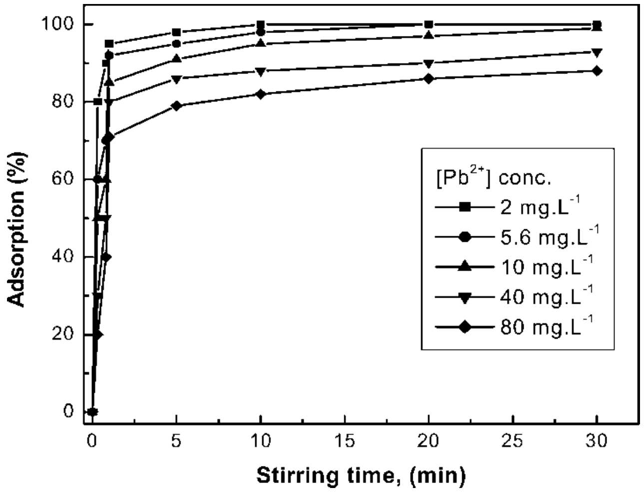

Figure 1. Influence of stirring time on the adsorption of various concentrations of Pb^{2+} ions by LS ($1000\,mg \cdot L^{-1}$) at pH 7.

be explained by a decrease in the number of adsorption sites having affinty toward Pb^{2+} ions.

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

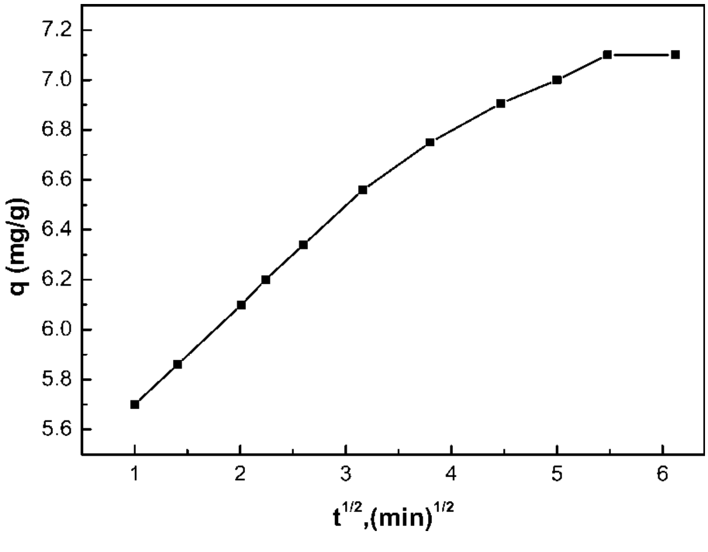

Figure 2. Plot of the amount of Pb^{2+} ions adsorbed onto LS ($1000\,mg \cdot L^{-1}$) vs. square root of time at pH 7.

Morris-Weber equation (23):

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

where q is the amount of Pb^{2+} ions adsorbed (mg/g). This indicates that an intrapore diffusion mechanism was involved in adsorption of Pb^{2+} ions by LS (Fig. 1). Figure 2 shows that two distinct regions were observed: an initial linear portion which may be due to the boundary layer effect (24), and a second portion which may be due to the intraparticle diffution effect (25). However, the fact that the line depicted in Fig. 2 does not pass through the origin indicates that intrapore diffusion is not the controlling step in sorption of Pb^{2+} ions by LS (20, 23). These data agree with those of Juang et al. (26) 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 intrapore diffusion. The value of the rate constant for the intrapore diffusion K_d was evaluated as 3.3×10^{-2} (mg/g min^{-1}) which give indication about the mobility of the Pb^{2+} ions toward the LS surface.

Again the kinetic data (Fig. 1) of the adsorption of Pb^{2+} ions by LS was examined by Bangham equation (27):

$$\text{Loglog}[C_i/(C_i - qm)] = \log(K_o m/2.303V) + \alpha \log t \tag{4}$$

where q, m, V, and C_i have been defined above, t is the time (min), K_o is the proportionality constant, and α is Bangham equation constant. Plot of $\text{Loglog}[C_i/(C_i - qm)]$ vs. log t gives a straight line (Fig. 3). These results show that the diffution of Pb^{2+} ions into LS pores played a role in the adsorption process and were similar to those described elsewhere (22, 28). The value of K_o and α constants deduced were 7.45, 4.14, respectively.

The kinetic data obtained in Fig. 1 for Pb^{2+} ion adsorption by LS were tested by Lagergren equation, as cited by Gupta and Shukla (29):

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

where q_e is the ammount of Pb^{2+} ion adsorbed at equilibrium (mg/g), K_{ads} is the first order rate constant for Pb^{2+} ions adsorption onto LS (min^{-1}), while q and t have been defined previously. The linear plot of Log $(q_e - q)$ vs. t (Fig. 4) shows 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 3.1 min^{-1}.

Effect of pH Value

It is well documented that solution pH is an important parameter that affects the metal-solution, adsorbent-surface and hence the sorption of heavy metal

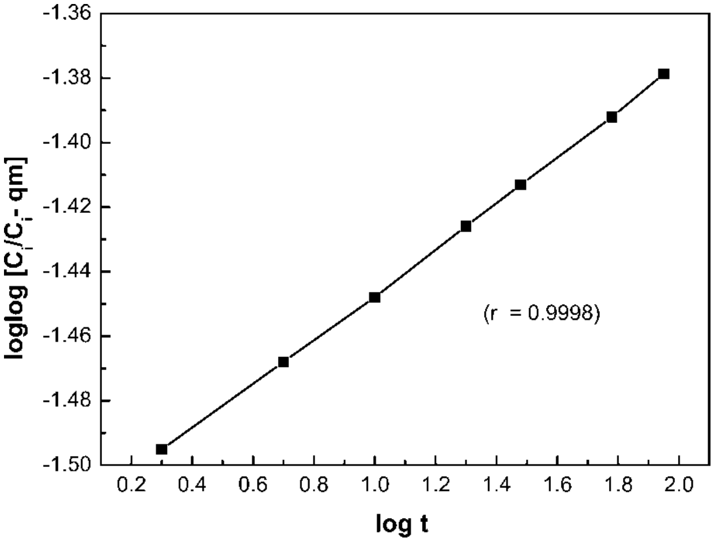

Figure 3. Plot of Loglog $[C_i/(C_i - qm)]$ vs. log t for the adsorption of Pb^{2+} ions by LS (1000 mg · L^{-1}) at pH 7.

ions (3, 13). Therefore, the influence of the solution pH on the Pb^{2+} ions adsorption by LS was studied. As a function of solution pH (3, 13), Pb^{2+} is the dominant species below pH 5.5. Between pH 6 and 10, Pb undergoes hydrolysis to $Pb(OH)^+$. Above pH 9, solid lead hydroxide $Pb(OH)_2$ is

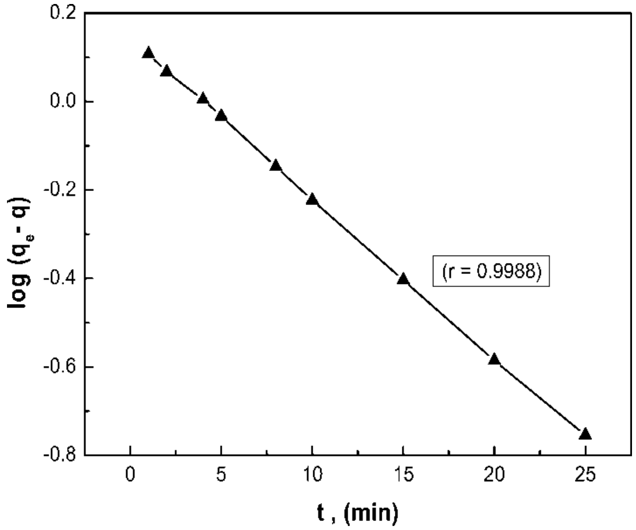

Figure 4. Plot of log $(q_e - q)$ vs. stirring time for Pb^{2+} ions adsorption onto LS.

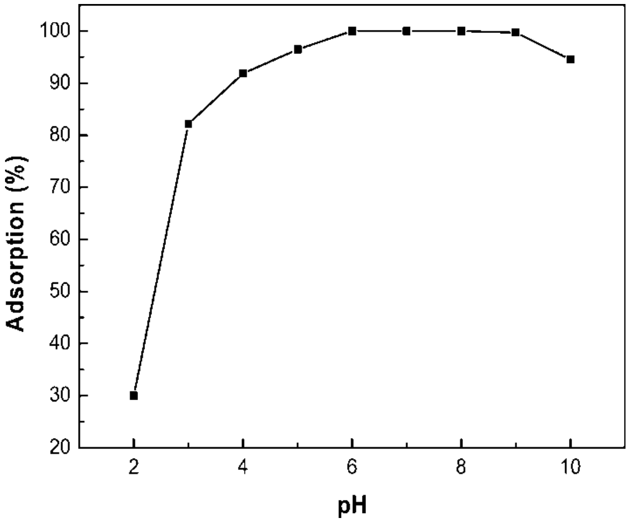

Figure 5. Adsorption (%) of Pb^{2+} ions (5 mg · L^{-1}) by LS (1000 mg · L^{-1}) vs. pH.

thermodynamically the most stable phase, while $Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$ are the predominant species at pH above 11.

In order to find the optimal pH value for the sorption process, the removal of Pb^{2+} ions in the pH range 2–10 was investigated and the data are depicted in Fig. 5. As can be seen, below pH 2, the removal of Pb^{2+} ions reaches zero which may be attributed to the complete solubility of LS (consists mainly from $CaCO_3$ and $MgCO_3$), thereby hindering the sorption of lead ions. Above pH 2, the removal efficiency increases sharply, reaching a maximum value (ca. ~100%) over the pH range 6–9 followed by decrease.

The removal of the Pb^{2+} ions at pH value <5 may be attributed to a possible ion-exchange mechanism between Pb^{2+} ions and calcium contaning LS in similar manner to that reported (30). Also, 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 (31). The enhanced removal of metal ion as the solution pH is increased (more than 5) can be attributed to adsorption of hydrolytic product $Pb(OH)^+$ (11) and/or surface precipitation of the metal as the insoluble carbonates, $PbCO_3$, forming successive layers on the sorbent surafce (32). The decrease in the removal efficiency at high pH values >9 may be attributed to the fact that the nagative species of lead, $Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$ are not capable of a combination with the negative surface of LS, as determined by ZPC ($pH_{ZPC} = 6.2$ after which the surface is negative). Moreover, this finding was confirmed by stirring LS with distilled water and the pH of its suspension was always decreased from 6.8 to 5.8. Therefore, pH 7 was recommended throughout all the other experiments.

Adsorption Isotherms

The Freundlich adsorption isotherm can be used successfully for modeling the equilibrium data in metal-surface systems. 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 is the amount of Pb^{2+} ions adsorbed at equilibrium (mg/g), C_e is the final equilibrium concentration (mg/l), 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 (Fig. 6). This demonstrates the applicability of the Freundlich model to lead adsorption onto limestone. The parameters n and K_F for adsorption of Pb^{2+} ions onto LS were calculated from the slope and intercept of the figure giving values of 1.84 and 378.9 L/g, respectively with a correlation coefficient ($r = 0.9998$). Favorable adsorption of Pb^{2+} ions by LS was demonstrated by the fact that the value of n is greater than unity (22, 33).

The linear form of the Langmuir equation applied to the Pb^{2+} ions adsorption data in Fig. 1 was

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

where K_L (mg/g) is the monolayer adsorption capacity and b (mL/mg) is the Langmuir constant. Figure 7, which is used only for comparative study, showed a deviation from the Langmuir model.

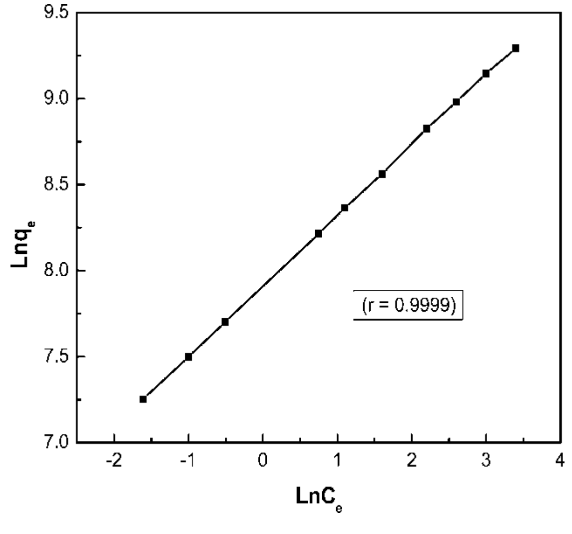

Figure 6. Freundlich plot for Pb^{2+} ions adsorption onto LS ($1000\ mg \cdot L^{-1}$).

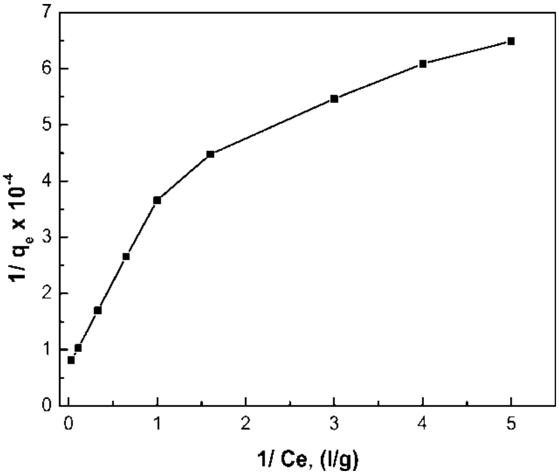

Figure 7. Langmuir plot for Pb^{2+}ions adsorption onto LS (1000 mg · L^{-1}).

Effect of Temperature

Another series of experiments was conducted to study the effect of the temperature on the adsorption of different Pb^{2+} ion concentrations (ca. 1, 2, 3, to 10 mg · L^{-1}) onto 1000 mg · L^{-1} of LS. The temperature was changed from 5 to 80°C. The obtained results showed that the change in temperature has no effect on the removal of the metal ions. The removal efficiency was in the range of 98–99%. Such results could suggest that the adsorption of Pb^{2+} ions onto LS involves chemical bond formation through ion exchange to form $PbCO_3$ (30, 31). Since most industrial effluents are usually hot, the simple adsorption procedure present here may find application in the industrial wastewater treatment for the removal of Pb^{2+} ions.

Effect of Various Ions

Under the optimized conditions determined for this investigation, the percentage removal of 5 mg · L^{-1} Pb^{2+} ions from a solution of pH 7 containing 800 mg · L^{-1} LS 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 nitrates 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 Pb^{2+} ions, are listed in Table 1. Inspection of the data indicates that the removal of Pb^{2+} ions is quantitative in all cases. However, it should be noted that higher concentrations of Cu^{2+}, Cd^{2+}, Hg^{2+}, or Zn^{2+} could have a harmful effect on the removal process. This may be due to a competition between cations and Pb^{2+} ions for

Table 1. Effect of some selected foreign ions on the percentage removal, Re (%), of 5 $mg \cdot L^{-1}$ Pb^{2+} ions from aqueous solutions using 1000 $mg \cdot L^{-1}$ LS at pH 7, and with shaking for 10 min at 250 rpm

Cations	Tolerance limit, × 10^3 $mg \cdot L^{-1}$	Re, %	Anions	Tolerance limit, × 10^3 $mg \cdot L^{-1}$	Re, %
Na^+	17.8	99.9	Cl^-	11.5	99.8
Ca^{2+}	20.1	99.7	I^-	63.0	99.9
Ba^{2+}	68.7	99.6	SO_4^{2-}	48.0	99.8
K^+	19.6	99.7	NO_3^-	31.0	99.7
$(NH_4)^+$	9.1	99.7	CO_3^{2-}	30.0	99.9
Mg^{2+}	12.2	99.8	$S_2O_3^{2-}$	56.0	99.8
Co^{2+} or Ni^{2+}	3.1	99.6	S^{2-}	16.0	99.8
Cu^{2+}	3.2	99.6	$Cr_2O_7^{2-}$	10.8	99.7
Cd^{2+}	1.2	99.5	CH_3COO^-	29.5	99.8
Hg^{2+}	1.0	99.7	$C_2O_4^{2-}$	22.0	99.7
Zn^{2+}	0.01	99.8			

adsorption on the active sites of LS. This problem could be overcome by increasing the amount of LS. Moreover, higher concentrations of some anions have no adverse effect on the removal of lead ions but they may enhance the process. This may be attributed to the precipitation of lead with most of the investigated anions on the surface of the limestone.

Adsorption Mechanism

Although adsorption from solution by solids is of great practical importance and a vast number of papers have been published, 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 preciptation 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 prevail (32, 34).
2. As a function of solution pH (3, 13), lead species may exist as soluble Pb^{2+} and hydroxo-species [$Pb(OH)^+$, $Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$] in addition to the insoluble lead hydroxide $Pb(OH)_2$.

3. The powdered limestone (LS) consists mainly of calcite ($CaCO_3$). When calcite (as a sparingly soluble salt-type mineral) is suspended 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 (35). Moreover, OH^-, H^+, and HCO_3^- are considered as potential determining ions in addition to Ca^{2+} and $CaCO_3$. 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 LS sorbent with distilled water for 1 h after which the suspenation pH decreases. This may be attributed to desorption of H^+ ions from sorbent surface or sorption of OH^- ions from the solution which agree with the literature data (19) and ZPC measurements that limestone surface is positively charged.

Therefore, the proposed mechanism may occur as follows: At pH < 5, the adsorption is less than 100% which may be due to repulsion between Pb^{2+} ions and positive surface charge, as determined from ZPC ($pH_{ZPC} = 6.2$) and stirring the LS sorbent with distilled water. Therefore, the removal of the Pb^{2+} ions may be attributed to a possible ion-exchange mechanism between Pb^{2+} ions and calcium containing LS in a manner similar to that reported in (30). Also, 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 (31). Also, adsorption may take place through precipitation of lead carbonate on LS surface according to the following equations (36):

$$\equiv CaCO_3^0 + M^{2+} + HCO_3^- = CaCO_3(s) + \equiv MCO_3^0 + H^+ \quad (8)$$

$$\equiv MCO_3^0 + M^{2+} + HCO_3^- = MCO_3(s) + \equiv MCO_3^0 + H^+ \quad (9)$$

In the pH range 6–9, where the maximal removal of Pb^{2+} ions occurred, adsorption may be electrostatic in nature and take place between $Pb(OH)^+$, the predominant species in this pH range, and the negatively charged surface of limestone, as determined by ZPC and precipitation of lead carbonate on LS surface.

In an alkaline medium, at pH > 9, the removal of Pb^{2+} ions decreases, which may be attributed to the incapability of adsorption of the negative species $Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$ onto the negative surface of the LS sorbent.

Application

To investigate the applicability of the recommended procedure, a series of experiments were performed to recover 4.0 and 6.4 mg of Pb^{2+} 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, and quantitative (~100%).

Table 2. Recovery of Pb^{2+} ions, (Re %) spiked to 1 L of various natural water samples using 1000 mg · L^{-1} LS at pH 7 with shaking for 10 min at 250 rpm

Sample (location)	Added Pb^{2+} ions (mg)	Found Pb^{2+} ions (mg)	Re, %
Distilled water	4.0	3.95	99.9
	6.4	6.395	99.9
Tap water (our laboratory)	4.0	3.95	99.9
	6.4	6.395	99.9
Nile water (Mansoura City)	4.0	3.92	99.8
	6.4	6.395	99.9
Sea water (Gamasah)	4.0	3.92	99.8
	6.4	6.389	99.8
Underground water (Salaka)	4.0	3.92	99.8
	6.4	6.393	99.9
Lake-water (El-Manzala)	4	3.92	99.8
	6.4	6.393	99.9

CONCLUSIONS

The powdered limestone has been investigated as a cheap and effective inorganic sorbent for the removal of Pb^{2+} ions from aqueous solutions. The experimental resultes revealed the following:

i. The adsorption occurred mainly at the surface of the solid limestone and slightly by the internal pores.
ii. The adsorption data were well described by the Freundlich model and deviated from that of Langmuir over the concentration range studied.
iii. It could occur through ion-exchange, adsorption of hydrolytic species, $Pb(OH)^+$, and the precipitation of lead carbonate onto LS sorbent depending on the solution pH.
iv. The procedure was successfully applied for the removal of Pb^{2+} ions from drinking and natural waters.
v. Moreover, the lead ions were essentially held by LS 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.

REFERENCES

1. Meunier, N., Laroulandie, J., Blais, J.F., and Tyagi, R.D. (2003) Coca shells for heavy metal removal from acidic solutions. *Bioresource Technol.*, 90 (3): 255–263.

2. Yan, G. and Viraraghavan, T. (2003) Heavy-metal removal from aqueous solution by fungus. *Mucor rouxii. Water Res.*, 37 (18): 4446–4496.
3. Sheng, P.X., Ting, Y-P., Chen, J.P., and Hong, L. (2004) Sorption of lead, copper, cadmium, zinc and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. *J. Colloid Interface Science*, 275 (1): 131–141.
4. Ho, Y.S., Ng, J.C.Y., and McKay, G. (2001) Removal of lead(II) from effluents by sorption on peat using second-order kinetics. *Sep. Sci. Technol.*, 36 (2): 241–261.
5. Freedman, R., Olson, L., and Hoffer, B.G. (1990) Toxic effects of lead on neuronal development and function. *Environ. Health Perspect.*, 89 (1): 27–34.
6. Goldstein, G.W. (1990) Lead poisoning and brain cell function. *Environ. Health Perspect.*, 89 (1): 91–94.
7. Grocetti, A.F., Mushak, P.F., and Schwartz (1990) Determination of number of lead-exposed women of child bearing age and pregnant women: an integrated summary of a report to the U.S. Congress on childhood lead poisoning. *Environ. Health Perspect.*, 89 (1): 109–120.
8. Aldrich, R., Wlodarczyk, J., and Hensley, M.J. (1993) Children blood lead levels and environmental lead contamination. *Med. J. Aust.*, 185 (7): 506–506.
9. Agency for Toxic Substances and Disease Registry (ATSDR) (1999). *Toxicological Profiles;* U.S. Department of Health and Human Services, Public Health Service: Atlanta.
10. Patterson, J.W. (1989) Industrial Waste Reduction. *Environ. Sci. Technol.*, 23 (9): 1032–1038.
11. Ghazy, S.E., Samra, S.E., Mahdy, A.M., and El-Morsy, S.M. (2005) Kinetic investigation of the removal of aluminum from water samples by adsorption onto powdered marble wastes. *Sep. Sci. Technol.*, 40 (9): 1797–1815.
12. Kumar, A., Rao, N.N., and Kaul, S.N. (2000) Alkali-treated straw and insoluble straw xanthate as law cost adsorbent for heavy metal removal–Preparation, characterization and application. *Bioresource Technol.*, 71 (2): 133–142.
13. Bradl, H.B. (2004) Adsorption of heavy metal ions on soils and soils constituent. *J. Colloid Interface Science*, 277 (1): 1–18.
14. Gómez del Río, J.A., Morando, P.J., and Cicerone, D.S. (2004) Natural materials for treatment of industrial effluents: comparative study of the reaction of Cd, Zn and Co by calcite and hydroxyapatite. Part I: batch experiments. *J. Environ. Management*, 71 (2): 169–177.
15. Komnitsas, K., Bartzas, G., and Paspaliarise, I. (2004) Efficiency of limestone and red mud barriers: laboratory column studies. *Minerals Engineering*, 17 (2): 183–194.
16. Bailey, S.E., Olin, T.J., Bricka, R.M., and Adrian, D.D. (1999) A review of potentially low-cost sorbents for heavy metals. *Water Res.*, 33 (11): 2469–2479.
17. Ghazy, S.E., Samra, S.E., and El-Morsy, S.M. (2001) Removal of copper(II) from aqueous solutions using limestone fines as the sorbent and oleic acid as the surfactant. *Adsorp. Sci. Technol.*, 19 (2): 175–185.
18. Bates, R.L. and Jackson, J.A. (1980) *Glossary of Geology*, 2nd Ed.; American Geological Institute: Falls Church, VA.
19. Somasundran, P. and Goddard, E.D. (1979) *Modern Aspects of Electrochemistry*; Nr. 13. Plenum Press: New York, 207.
20. Al-Asheh, S. and Banat, F. (2001) Adsorption of zinc and copper ions by the solid waste of the olive oil industry. *Adsorp. Sci. Technol.*, 19 (2): 117–129.

21. Yubin, T., Fangyan, C., and Honglin, Z. (1998) Adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} ions on to waste fluidized catalytic cracking (FCC) catalyst. *Adsorp. Sci. Technol.*, 16 (8): 595–606.
22. Akhtar, S. and Qadeer, R. (1997) Active carbon as an adsorbent for lead ions. *Adsorp. Sci. Technol.*, 15 (10): 815–824.
23. Weber, W.J., Jr. and Morris, S.c. (1963) Intraparticle diffusion during the sorption of surfactants onto activated carbon. *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.*, 89 (1): 53–61.
24. Crank, J. (1965) *The Mathematics of Diffusion*; Carlendon Press: Oxford, London.
25. McKay, G., Otterbern, M.S., and Sweeney, A.G. (1980) The removal of color from effluent using various adsorbents -III. Silica: Rate processes. *Water Res.*, 14 (1): 15–20.
26. Juang, R., Wu, F., and Tseng, R. (2000) Mechanism of adsorption of dyes and phenols from water using activated carbons prepared from plum kernels. *J. Colloid Interface Sci.*, 227 (2): 437–444.
27. Bangham, D.H. and Burt, F.P. (1924) The behavior of gases in contact with glass surfaces. *Proc. Roy. Soc.*, (London) Ser, 105 (A): 481–488.
28. Qadeer, R. and Hanif, J. (1994) Kinetics of uranium(VI) adsorption on activated charcoal from aqueous solutions. *Radiochim. Acta*, 65 (4): 259–263.
29. Gupta, G.S. and Shukla, S.P. (1996) An inexpensive adsorption technique for the treatment of carpet effluents by low cost materials. *Adsorp. Sci. Technol.*, 13 (1): 15–26.
30. Mandjiny, S., Zouboulis, A.I., and Matis, K.I. (1995) Removal of cadmium from dilute solutions by hyroxyapatite. Part I. Sorption studies. *Sep. Sci. Technol.*, 30 (15): 2963–2978.
31. Chermiak, D.J. (1997) An experimental study of Sr and Pb diffusion in calcite and its implications for carbonate diagenesis and metamorphism. *Geochimica et Cosmochimica Acta*, 61 (19): 4173–4179.
32. Apak, R., Tutem, R., Hugul, M., and Hizal, J. (1998) Heavy metal cation retention by conventional sorbents (red mud and fly ashes). *Water Res.*, 32 (2): 430–440.
33. Nassar, M.M., Hamoda, M.F., and Radwan, G.H. (1996) Utilization of palm-fruit bunch particles for the adsorption of dyestuff wastes. *Adsorp. Sci. Technol.*, 13 (1): 1–6.
34. Zouboulis, A.I., Kydros, K.A., and Matis, K.A. (1995) Removal of hexavalent chromium anions from solutions by pyrite fines. *Water Res.*, 29 (7): 1755–1760.
35. Somasundran, P. and Agar, G.E. (1967) Zero point of charge of calcite. *J. Colloid Interface Sci.*, 24 (4): 433–440.
36. Zhu, C. (2002) Estimation of surface precipitation constants for sorption of divalent metals onto hydrous ferric oxide and calcite. *Chem. Geol.*, 188 (1–2): 23–32.