Removal of Lead Ions from Aqueous Solution by Sorptive-Flotation Using Limestone and Oleic Acid

Shaban E. Ghazy *+

Department of Chemistry, Faculty of Science, Mansoura University, P.O. Box 66, Mansoura, EGYPT

Ahmed H. Ragab

New Mansoura Water Treatment Plant, Mansoura City, EGYPT

ABSTRACT: *A simple, rapid and economic procedure was presented to remove lead(II) from aqueous solution under the optimized conditions. It is based on the sorption of Pb^{2+} ions from aqueous solutions onto limestone fines (LS), which is an inexpensive and widespread over the globe, followed by flotation with oleic acid (HOL) surfactant. The different parameters (namely: solution pH, sorbent, surfactant and lead concentrations, shaking times, ionic strength, temperature and the presence of foreign ions) influencing the sorptive-flotation process were examined. Nearly, 99% of Pb^{2+} ions were removed from aqueous solutions at pH 7 after shaking for 5 min and at room temperature (~25 ^{o}C). The procedure was successfully applied to recover lead(II) spiked to some natural water samples. A mechanism for sorption and flotation is suggested.*

KEY WORDS: *Lead, Sorptive-flotation, Limestone, Oleic acid*

INTRODUCTION

Lead is a natural compound that exists in elemental, inorganic, and organic forms. It is present in trace amounts in all soils, water, and foods. It is soft, malleable, blue-gray in color, and is highly resistant to corrosion. These properties, along with the poor ability of lead to conduct heat and electricity, probably contributed to its use in mining, smelting, refining, battery manufacturing, soldering, electrical wiring, home demolition and construction, painting, ceramic glazing, and the making of stained glass.

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 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 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]. Therefore, cost-effective treatment technologies are needed to meet these requirements of recovery and/or removal of metal ions.

During the last years, increasing attention has been focused on the separation, pre-concentration and/or determination of trace metal ions in the environment. This field of interest is becoming a real challenge due to the specificity, accuracy and sensitivity required by more and more stringent regulations [10,11]. Numerous techniques are available in this concern and have been reported [12-15]. These techniques may involve: chemical precipitation, ion exchange, reverse osmosis, electro-deposition, adsorption, solvent extraction and flotation separation processes. Of these, adsorption has proved to be an effective technique, but it may suffer from economic limitations owing to difficulties encountered in separating sorbent from suspension in order for it to be regenerated [15]. Therefore, attempts have been made to develop separation techniques.

Flotation as a solid/liquid or liquid/liquid (or both) separation process has recently received a considerable interest owing to: simplicity, rapidity, economic, good separation yields (R > 95 %) for small impurity agent concentrations (10^{-6}-10^{-2} mol.l^{-1}), a large possibility of application for species having different nature and structure, flexibility and friability of equipment and processing for recovery purposes [16,17]. It is believed that this process will soon be incorporated as a clean technology to treat water and wastewater [18]. For the aforementioned reasons a combination of adsorption and flotation into a unified operation termed sorptive-flotation could be considered as a vital process.

In recent years there has been a 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 [19]. 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 retaining heavy metals and the subsequent clean up of industrial effluents, leachates and contaminated ground water [19-21]. Hence, the present work aims to establish a selective, rapid and simple sorptive-flotation procedure using LS (which is naturally occurring or readily available and alternative to existing commercial adsorbents) as a sorbent and oleic acid as a surfactant for removing lead ions from aqueous solutions and natural waters under the recommended conditions.

EXPERIMENTAL
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 10-15 µm particle size range was used in the experiments. The sample contained [22], 92% calcite ($CaCO_3$) and 3% dolomite ($MgCO_3$), with the reminder being composed of common minor constituents such as silica, clays, feldspar, pyrite, and sedrite [23]. 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 3.88 m^2.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 agreed with the previously reported data [24].

Reagents

All the solutions were prepared from certified reagent grade chemicals. A lead nitrate $Pb(NO_3)_2$ stock solution (780 mg.l^{-1}) was prepared and the working solutions were made by diluting the former with doubly distilled water. An oleic acid (HOL) stock solution, 6.36×10^{-2} mol. l^{-1}, was prepared from food grade with sp. gr. 0.895 (provided by J.T. Baker Chemical Co.) by dispersing 20 cm^3 of HOL in 1 l kerosene. Aqueous solutions of HNO_3 and NaOH were used for pH adjustments.

Apparatus

A Pekin-Elmer 2380 Atomic Absorptions Spectro-photometer 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. The flotation procedure was carried out in a flotation cell, which was a cylindrical tube of 1.5 cm inner diameter and 29 cm length fitted with a stopcock at the bottom and a stopper at the top [25].

Procedure

To study the various parameters affecting the sorption-flotation process, a 20 ml aliquot of a suspension containing 3.0 mg.l^{-1} Pb^{2+} ions and 1000 mg.l^{-1} sorbent (LS) of initial pH 7 was introduced into the flotation cell. The cell was shaken for 5 min (optimized time) to ensure complete adsorption of Pb^{2+} ions by LS. Then 3 ml of 1×10^{-3} mol. l^{-1} HOL was added. The cell was again inverted 20 times by hand and allowed to stand for 5 min to complete flotation.

The residual Pb^{2+} ion concentration in the mother liquor was analyzed using a Perkin-Elmer 2380 atomic absorption spectrophotometer at a wavelength of 217.0 nm. The percentage floatability of Pb^{2+} ions (%F) was calculated from the relationship:

$$\%F = (C_i - C_r) / C_i \times 100 \qquad (1)$$

where C_i and C_r denote the initial and residual Pb^{2+} ion concentrations.

To study the flotation of LS alone, the previous procedural steps were conducted in the absence of Pb^{2+} ions. After complete flotation, the LS-containing float was filtered through a G$_5$ sintered-glass filter (porosity, 1-1.5 μm) and dried to constant weight in an oven at 125 ℃. The percentage floatability of LS (%F), was calculated from:

$$\%F = C_f / C_i \times 100 \qquad (2)$$

where C_i and C_f denote the initial and float concentrations of the LS sorbent. All experiments were carried out at room temperature (~ 25 ℃).

To asses the applicability of the procedure, another series of experiments were conducted on 1 l suspension of natural water samples (placed in a 2 l glass beaker) containing 3.0 or 5.0 mg Pb^{2+} ions, 1000 mg.l^{-1} LS and 10 ml of 1×10^{-3} mol. l^{-1} HOL with an initial pH of 7. The suspension was stirred magnetically for 10 min at 250 rpm where it was noted that the Pb-LS- HOL system was self-floatable without a stream of air bubbles being necessary.

RESULTS AND DISCUSSION
Floatability of powdered limestone

A preliminary series of experiments (using a constant concentration of HOL equal to 1×10^{-3} mol.l^{-1} at pH 7) was undertaken to float various concentrations of LS. The results obtained are depicted in Fig. 1 from which it is clear that a maximum flotation (~ 100 %) for LS was attained over a wide concentration range up to 4000 mg.l^{-1}. Hence, the concentration of powdered limestone favorable for lead(II) removal was presumed to be 1000 mg.l^{-1} at pH 7.

Another series of experiments was conducted to study the effect of pH on the flotation of 1000 mg.l^{-1} of LS using 1×10^{-3} mol.l^{-1} HOL. The results are depicted in Fig. 2 and show that maximum flotation of LS (~100 %) was attained over the pH range 4-10. It should also be noted that at pH values less than 3, the process was not effective due to the partially dissolution of the LS sorbent. For this reason, a pH value of 7 was used in all subsequent measurements.

To find out the suitable concentration of HOL for the complete flotation of 1000 mg.l^{-1} of LS a series of experiments was performed using different concen-trations of HOL in acidic, neutral and alkaline media. The results shown in Fig. 3 indicate that the floatability of LS did not exceed ~85 % at pH 3, but attained maximum value (~ 100%) in the HOL concentration range 1×10^{-4} - 2.5×10^{-2} mol.l^{-1} at pH values of 7 and 9. For simplicity, 1×10^{-3} mol.l^{-1} HOL was used in other experiments at an initial pH 7.

The removal of lead(II) ions
Effect of pH

Generally, adsorption and flotation are sensitive to variations in the pH of the medium and knowledge of how the pH value affects each system was a prerequisite to studies employing these methods. As a function of solution pH [3, 26], 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 thermodynamically the most stable phase, while Pb(OH)$_3^{-}$ is predominant at pH above 11.

The influence of pH on the combined process (sorption and flotation) for the removal of 3 mg.l^{-1}of Pb^{2+} ions was investigated in the absence and presence of 400 and 1000 mg.l^{-1} of LS using 1×10^{-3} mol.l^{-1} of HOL without or with shaking for 5 min. The pH of solutions
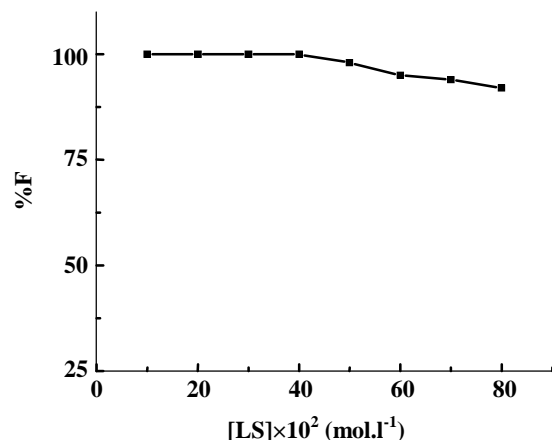
Fig. 1: Floatability of different concentrations of LS using 1×10^{-3} mol.l^{-1} HOL at pH 7.

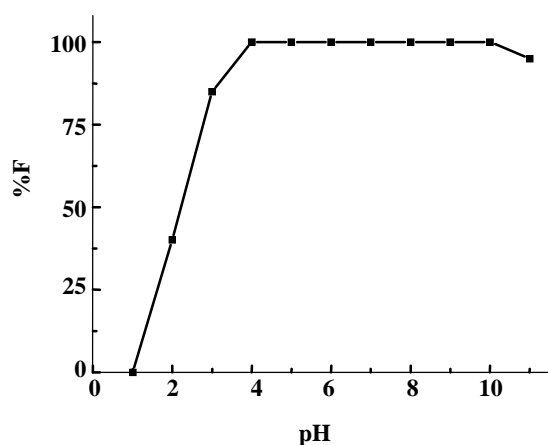
Fig. 2: Floatability of 1000 mg.l^{-1}of LS at different pH values using 1×10^{-3} mol.l^{-1}HOL.
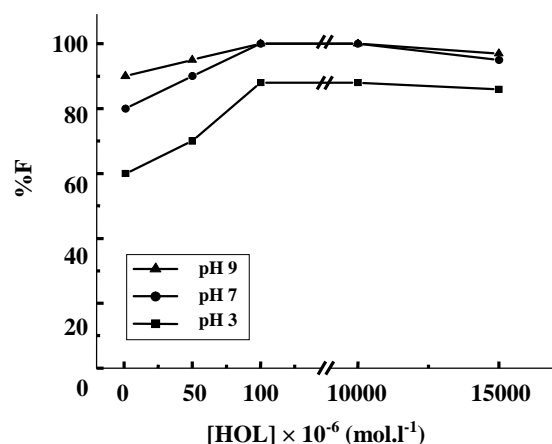

Fig. 3: Floatability of 1000 mg.l^{-1}of LS at different concentrations of HOL using different pH values.

was adjusted with HNO$_3$, HCl, H$_2$SO$_4$ and/or NaOH. The results are presented in Fig. 4 and indicate that the removal of Pb^{2+} ions from aqueous solutions with HOL only did not exceed ~ 25%. For this reason, a mean of enhancing the process was required.

Inspection of the figure indicated that the use of LS as a sorbent increased the removal of Pb^{2+} ions as the pH increased, reaching a maximum value (~ 100% after shaking for 5 min) at pH $\geq$ 4. At pH values less than 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.

The removal of the Pb^{2+} ions at pH values < 4 may be attributed to a possible ion-exchange mechanism between Pb^{2+} ions and calcium containing LS in similar manner to that reported [27]. Adsorbed lead ions generally occupy calcium sites within the calcite lattice [28]. Moreover, Pb^{2+} ions may be adsorbed electrostatically with the negatively charged surface of limestone [22]. The enhanced removal of metal ion as the solution pH is increased (more than 4) can be attributed to adsorption of hydrolytic product Pb(OH)$^+$ and/or surface precipitation of the metal as the insoluble hydroxides, Pb(OH)$_2$, forming successive layers on the sorbent surface [29].

It is also clear that the shaking for 5 min is necessary. Moreover, adjusting the pH with HNO$_3$ in the acidic medium is favorable than with HCl or H$_2$SO$_4$. Therefore, pH 7 was recommended throughout all other experiments.

Effect of surfactant concentration

In order to find a suitable concentration of HOL for removing 3 mg.l^{-1}of Pb^{2+} ions from aqueous solutions, a series of experiment was conducted at pH 7 in the absence and presence of 400 and 1000 mg.l^{-1} LS using different concentrations of HOL. The results obtained are presented in Fig. 5. It can be seen that the removal of Pb^{2+} ions attained a maximum values (~ 25%) in the absence of LS and (ca. ~ 90% and ~ 95%) in the presence of 400 and 1000 mg.l^{-1} of LS, respectively. An enhancement in the flotation efficiency of Pb^{2+} ions to ~ 100% was achieved after shaking for 5 min. These maximal values were attained over the HOL concentration range of 1×10^{-4} - 2.5×10^{-2} mol.l^{-1}.

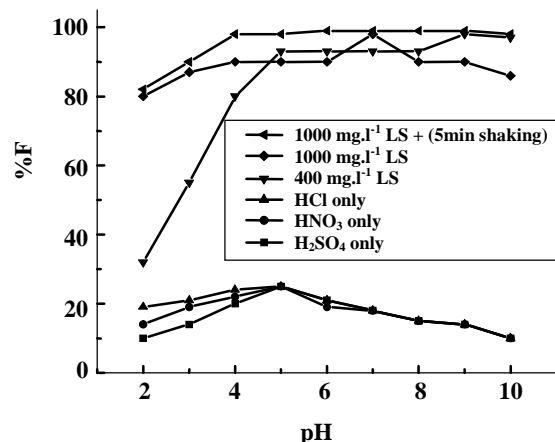Higher concentrations of the surfactant impaired flotation. This impairment has been discussed by some

Fig. 4: Floatability of 3 mg.l⁻¹of Pb²⁺ at different pH values with or without shaking using different concentrations of LS and 1×10⁻³ mol.l⁻¹ of HOL.
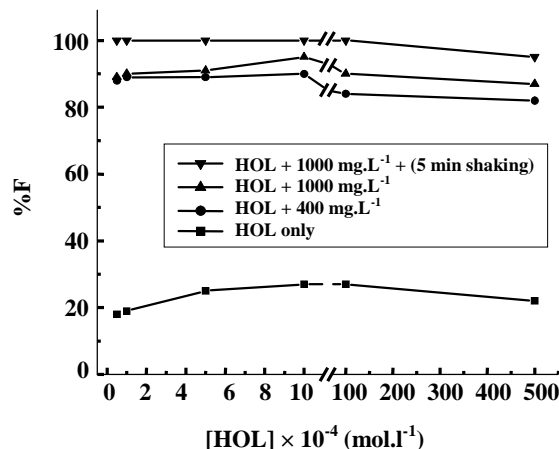

Fig. 5: Floatability of 3 mg.l⁻¹ Pb²⁺ ions versus HOL at pH 7 using different concentrations of LS.
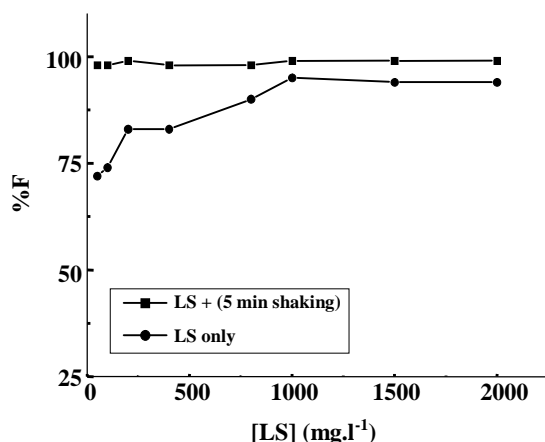
Fig. 6: Floatability of 3 mg.l⁻¹ Pb²⁺ ions versus LS concentrations at pH 7 using 1×10⁻³ mol.l⁻¹ HOL.
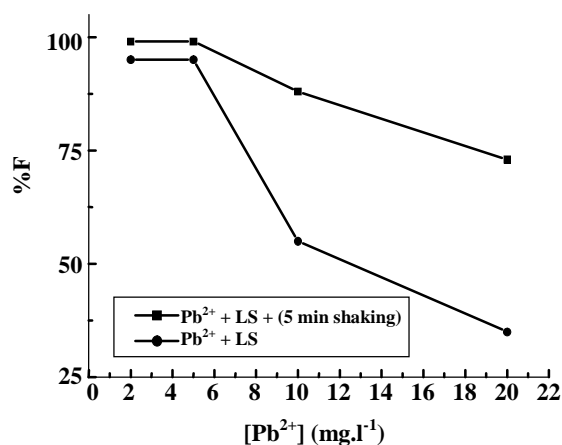
Fig. 7: Floatability of different concentrations of Pb²⁺ ions at pH 7 using 1000 mg.l⁻¹ of LS and 1×10⁻³ mol.l⁻¹ HOL.

workers [22] who concluded that poor flotation at high surfactant concentration was caused by the formation of air bubbles on the surface of stable, hydrated envelope of surfactant or, perhaps, by the formation of a hydrated micelle coating on the solid surface. As a result, the hydro-phobicity of the resulting surface was not satisfactory for flotation. Consequently, the concentration of HOL employed was fixed at 1×10^{-3} mol.l^{-1} throughout all other studies.

Effect of sorbent and metal ion concentration

Two parallel series of experiments were conducted to study the influence of powdered limestone concentration (Fig. 6) and changing the lead ion concentration (Fig. 7) on the removal percentage of Pb²⁺ ions from aqueous

solutions at pH 7 using 1×10^{-3} mol.l^{-1} of HOL without or with shaking for 5 min. As can be seen from Fig. 6, the removal percentage of Pb²⁺ ions increased as the LS dose increased, while it decreased as the concentration of the metal ion increased (Fig. 7). The reason for attaining a maximum removal of Pb²⁺ ions (~ 100 %) at higher LS dose, after shaking for 5 min may be due to an increase in the number of binding sites on the sorbent available to Pb²⁺ ions. Hence, 1000 mg.l⁻¹ of LS may be a suitable dose for the removal of Pb²⁺ ions having a concentration of ≤ 5 mg.l⁻¹ after shaking for 5 min.

Effect of temperature

Studies of the influence of temperature on the flotation efficiency of Pb²⁺ ions seemed to be important

Table 1: Effect of temperatures on the floatability (%) of 3 mg.l⁻¹ Pb²⁺ ions at pH 7 using 1000 mg.l⁻¹ of LS and 1×10⁻³ mol.l⁻¹ of HOL with or without shaking for 5 min.

Temperature, $^{\circ}$C	% F without shaking	% F with shaking, 5 min
3	90.0	99.2
5	94.0	99.9
10	95.0	99.9
30	95.9	100.0
40	97.2	99.9
60	96.3	99.7
70	96.4	99.6
90	91.1	99.5

Table 2: Floatability (%) of 3 mg.l⁻¹ Pb²⁺ ions from different solution volumes at pH 7 using 1000 mg.l⁻¹ of LS and 1×10⁻³ mol.l⁻¹ of HOL with or without shaking for 5 min.

Volume, ml	% F without shaking	% F with shaking, 5 min
10	90.0	99.9
20	94.0	99.9
50	95.1	98.9
100	95.9	98.0
250	97.2	97.9
500	96.3	97.7
1000	90.4	97.6

from a practical viewpoint, especially in the case of hot industrial effluents. For such studies, one solution containing 3 mg.l⁻¹ Pb²⁺ ions and 1000 mg.l⁻¹ of LS and a second solution containing 1×10⁻³ mol.l⁻¹ of HOL were either heated or cooled to the same temperature using a water bath. The surfactant solution was quickly poured onto the Pb²⁺ solution contained within a flotation cell jacketed with 1-cm thick fiberglass insulation. The mixture was then floated using the previously described procedure. The results obtained (table 1) indicated that the percentage removal of Pb²⁺ ions (~ 100%) was not markedly affected by raising the temperature from 3 to 90 $^{\circ}$C after shaking for 5 min. Therefore, the simple procedure presented here may find application in the removal of Pb²⁺ ions from hot industrial wastewater.

Effect of shaking time

The effect of manually shaking time (2-30 min) on the floatability of 3 mg.l⁻¹ Pb²⁺ ions was investigated at pH 7 using 1×10⁻³ mol.l⁻¹ of HOL. The data obtained showed the removal of Pb²⁺ ions almost quantitatively (~ 100%) after shaking from 5 to 30 min. So, 5 min shaking was recommended for all experiments in this investigation.

Floatability of lead(II) ions from different volumes

The floatability (%) of 3 mg.l⁻¹ Pb²⁺ ions from different solution volumes (10 - 1000 ml) using 1000 mg.l⁻¹ of LS and 1×10⁻³ mol.l⁻¹ HOL at pH 7 with or without shaking for 5 min was investigated. The data obtained (table 2) revealed that after shaking for 5 min the floatability percentage of Pb²⁺ ions was satisfactory up to 1000 ml

solution. This means that the simple recommended procedure may be expected to apply on a large scale.

Effect of foreign ions

Under the optimized conditions determined as above, the percentage removal of 3 mg.l⁻¹ Pb²⁺ ions from a solution of pH 7 containing 1000 mg.l⁻¹ of LS and 1×10⁻³ mol.l⁻¹ HOL was studied (with and without shaking for 5 min) in the presence of high concentrations of various cations and anions, usually found in some water samples. All cations were used as their nitrates whereas the anions were used as their sodium or potassium salts. The cations and anions were investigated separately not in combination. The tolerable amounts of each ion giving a maximum error of $\pm$ 2% in the flotation efficiency are summarized in table 3. An inspection of the data indicates that all the investigated cations and anions did not interfere. However, it should be noted that higher concentrations of Al³⁺, Cr³⁺, Co²⁺ or Ni²⁺ could have harmful effect on the removal process. This may be due to competition between these cations and Pb²⁺ ions for sorption onto the active sites of LS. This problem could be overcome by increasing the amount of sorbent. Thus, the recommended procedure could be fairly employed for the removal of Pb²⁺ ions from various complex water samples.

Application

To investigate the applicability of the recommended procedure, a series of experiments was performed to recover 3.0 and 5.0 mg of Pb²⁺ ions added to aqueous and

Table 3: Effect of some selected foreign ions on the floatability (%) of 3 mg.l^{-1} Pb^{2+} ions at pH 7 using 1000 mg.l^{-1} LS , and 1×10^{-3} mol.l^{-1} HOL , with or without shaking for 5 min.

Cation	Concentration, ×10^3 (mg.l^{-1})	% F		Anions	Concentration, ×10^3 (mg.l^{-1})	% F	
		Without shaking	With 5 min shaking			Without shaking	With 5 min shaking
Na$^+$	11.5	82	98	Cl$^-$	17.8	81	99
Ba^{2+}	6.9	87	99	I$^-$	65.3	92	99
NH$_4^+$	9	88	99	CO$_3^{2-}$	3	72	99
K$^+$	19.5	92	99	SO$_4^{2-}$	48	94	99
Mg^{2+}	12.2	72	98	NO$_3^{2-}$	31	83	99
Ca^{2+}	2	83	97	S^{2-}	16	81	98
Co^{2+}	0.3	80	98	CH$_3$COO$^-$	5.5	80	99
Ni^{2+}	0.3	80	98	Cr$_2$O$_7^{2-}$	108	83	98
Cu^{2+}	1.8	75	98	Citrate	29	85	99
Cd^{2+}	1.13	87	99	S$_2$O$_3^{2-}$	5.6	80	97
Mn^{2+}	1.2	85	97				
Al^{3+}	0.04	73	97				
Cr^{3+}	0.04	73	97				

some natural water samples. The sorpetive-flotation experiments were carried out using 1 l of clear, filtered, uncontaminated sample solutions after adjusting their pH values to 7.0. The results obtained are listed in table 4 and show that the recovery was satisfactory and quantitative (~ 100 %). Moreover, the data indicated that the method could be successfully applied for the separation of Pb^{2+} ions from natural water samples containing large amounts of salt matrix under the recommended conditions.

Adsorption and flotation mechanism

Before discussing the possible sorptive-flotation mechanism involved, the following points need to be taken into consideration:

1- Most metal cations are removed by: i) adsorption on solid phases via coprecipitation of their insoluble hydroxides; ii) flocculation by adsorption of hydrolytic products; iii) ion exchange or iv) complexation with specific surface sites, provided that the appropriate conditions prevail [29, 30].

2- As a function of solution pH [3, 26], lead species may exist as soluble Pb^{2+}and hydroxo-species [Pb(OH)$^+$ and Pb(OH)$_3^-$] in addition to the insoluble lead hydroxide Pb(OH)$_2$.

3- The powdered limestone (LS) consists mainly of calcite (CaCO$_3$). When calcite (as 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 [24]. 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 by stirring the LS 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 well agree with the literature data that most natural surfaces are negatively charged [31].

4- Oleic acid (HOL) surfactant begins to dissociate at pH ≥ 5.2 [22].

Therefore, the proposed mechanism may occur as follows. At pH < 4, 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 similar manner to that reported [27]. Adsorbed lead ions generally occupy calcium sites within the calcite lattice [28]. Also, adsorption may take place through precipitation of lead

Table 4. Recovery of Pb^{2+} ions from various natural water samples of pH 7 using 1000 $mg.l^{-1}$ of LS and 1×10^{-3} $mol.l^{-1}$ HOL after shaking for 5 min.

Sample (location)	Added Pb^{2+} ($mg.l^{-1}$)	Found Pb^{2+} ($mg.l^{-1}$)	% F
Tap water (our laboratory)	2.997 5.000	5.8 7.8	99.9 100.0
Nile water (Mansoura City)	2.994 4.995	5.82 7.7	99.8 99.9
Sea water (Gamasah)	2.991 4.990	5.6 7.5	99.7 99.8
Underground water (Salaka)	2.967 4.965	5.7 7.8	98.9 99.3
Lake water (El-Manzala)	2.943 4.950	5.75 7.65	98.1 99.0

carbonate on LS surface according to the following equations [32]:

$$CaCO_3^0 + M^{2+} + HCO_3^- = CaCO_3 (s) + \equiv MCO_3^0 + H^+ \quad (3)$$

$$\equiv MCO_3^0 + M^{2+} + HCO_3^- = MCO_3 (s) + \equiv MCO_3^0 + H^+ \quad (4)$$

The adsorbent-adsorbate system is made hydrophobic by combination with un-dissociated oleic acid molecules. Such combination may occur through hydrogen bonding of the hydroxide group of HOL as confirmed by the appearance of an absorption band at 2926 cm^{-1} during IR spectral analysis of LS - HOL system.

In the pH range 4-10, where the maximal removal of Pb^{2+} ions occurred, adsorption may take place between $Pb(OH)^+$, the predominant species in this pH range, and the surface of limestone via hydrogen bonding. The aggregates of LS-Pb^{2+} being made hydrophobic by combination with un-dissociated oleic acid through hydrogen bonding and/or chemically with oleate anions. These hydrophobic aggregates are floated to solution surface with the aid of air bubbles.

At pH > 10, the removal of Pb^{2+} ions decreases, which may be attributed to the incapability of adsorption of the negative species, $Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$ and/or negative oleate ions on the negative surface of LS sorbent as confirmed by zeta potential measurements.

CONCLUSIONS

This investigation presented powdered limestone as inorganic sorbent which is abundant in nature, low in cost and have minimal environmental impact for restoration or remediation of natural resources. It is effective in removing Pb^{2+} ions from aqueous solutions, tap water and natural water samples. The experimental results revealed that this simple sorptive-flotation procedure, using LS as

a sorbent and oleic acid as a surfactant, succeeded in removing nearly 99% of Pb^{2+} ions from aqueous solutions at pH 7 after shaking for 5 min and at room temperature (~25 ^{o}C). The sorption of lead ions onto LS may proceed via cation exchange, precipitation of lead hydroxide and/or lead carbonate. The adsorbent-adsorbate system is made hydrophobic by combination with un-dissociated oleic acid molecules perhaps through hydrogen bonding. 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., Coca Shells for Heavy Metal Removal from Acidic Solutions, *Bioresource Technol.*, **90**, 255 (2003).

[2] Yan, G. and Viraraghavan, T., Heavy Metal Removal from Aqueous Solution by Fungus *Mucor rouxii*, *Water Res.*, **37**, 4446 (2003).

[3] Sheng, P.X., Ting, Y.P., Chen, J.P., and Hong, L., Sorption of Lead, Copper, Cadmium, Zinc and Nickel by Marine Algal Biomass: Characterization of Biosorptive Capacity and Investigation of Mechanisms, *J. Colloid Interface Sci.*, **275**, 131 (2004).

[4] Ho, Y.S., Ng, J.C.Y., and McKay, G. Removal of Lead(II) from Effluents by Sorption on Peat Using Second Order Kinetics, *Sep. Sci. Technol.*, **36**, 241 (2001).

[5] Freedman, R., Olson, L., and Hoffer, B.G., Toxic Effects of Lead on Neuronal Development and Function, *Environ. Health Perspect.*, **89**, 27 (1990).

[6] Goldstein, G.W., Lead Poisoning and Brain Cell Function, *Environ. Health Perspect*, **89**, 91 (1990).

[7] Grocetti, A. F., Mushak, P. F. and Schwartz, A. D., 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**, 109 (1990).

[8] Aldrich, R., Wlodarczyk, J. and Hensley, M.J., Children Blood Lead Levels and Environmental Lead Contamination, *Med. J. Aust.*, **185**, 506 (1993).

[9] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profiles, U.S. Department of Health and Human Services, Public Health Service, Atlanta (1999).

[10] van den Brandt, P., Voorrips, L., Hertz Picciotto, I., Shuker, L., Boeing, H., Speijers, G., Guittard, C., Knowles, M., Wolk, A. and Goldbohm, A., The Contribution of Epidemiology, *Food Chem. Toxicol.*, **40**, 387 (2002).

[11] Brach Papa, C., Coulomb, B., Boudenne, J.L., Cerda, V. and F. Theraulaz F., Spectrophotometric Determination of Aluminum in Drinking Waters by Sequential Injection Analysis, *Anal. Chem. Acta*, **457**, 311 (2002).

[12] Leyden, D.E. and Wegscheider, W., Preconcentration for Trace Element Determination in Aqueous Samples, *Anal. Chem.*, **53**, 1059A (1981).

[13] Mizuike, A., Fresenius, Z., Preconcentration Techniques for Inorganic Analysis, *Anal. Chem.*, **324**, 672 (1986).

[14] Ghazy, S. E., Samra, S. E., Mahdy, A. M. and El-Morsy, S.M., Removal of Aluminum from Water Samples by Sorptive-Flotation Using Powdered Modified Activated Carbon as a Sorbent and Oleic Acid as a Surfactant, *Anal. Sci.,* **22**, 377 (2006).

[15] Zouboulis, A.I., Lazaridis, N.K., Zamboulis, D., Powdered Activated Carbon Separation from Water by Foam Flotation, *Sep. Sci. Technol.*, **29**, 385 (1994).

[16] Stoica, L., Dinculescu, M., Plapcianu, C.G., Mn(II) Recovery from Aqueous Systems by Flotation, *Water Res.*, **32**, 3021 (1998).

[17] Ghazy, S.E., Samra, S.E., Mahdy, A.M. and El-Morsy, S.M., Flotation-Separation of Aluminum from some Water Samples Using Powdered Marble Waste and Oleic Acid, *Anal. Sci.*, **19**, 1401 (2003).

[18] Rubio, J., Souza, M. L., Smith, R. W., Overview of Flotation as a Wastewater Treatment Technique, *Minerals Eng.*, **15**, 139 (2002).

[19] Gómez del Río, J.A., Morando, P.J. and Cicerone, D.S., 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**, 169 (2004).

[20] Komnitsas, K., Bartzas, G. and Paspaliarise, I., Efficiency of Limestone and Red Mud Barriers: Laboratory Column Studies, *Minerals Eng.*, **17**, 183 (2004).

[21] Bailey, S.E., Olin, T.J., Bricka, R.M. and Adrian, D.D., A Review of Potentially Low Cost Sorbents for Heavy Metals, *Water Res.*, **33**, 2469 (1999).

[22] Ghazy, S.E., Samra, S.E., El-Morsy, S.M., Removal of Copper(II) from Aqueous Solutions Using Limestone Fines as the Sorbent and Oleic Acid as the Surfactant, *Adsorp. Sci. Technol.*, **19** 175 (2001).

[23] Bates, R.L., Jackson, J.A., "Glossary of Geology", 2nd Ed., American Geological Institute: Falls Church, VA, (1980).

[24] Somasundran, P. and Agar, G.E., Zero Point of Charge of Calcite, *J. Colloid Interface Sci.,* **24** 433 (1967).

[25] Ghazy, S.E., Removal of Cadmium, Lead, Mercury, Tin, Antimony, and Arsenic from Drinking and Seawaters by Colloid Precipitate Flotation, *Sep. Sci. Technol.*, **30**, 933 (1995).

[26] Bradl, H.B., Adsorption of Heavy Metal Ions on Soils and Soils Constituent, *J. Colloid Interface Sci.*, **277**, 1 (2004).

[27] Mandjiny, S., Zouboulis, A.I. and Matis, K.I., Removal of Cadmium from Dilute Solutions by Hyroxyapatite, Part I. Sorption Studies, *Sep. Sci. Technol.*, **30**, 2963 (1995).

[28] Chermiak, D.J., An Experimental Study of Sr and Pb Diffusion in Calcite and Its Implications for Carbonate Diagnosis and Metamorphism., Geochimica et Cosmochimica Acta, **61**, 4173 (1997).

[29] Apak, R., Tutem, R, Hugul, M. and Hizal, J., Heavy Metal Cation Retention by Conventional Sorbents (Red Mud and Fly Ashes), *Water Res.*, **32**, 430 (1998).

[30] Zouboulis, A.I., Kydros, K.A. and Matis, K.A., Removal of Hexavalent Chromium Anions from Solutions by Pyrite Fines, *Water Res.*, **29**, 1755 (1995).

[31] Rosen, MJ., "Surfactants and Interface Phenomena", 2nd Ed., John Wiley & Sons Inc.: New York, (1989).

[32] Zhu, C., Estimation of Surface Precipitation Constants for Sorption of Divalent Metals onto Hydrous Ferric Oxide and Calcite, *Chem. Geol.*, **188**, 23 (2002).