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Adsorption of Lead(II) Ions by Sorptive-Flotation Technique from Synthetic Solution Using Powdered Palm Fronds and Oleic Acid

Salem M. El-Nakeib

Department of Chemistry, Alasmarya Islamic University, Zliten City, Libya.
E-mail: sma7228@yahoo.com

امتزاز أيونات الرصاص بواسطة تقنية التعويم الإمتزازي من محاليل صبغية باستخدام مسحوق سعف النخيل وحمض الآوليك كعامل سطحي نشط

سالم محمد النقيب

قسم الكيمياء، الجامعة الأسمرية الإسلامية، زليتن، ليبيا

Abstract

Heavy metals are the largest class of contaminants and also the most difficult to treat. Lead Pollution impacts all the systems of the human body. Many of the methods were utilized to remove lead from west water. Therefore, this study was carried out to examine the potential and effectiveness of using powdered palm fronds, which were prepared from palm fronds (a cheap agricultural and non-toxic material) to remove lead from water. A series of bench–scale experiments were conducted in the laboratory, aiming to assess the feasibility of using powdered palm fronds (PF) as an effective biosorbent and oleic acid (*HOL*) as a surfactant. The effects of the process variables such as; initial solution pH, sorbent, surfactant, lead concentration, and shaking time that influences the biosorption–flotation process were examined. Promising results were obtained under the optimum conditions, according to which nearly 100% of lead, at pH 7 at room temperature (~25°C) was removed. Moreover, a sorption and flotation mechanism is suggested.

Keywords: *Lead, Sorptive-Flotation, Powdered palm fronds, Oleic acid.*

الملخص

تلوث العناصر الثقيلة يكون أكبر طبقة من الملوثات وهو صعب جداً في المعالجة , وتلوث الرصاص يؤثر علي كل الأنظمة في جسم الأنسان، ولذلك تم في هذا البحث اختبار كفاءة مسحوق سعف النخيل وهي مواد طبيعية رخيصة الثمن وغير مكلفة لإزالة أيونات الرصاص الثنائي, وتم عمل تجارب معملية بهدف إزالة أيونات الرصاص الثنائي من الوسط المائي ولقد اعتمدت التجارب علي استخدام مسحوق سعف النخيل كسطح امتزاز فعال وتم استخدام حمض الآوليك كعامل سطحي نشط, كما تم دراسة تأثير العوامل المختلفة والتي تؤثر تأثيراً مباشراً علي عملية التعويم الامتزازي الحيوي مثل (الأس الهيدروجيني, تركيزات كل من الرصاص الثنائي, سطح الامتزاز، العامل السطحي النشط, درجة الحرارة, ووقت الرج). تم الحصول على نتائج جيدة وذلك عند أس هيدروجيني (7)، وعند درجة حرارة الغرفة (25±2مº) وكانت عملية الفصل 100%. أخيراً تم اقتراح ميكانيكية لعملية الامتزاز.

كلمات دلالية: الرصاص، التعويم الإمتزازي، مسحوق سعف النخيل، حمض الآوليك.

1. Introduction

Heavy metal contamination of water is an important environmental problem that poses a threat to human health. Lead is a priority toxic pollutant in wastewater discharged from industries such as metal mining, melting, planting, batteries, pesticides, oil paint, pigments, and alloys (Sulaymon *et al*., 2013a; and Sulaymon *et al*., 2013b). At certain exposure levels, lead is a poisonous substance to human. It damages nervous system and causes blood and brain disorders. Long-term exposure to lead or its salts can cause nephropathy, and colic-like abdominal pains (Shakir *et al*., 2010).

The environmental significant of these metals is partly attributed to their presence in industrial effluent and other sources of waste (Yadla *et al*., 2012). Therefore, the removal of these metal ions is necessary in order to forestall the manifestation of their toxic impact through bioaccumulation and biomagnification along the food chain (Stoica *et al*., 2012). These techniques may involve: chemical precipitation, ion exchange, reverse osmosis, electrodeposition, adsorption, solvent extraction and flotation separation processes. So, adsorption has proved to be an effective technique, but it may suffer from economic palm fronds owing to difficulties encountered in separating sorbent from suspension in order for it to be regenerated (Sulaymon and Mohammed, 2010). 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, and good separation yields (R>95%) for small impurity agent concentrations ranged between (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 (Aboabboud *et al*., 2013; Okasha *et al.*, 2012; Abo-El-Enein *et al*., 2011; Okasha and Ibrahim, 2010; Al-Meshragi *et al.*, 2009; and Ghazy *et al.*, 2001). It is believed that this process will soon be incorporated as a clean technology to treat water and wastewater (Liao *et al*., 2010).

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 (Yanqing *et al.*, 2012). Palm fronds (PF), which is produced in large quantities in many countries (among them is Libya), is a low-cost reactive medium that can be used for retaining heavy metals and the subsequent cleanup of industrial effluents, leachates and contaminated ground water (Murugesan *et al.*, 2011). Hence, the present work aims to establish a selective, rapid and simple sorptive-flotation procedure using PF (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.

2. Materials and Methods

2.1. Sorbent

Palm fronds were provided from Zliten area north Tripoli City, (Libya). The palm fronds were first dried to obtain minimum humidity. Then, the dried sample was washed several times with double distilled water. After collecting sufficient quantities, the washed adsorbent was heated in a furnace an over at temperature of 120 ^{o}C for time of two days. The samples were crushed and pulverized in the laboratory and 500 μm particle size range was used in the experiments. The sample contained (Yanqing *et al.*, 2012), 92% calcite ($CaCO_3$) and 3% ($MgCO_3$), the prepared samples were stored in air tight bottles and placed $CaCl_2$ desiccators until use in experiments (Murugesan *et al.,* 2011).

2.1.1. Sorbent Characteristics

Surface carbon-oxygen groups and used to obtain information about the nature of possible interaction between the functional groups present on PF surface with pb^{2+}. The PF sample was diluted with *KBr*, compressed into wafer and FT-IR spectrum was recorded by (FT-IR-6100 type A) spectrophotometer. The results obtained is given in Figure (1). A variety of *C-O* (carbon oxygen) surface functional groups were observed in the PF sample: *O-H* stretching mode of hydroxyl groups and adsorbed water, carbonyl group, *C-O* stretching in acids, alcohols, phenols, ethers, and esters.

2.1.1.1. Fourier Transform- Infrared Spectroscopy (FT-IR)

FT-IR investigates the surface carbon-oxygen groups and used to obtain information about the nature of possible interaction between the functional groups present on PF surface with Pb^{2+}. The PF sample was diluted *KBr*, compressed into wafer and FT-IR spectrum was recorded by (FT-IR-6100 type A) spectrophotometer. The results obtained is given in Figure (1). A variety of *C-O* (carbon oxygen) surface functional groups were observed in the PF sample: *O-H* stretching mode of hydroxyl groups water, carbonyl group, *C-O* of phenolic, carbonyl and carboxylic groups were present in the FT-IR spectrum of activated carbon. The presence of such methylene groups induces hydrophobicity into the PF sample.

2.1.1.2. Surface Morphology

A scanning electron microscope (SEM) was used to examine the surface of PF sample in Figure (2), and EDX pattern of PF after lead adsorption in Figure (3). The SEM image show a porous morphology of the surface with pores of different sizes and shapes. These pores act as active sites for lead adsorption.

2.1.1.3. Surface Area Determination

The surface area of the sorbent was determined from the respective nitrogen adsorption isotherms by applying the conventional BET equation and found to be 138 $m^2.g^{-1}$.

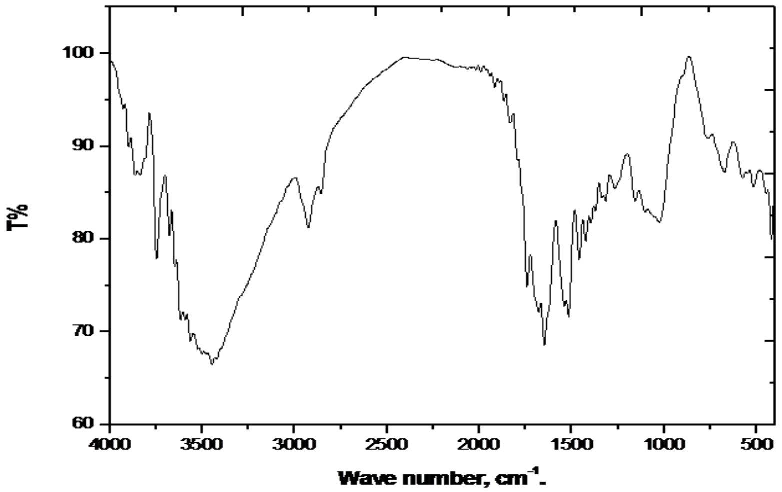

Figure 1. FT-IR spectrum of PF sample

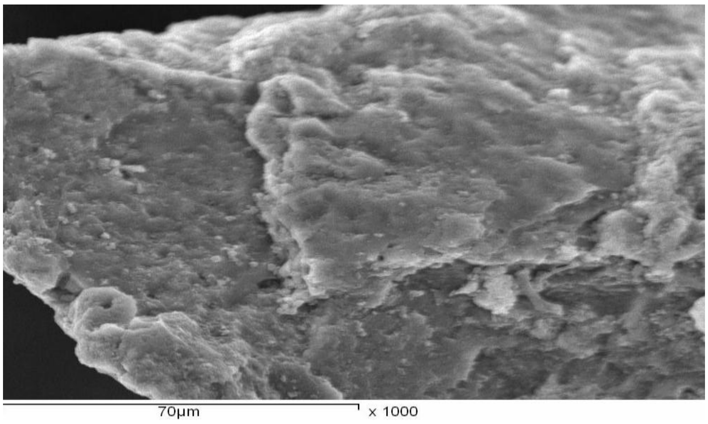

Figure 2. SEM image of PF sample after treatment with *Pb(II)*

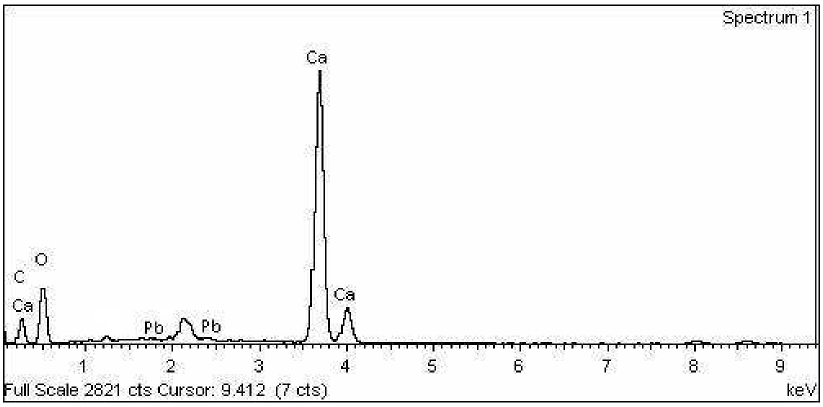

Figure 3. EDX image of PF sample after treatment with *Pb(II)*

2.2. Solutions

All the solutions were prepared from certified reagent grade chemicals. A lead nitrate $Pb(NO_3)_2$ stock solution (1000 $mg.l^{-1}$) 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 *ml* of *HOL* in 1 *l* of kerosene. Aqueous solutions of *HCl* and *NaOH* were used for pH adjustments.

2.3. Experimental Set-up

The residual *Pb(II)* concentrations in the filtrate was analyzed by AAS spectrometry at 327.4 *nm* using a perkin-Elmer Atomic Absorption Spectrophotometer with air-acetylene flame. Also to study the various parameters affecting the sorption-flotation process, a 10 *ml* aliquot of a suspension containing 3.0 $mg.l^{-1}$ of Pb^{2+} ions and 1000 $mg.l^{-1}$ of sorbent (PF) 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 PF. Then 3 *ml* of 1×10^{-3} $mol.\ l^{-1}$ *HOL* was added. The cell was again inverted twenty times by hand and allowed to stand for 5 *min.* to complete flotation.

The residual Pb^{2+} ion concentrations in the mother liquor was analyzed using a Perkin-Elmer atomic absorption and spectrophotometer. The removal percentage of Pb^{2+} ions (%*R*) was calculated from the relationship;

$$R\,\% = (C_i - C_r)/C_i\times100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (1)$$

Where C_i and C_r denote the initial and residual Pb^{2+} ion concentrations. After complete flotation, the PF-containing float was filtered through a G5 sintered-glass filter (porosity, 1-1.5 μm) and dried to constant weight in an oven at 125 ºC. The percentage floatability of PF (%*F*), was calculated from;

$$F\,\% = C_f/C_i\times100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

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

3. Results and Discussion

3.1. Floatability of Powdered Palm Fronds

The removal of fine particles of (PF) sorbent from aqueous solution (particularly those that passed through a filtration medium) was an obvious economic measure for the undertaken studies.

3.1.1. 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 preliminary of the experiments was conducted to float 60 *mg.l*$^{-1}$ of PF over a wide range of pH values (1-10) using 1×10^{-3} *mol.l*$^{-1}$ of *HOL*. The obtained results are depicted in Figure (4), from which it is clear that flotation percentage increased as pH increased from 1 to 5 then a maximum flotation (~100%) for PF was attained over a wide pH range 6-9.

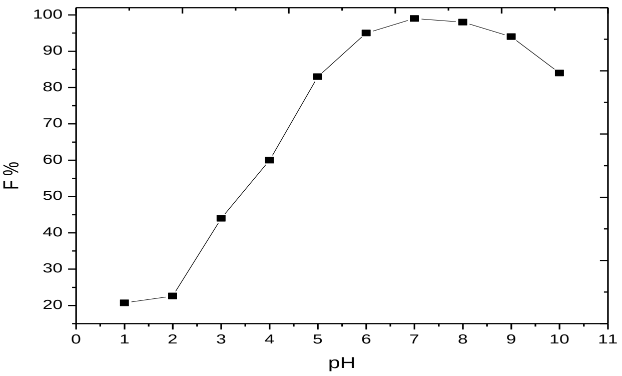

Figure 4. Floatability of 60 *mg.l*$^{-1}$ of PF using 1×10^{-3} *mol.l*$^{-1}$ of *HOL* at different pH values.

3.1.2. Effect of Surfactant Concentration

The separation of 60 *mg.l*$^{-1}$ of PF using different concentration of oleic (*HOL*) surfactant at pH 7 is presented in Figure (5). The results proved that oleic acid is an effective surfactant for a quantitative removal (~100%) of the sorbent at lower concentration ($1\sim2\times10^{-3}$ *mol.l*$^{-1}$). In general, it was found that for the undertaken studies the recommended *HOL* concentration was (1×10^{-3} *mol.l*$^{-1}$).

3.1.3. Effect of Sorbent Concentration

Two parallel series of experiments were conducted to study the influence of powdered Palm fronds concentration as shown in Figure (6). Another series of experiments was carried out to float different concentration of PF sample using 1×10^{-3} *mol.l*$^{-1}$ of *HOL* at pH 7. Quantitative separation (~100%) of the sorbent was attained over a wide concentration range (up to 100 *mg.l*$^{-1}$) then the flotation percentage decreased after 100 *mg.l*$^{-1}$. Hence, for all experiments the recommended concentration of PF is 60 *mg.l*$^{-1}$.

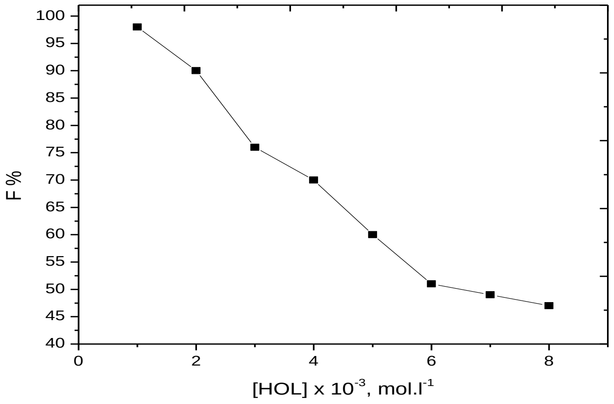

Figure 5. Flotation of 60 *mg.l^{-1}* of PSG at pH 7 using different concentration of *HOL*.

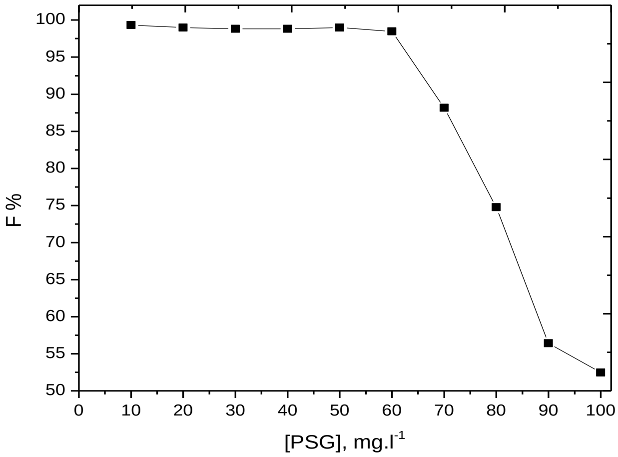

Figure 6. Floatability of different concentration of PF using 1×10^{-3} *mol.1^{-1} HOL* at pH 7.

3.1.4. Effect of Temperature

In order to find the suitable temperature for flotation of 60 *mg.l^{-1}* of PF at pH using (1×10^{-3} *mol.l^{-1}*) *HOL*, an extensive series of experiments was carried out at different temperatures. The results recorded in Figure (7). Show that the floatability of sorbent not affected by increasing the temperature up to 80 *^{o}C*.

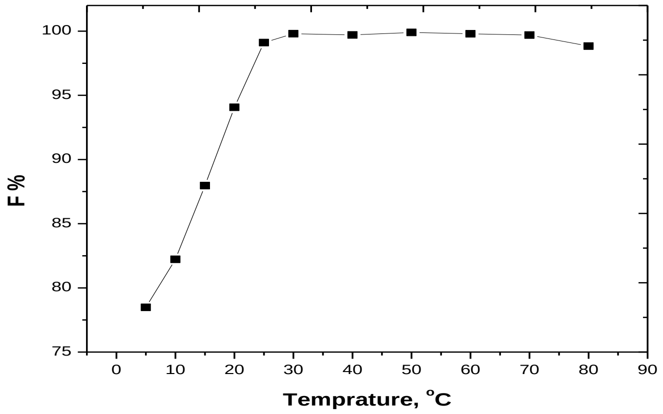

Figure 7. Effect of temperature on the flotation of 60 *mg.l*$^{-1}$ of PF using (1×10^{-3} *mol.l*$^{-1}$) *HOL* at pH 7.

From the previous results it is obvious that the process is economic and effective (F~ 100%) since it needs small concentration of surfactant (1×10^{-3} *mol.l*$^{-1}$) from *HOL* to float high concentration of PF (60 *mg.l*$^{-1}$) and acting at a wide range of pH from 6 to 9 and temperature range between (20-80 ^{o}C).

3.2. Removal of Lead Ions

3.2.1. Effect of pH

In order to find the optimal pH value for the biosorptive-flotation process, the removal efficiency of Pb^{2+} ions over the pH range (1-10) was studied as presented in Figure (8) illustrates the influence of the pH on the combined process of sorption and flotation for the removal of 30 *mg.l*$^{-1}$ of Pb^{2+} ions using 60 *mg.l*$^{-1}$ of PF and (1×10^{-3} *mol.l*$^{-1}$) of *HOL*.

It should be noted that the removal of Pb^{2+} ions was diminished at (pH< 5.0), which may be attributed to the fact that at strong acidic medium at higher H^+ ions concentration, the adsorbent surface becomes more positively charged thus reducing the attraction between adsorbent and metal ions.

When the pH increases, the concentration of hydronium ion (H_3O^+) is very low, biosorbent surface was more negatively charged, and function group of biomass were more deprotonated in a wide range of pH from 5 to 9, thus the sites are easily available for metal ion bonding. So the proton competition was decreased, and the removal percentage of metal ions is increased. The decrease in the removal rate at high pH values (>9) may be attributed to the fact that oleate anions ion are not capable of combination with the negative surface of PF. Therefore, pH 7 was recommended throughout all other experiments.

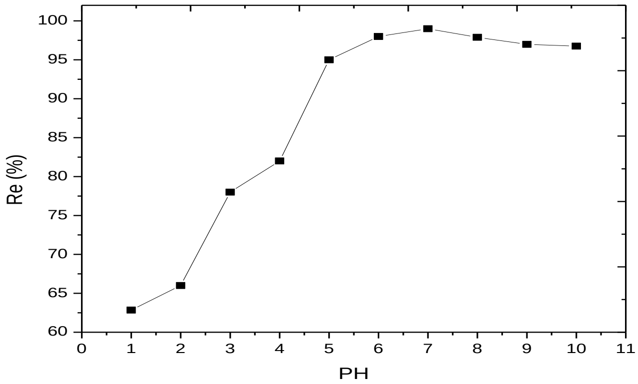

Figure 8. The effect of pH on the removal of Pb^{2+}.

3.2.2. Effect of Sorbent and Metal Ion Concentration

Two parallel series of experiments were conducted to study the influence of powdered Palm fronds concentration (Figure 9) and changing the lead ion concentration (Figure 10) on the removal percentage of Pb^{2+} ions from aqueous solutions at pH 7 using 1×10^{-3} *mol.l*$^{-1}$ of *HOL* without or with shaking for 5 *min.* As shown in Figure (9), the removal percentage of Pb^{2+} ions increased as the PF dose increased, while it decreased as the concentration of the metal ion increased as presented in Figure (10). The reason for attaining a maximum removal of Pb^{2+} ions (~100 %) at higher PF dose, after shaking for 5 *min.* may be due to an increase in the number of binding sites on the sorbent available to Pb^{2+} ions. Hence, 60 *mg.l*$^{-1}$ of PF may be a suitable dose for the removal of Pb^{2+} ions having a concentration of ≤ 30 *mg.l*$^{-1}$ after shaking for 5 *min.*

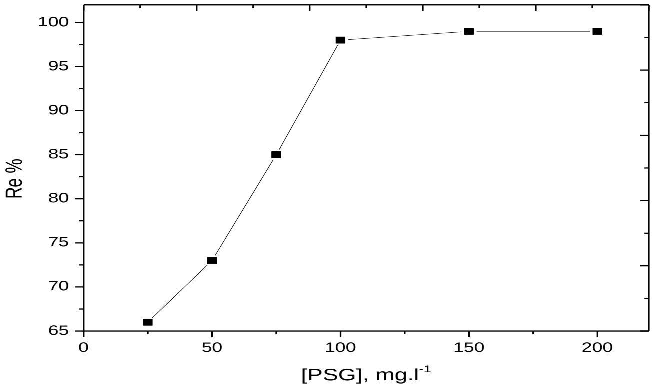

Figure 9. Effect of adsorbent dosage on the removal of Pb^{2+}.

3.2.3. Effect of Surfactant Concentration

A series of experiment was conducted at pH 7 in the absence and presence 60 *mg.l*$^{-1}$ PF using different concentrations of *HOL*. The results obtained are presented in Figure (10). It can be seen that the removal of Pb^{2+} ions attained a maximum value (~100 %) in the absence of PF. An enhancement in the flotation efficiency of Pb^{2+} ions to (~100%) was achieved after shaking for 5 *min*. These maximal workers (Murugesan *et al*., 2011) 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 experiments.

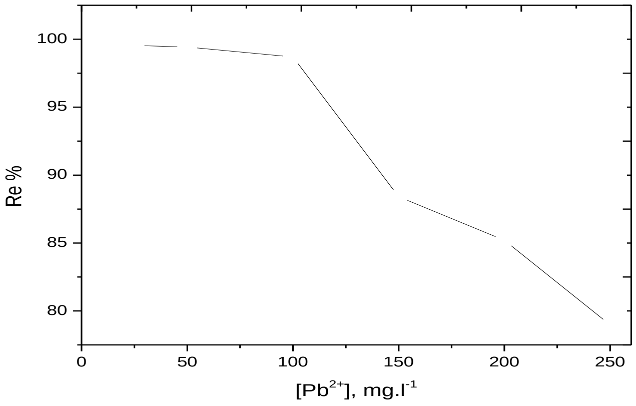

Figure 10. Effect of initial metal ion concentration on the removal of Pb^{2+}.

3.2. 4 Effect of Shaking Time

The effect of manually shaking time (1-10 *min*.) on the floatability of 30 $mg.l^{-1}$ of Pb^{2+} ions was investigated at pH 7 using 1×10^{-3} $mol.l^{-1}$ of *HOL*. The results obtained in Figure (11) showed the removal of Pb^{2+} ions almost quantitatively (~100%) after shaking from 5 to 30 *min*. So, 5 *min.* shaking was recommended for all experiments in this investigation.

3.2.5. Effect of temperature

Studies of the influence of temperature on the separation process seemed to be important from a practical viewpoint, especially in the case of hot industrial effluents. For such studies, one solution containing 30 $mg.l^{-1}$ of pb^{2+} ions and 60 $mg.l^{-1}$ of PF 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 Pb^{2+} solution contained within a flotation cell jacketed with 1*cm* thick fiber glass insulation. The obtained results in Figure (12) indicated that the removal percentage of Pb^{2+} ions may proceed through chemical bond formation and the creation of new active sites on the surface of PF available for Pb^{2+} ions adsorption (Yanqing *et al*., 2012).

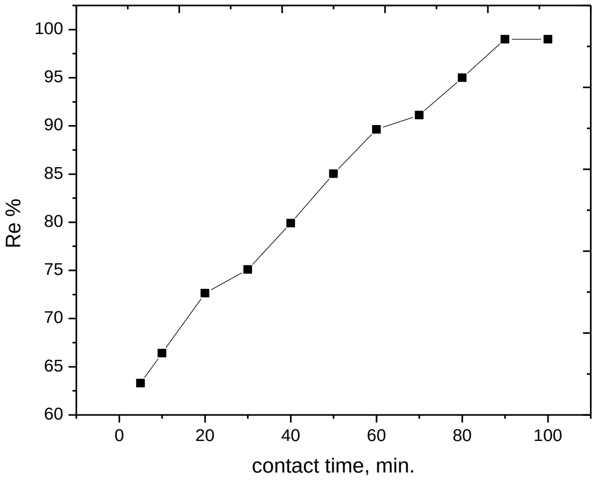

Figure 11. Effect of contact time on the removal of Pb^{2+}.

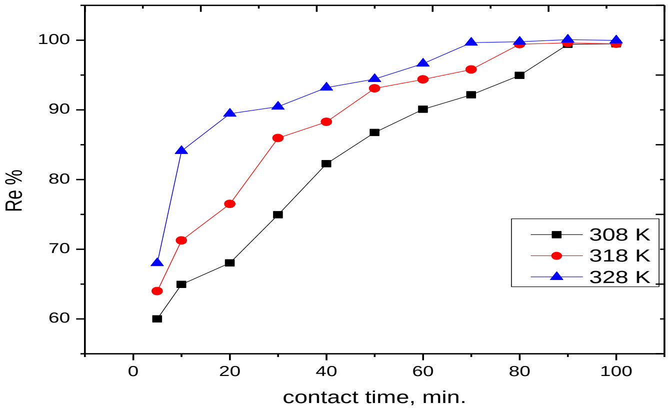

Figure 12. Effect of temperature on the removal of Pb^{2+}.

3.3. Application

To investigate the applicability of the recommended procedure, a series of experiments was performed to recover 10 $mg.l^{-1}$ of Pb^{2+} ions added to aqueous and some natural water samples. The sorptive-flotation experiments were carried out using 50 *ml* clear, filtered, uncontaminated sample solutions after adjusting their pH values to 7.0. The results shown in Table (1) 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.

Table 1. Recovery of Pb^{2+} ions added to some water samples using 60 $mg.l^{-1}$ of PF at pH 7

Serial No.	**Sample Location**	**Added Pb^{2+} Ions ($mg.l^{-1}$)**	***R* %**
1	Distilled Water	10	99.5
2	Tap Water	10	98.2
3	Industrial Exchange (Zliten City)	10	96.7
4	Ground Water (Zliten City)	10	99.2
5	Sea Water (Zliten City)	10	95.1
6	Wadi Ka'am (Zliten City)	10	97.3
7	Factory of Cement (Zliten City)	10	99.3

3.3.1. 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 (Liao *et al.*, 2010).
2. As a function of solution pH, 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 Palm fronds (PF) 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.

   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 PF sorbent with distilled water for 4 *hr* 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 will agree with the literature data that most natural surfaces are negatively charged (Gupta *et al.*, 2010).
4. Oleic acid (*HOL*) surfactant begins to dissociate at pH ≥ 5.2 (Yanqing *et al.*, 2012).

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- adsorption may take place through precipitation of lead. The adsorbent-adsorbate system is made hydrophobic by combination with un-dissociated oleic acid exchange mechanism between Pb^{2+} ions and calcium containing PF in similar manner to that reported (Murugesan *et al.*, 2011). Adsorbed lead ions generally occupy calcium sites within the calcite lattice. Also, molecules, such combination may occur through hydrogen bonding of the hydroxide group of *HOL* as confirmed by the appearance of an absorption band at 2829 cm^{-1} during IR spectral analysis of PF-*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 Palm fronds via hydrogen bonding. The aggregates of PF-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 PF sorbent as confirmed by zeta potential measurements.

4. Conclusion

This investigation presented powdered Palm fronds 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 PF 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 ^oC). The sorption of lead ions onto PF 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 PF 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.

Flotation technique which has advantages (compared with other separation methods) of being simple, inexpensive, less time consuming and expected to be soon incorporated as a clean technology to treat water and wastewater been applied in this investigation. Moreover, the removal of Pb^{2+} ions attained (~100%) in the presence of oleic acid as a cheap surfactant.

Reference

Aboabboud M., Ibrahim H.G., Okasha A., & Elatrash M.S. (2013). Investigation of Chromium Removal by Adsorption/Precipitation Techniques using Solid Waste Material. *Journal of Selcuk University Natural and Applied Science*, 2(2), 538-545.

Al-Meshragi M., Ibrahim H.G., & Okasha A.Y. (2009, May). Removal of trivalent chromium from aquatic environment by cement kiln dust: Batch studies. In: *AIP Conference Proceedings* (Vol. 1127, No. 1, pp. 74-85). American Institute of Physics.

Ghazy S.E., Samra S.E., and El-Morsy S.M. (2001). Removal of copper(II) from aqueous solutions by flotation using limestone fines as the sorbent and oleic acid as the surfactant. *Adsorption Science and Technology*, 19(2): 175–185.

Gupta V.K., Rastogi A., and Nayak A. (2010). Biosorption of nickel onto treated alga (*Oedogonium hatei*): Application of isotherm and kinetic models. *Journal of Colloid and Interface Science*, 342(2): 533–539.

Liao D., Zheng W., Li X., Yang Q., Yue X., Guo L., and Zeng G. (2010). Removal of lead(II) from aqueous solutions using carbonate hydroxyapatite extracted from eggshell waste. *Journal of Hazardous Materials*, 177: 126–130.

Murugesan A., Ravikumar L., Sathya Selva Bala V., Senthil-Kumar P., Vidhyadevi T., Dinesh Kirupha S., Kalaivani S.S., Krithiga S., and Sivanesan S. (2011). Removal of *Pb(II), Cu(II)* and *Cd(II)* ions from aqueous solution using polyazomethineamides, Equilibrium and kinetic approach. *Desalination*, 271: 199–208.

Okasha A.Y. & Ibrahim H.G. (2010). Removal of Cu^{2+} ions from aqueous solutions by adsorption on Libyan soil. *Journal of environmental science and engineering*, 4(10): 9-15.

Okasha A.Y., Ibrahim H.G., Elatrash M.S., & Marie A. (2012). Removal of cadmium from aqueous solutions using adsorption technique: kinetics and equilibrium. *Int J Environ Bioenergy*, 1: 105-118.

Shakir K.A., Elkafrawy F.H., Ghoneimy F.S., Elrab Beheir G., and Refaat M. (2010). Removal of rhodamine B (a basic dye) and thoron (an acidic dye) from dilute aqueous solutions and wastewater simulants by ion flotation. *Water Research*, 44(5): 1449–1461.

Stoica L., Dima G., Micu O., Oancea D., and Oproiu G. (2012). Heavy Metal Ions Removal by Biosorption—Flotation on Mycelial Wastes. *International Mine Water Association*, Granada, Spain.

Sulaymon A.H., and Mohammed A.A. (2010). Separation and hydrodynamic performance of air-kerosene-water system by bubble column. *International Journal of Chemical Reactor Engineering*, 8: 1–15.

Sulaymon A.H., Ebrahim S.E., and Mohammed-Ridha M.J. (2013b). Equilibrium, kinetic, and thermodynamic biosorption of *Pb(II), Cr(III),* and *Cd(II)* ions by dead anaerobic biomass from synthetic wastewater. *Environmental Science and Pollution Research*, 20(1): 175-187.

Sulaymon A.H., Mohammed A.A., and Al-Musawi T.J. (2013a). Competitive biosorption of lead, cadmium, copper, and arsenic ions using algae. *Environmental Science and Pollution Research*, 20(5): 3011-3023.

Yadla, S.V., Sridevi, V., and Lakshmi, M.C. (2012). Adsorption performance of fly ash for the removal of lead. *In International Journal of Engineering Research and Technology*, 1(7): (September-2012). ESRSA Publications.

Yanqing T., Chen M., and HaoY. (2012). High efficient removal of *Pb(II)* by amino functionalized Fe_3O_4 magnetic nano-particles, *Chemical Engineering Journal*, 191: 104– 111.