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

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Abstract

Heavy metals are the largest class of contaminants and also most difficult to treat. Lead Pollution impacts all the systems of the human body. Many of the methods 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 was 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 and lead concentration and shaking time that influence the biosorptive–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.
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 (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 over at temperature of 120 °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 (CaCO₃) and 3% (MgCO₃), the prepared samples were stored in air tight bottles and placed CaCl₂ 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 Pb²⁺. 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 Pb²⁺. 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 and adsorbed water, carbonyl group, C-O stretching in acids, alcohols, phenols, ethers, and esters.

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 m².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) was prepared and the working solutions were made by diluting the former with doubly distilled water. An oleic acid \( (HOL) \) stock solution \( 6.36 \times 10^{-2} \text{ mol.l}^{-1} \), 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 of \( Pb^{2+} \) ions and 1000 mg/l 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 \( 1 \times 10^{-3} \text{ mol. l}^{-1} \) 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;

\[
R \% = \frac{C_i - C_r}{C_i} \times 100
\]

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 \( \mu m \)) and dried to constant weight in an oven at 125 \( ^\circ \text{C} \). The percentage floatability of PF \((\% F)\), was calculated from;

\[
F \% = \frac{C_f}{C_i} \times 100
\]

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 \( ^\circ \text{C} \)).

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](image)

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 (1~2×10⁻³ 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.
3.1.4. Effect of Temperature

In order to find the suitable temperature for flotation of $60 \text{ mg} \cdot \text{l}^{-1}$ of PF at pH using $(1 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1})$ 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 $80 \degree \text{C}$. 

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

**Figure 6.** Floatability of different concentration of PF using $1 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ 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 \((1 \times 10^{-3} \text{ mol.L}^{-1})\) from HOL to float high concentration of PF \((60 \text{ mg.L}^{-1})\) and acting at a wide range of pH from 6 to 9 and temperature range between \((20-80^\circ C)\).

### 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 \(\text{Pb}^{2+}\) 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 \(\text{Pb}^{2+}\) ions using 60 mg.L\(^{-1}\) of PF and \((1 \times 10^{-3} \text{ mol.L}^{-1})\) of HOL.

It should be noted that the removal of \(\text{Pb}^{2+}\) ions was diminished at \((\text{pH} < 5.0)\), which may be attributed to the fact that at strong acidic medium at higher \(\text{H}^+\) 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 \((\text{H}_3\text{O}^+)\) 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.
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 \( \text{Pb}^{2+} \) ions from aqueous solutions at pH 7 using \( 1 \times 10^{-3} \text{ mol.l}^{-1} \) of HOL without or with shaking for 5 min. As shown in Figure (9), the removal percentage of \( \text{Pb}^{2+} \) 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 \( \text{Pb}^{2+} \) 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 \( \text{Pb}^{2+} \) ions. Hence, 60 mg.l\(^{-1}\) of PF may be a suitable dose for the removal of \( \text{Pb}^{2+} \) ions having a concentration of \( \leq 30 \text{ mg.l}^{-1} \) after shaking for 5 min.

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**Figure 8.** The effect of pH on the removal of \( \text{Pb}^{2+} \).

**Figure 9.** Effect of adsorbent dosage on the removal of \( \text{Pb}^{2+} \).
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 Pb²⁺ ions attained a maximum values (~100 %) in the absence of PF. An enhancement in the flotation efficiency of Pb²⁺ 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 Pb²⁺.](image)

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 Pb²⁺ 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 Pb²⁺ 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 Pb²⁺ 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 Pb²⁺ solution contained within a flotation cell jacketed with 1cm thick fiber glass insulation. The obtained results in Figure (12) indicated that the removal percentage of Pb²⁺ 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 \( Pb^{2+} \).](image)

![Figure 12. Effect of temperature on the removal of \( Pb^{2+} \).](image)

3.3. Application

To investigate the applicability of the recommended procedure, a series of experiments was performed to recover 10 mg.\text{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 Pb²⁺ ions from natural water samples containing large amounts of salt matrix under the recommended conditions.

Table 1. Recovery of Pb²⁺ ions added to some water samples using 60 mg.l⁻¹ of PF at pH 7

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Sample Location</th>
<th>Added Pb²⁺ Ions ( mg.l⁻¹)</th>
<th>R %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Distilled Water</td>
<td>10</td>
<td>99.5</td>
</tr>
<tr>
<td>2</td>
<td>Tap Water</td>
<td>10</td>
<td>98.2</td>
</tr>
<tr>
<td>3</td>
<td>Industrial Exchange (Zliten City)</td>
<td>10</td>
<td>96.7</td>
</tr>
<tr>
<td>4</td>
<td>Ground Water (Zliten City)</td>
<td>10</td>
<td>99.2</td>
</tr>
<tr>
<td>5</td>
<td>Sea Water (Zliten City)</td>
<td>10</td>
<td>95.1</td>
</tr>
<tr>
<td>6</td>
<td>Wadi Ka'am (Zliten City)</td>
<td>10</td>
<td>97.3</td>
</tr>
<tr>
<td>7</td>
<td>Factory of Cement (Zliten City)</td>
<td>10</td>
<td>99.3</td>
</tr>
</tbody>
</table>

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 Pb²⁺ and hydroxo-species $[Pb(OH)⁺$ and $Pb(OH)²⁻]$ in addition to the insoluble lead hydroxide Pb(OH)₂.
3. The powdered Palm fronds (PF) consists mainly of calcite ($CaCO₃$). When calcite (as sparingly soluble salt type mineral) is suspended with water, $HCO₃⁻$, $Ca²⁺$, $CaHCO₃⁺$ and $CaHO⁺$ are formed as surface-charged species and their presence is a function of solution pH. Moreover, OH⁻, $H⁺$ and $HCO₃⁻$ are considered as potential determining ions in addition to $Ca²⁺$ and $CaCO₃$. 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 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 $Pb(OH)\cdot\cdot\cdot$, 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, $Pb(OH)\cdot\cdot\cdot$ 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 °C). 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


