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Sorptive-Flotation Of Lead Using Powdered Modified Activated Carbon Sorbent Prepared From Olive Stones

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ABSTRACT

Environmental pollution, mainly in the aquatic systems, due to developments in industry, is one of the most significant problems of this century. Many industrial wastewater streams (ca. the metal working, semiconductor, and copper industries, mine water, etc.) contain heavy metals, which are of great environmental concern and must be removed prior to water discharge or water recycling. The present study aims to develop a simple, rapid and economic procedure for lead(II) removal under the optimum conditions. Laboratory-scale experiments were conducted in the laboratory, aiming to remove lead from water. They were based on using powdered activated carbon (PACI), which was prepared from olive stones generated as plant wastes and modified with aqueous oxidizing agent as $(NH_4)_2S_2O_8$, as an effective sorbent and oleic acid (HOL) as a surfactant. The main parameters (namely: initial solution pHs, sorbent, surfactant and aluminum concentrations, shaking time, ionic strength and the presence of foreign ions) that influence the sorptive-flotation process were examined. Good results were obtained at the optimum conditions, according to which nearly 100% of lead, at pH 7 and at room temperature (~25°C), was removed. The procedure was successfully applied to recover lead spiked to some natural water samples. Moreover, a sorption and flotation mechanism is suggested.

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 $mg{\cdot}l^{-1}$ 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 few 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, electrodeposition, adsorption, solvent extraction and flotation separation processes. Of these, adsorption has proved to be an effective technique. Activated carbons are unique and versatile adsorbents because of their extended surface area, micro-porous structure, high adsorption capacity and high degree of surface reactivity[16-20]. They find their wide applications in the removal of color, odor, taste and other undesirable organic and inorganic impurities from different aqueous media[15,21]. They are being increasingly used in the field of hydrometallurgy for the recovery of gold, silver, other in-organics and as catalyst supports[22]. Their use in medicine to combat certain types of bacterial ailment is also well known[22]. Moreover, they are usually considered to be the adsorbents against which others are assessed[21]. However, the adsorption may suffer from economic limitations owing to difficulties encountered in separating sorbent from suspension in order for it to be regenerated[17]. 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 its simplicity, rapidity, good separation yields ($R > 95\%$) for small impurity agent concentrations (10^{-6}-10^{-2} $mol{\cdot}l^{-1}$), a large possibility of application for species having different nature and structure, flexibility and friability of equipment and processing for recovery purpose[23,24]. It is believed that this process will be soon incorporated as a clean technology to treat water and wastewater[25]. For the aforementioned reasons a combination of adsorption and flotation into a unified operation termed sorptive-flotation could be considered as a vital process[26].

In developing countries, the pollution control measures frequently need to be based on lower-cost technologies. In this context, one area which is being explored is the use of naturally occurring materials which have the potential for adsorbing pollutants[21]. Accordingly, this investigation aims to establish a selective, rapid and simple procedure for the removal of lead ions from aqueous solutions using powdered activated carbon, obtained from olive stones, as an organic sorbent (which may be inexpensive, readily available and as alternative to existing commercial adsorbents) and oleic acid as a surfactant at the recommended conditions.

EXPERIMENTAL

Samples

Modified powdered activated carbon was prepared from olive stones after washing with 5% aqueous solution of HCl, followed several times by distilled water and drying at 125°C, and then subjected to destructive distillation for 5 h at 600°C under a flow of nitrogen. The resulting material was subsequently activated by gasification with steam at 900°C. The modified activated carbon sample was prepared by treatment with $(NH_4)_2S_2O_8$. The suspension was shaken for 48 h at room temperature, after which the modified activated carbon sample was removed by filtration, washed with distilled water and dried in an air oven for 24 h at 125°C. Whilest hot, the treated carbon sample was then quickly transferred into a desiccator and subjected to low-pressure evacuation. A mean particle size of ca.12∝m was employed in subsequent experiments. Experimental characterization of the carbon sample under investigation (TABLE 1) revealed that: the surface area of PACI is 249.1 m^2/g (employing the conventional BET equation), its ash content was 5.7% and its suspension pH after 4h stirring (water pH=6.8) was 2.5 The base neutralization capacities (m equiv.g^{-1}) for $NaHCO_3$, Na_2CO_3 and NaOH were 0.05, 0.16 and 0.20, respectively. Moreover, the IR analysis of PAC sample (using KBr disc method) revealed the appearance of two absorption bands at 1401 cm^{-1} and 3420 cm^{-1} assigned to ν(COOH) and ν(OH), respectively.

TABLE 1: Surface characterization of carbon samples

Type of characterization		PACI
Ash content (%)		5.7
Surface area (m^2/g) by BET equation		249.1
Suspension pH after 4 h stirring (water pH = 6.8)		2.5
Base neutralization capacities (m equiv g^{-1})		
$NaHCO_3$		0.05
Na_2CO_3		0.16
NaOH		0.20
IR bands cm^{-1} (in KBr disc)		
without HOL	ν(COOH)	1401
	ν(OH)	3420
With HOL	ν(COOH)	1712
	ν(C-H)	2922
	ν(OH)	3428

Reagents

All the solutions were prepared from certified reagent-grade chemicals. lead stock solution ($1mg\cdot ml^{-1}$) was prepared from $Pb(NO_3)_2$ (BDH Ltd, Poole, England) by dissolving the calculated amount in doubly distilled water containing 1 ml of concentrated HNO_3, and diluting to 1 l. An oleic acid (HOL) stock solution, 6.36×10^{-2} $mol\cdot l^{-1}$, was prepared from the food grade with sp.gr. 0.895 (provided from J.T. Baker Chemical Co.) by dispersing 20 ml HOL in 1 l kerosene. Aqueous solutions of HCl and NaOH were used for pH adjustments. Further dilutions were prepared daily as required.

Apparatus

A Pekin-Elmer 2380 atomic absorptions spectrophotometer 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 the KBr disc method. A flotation procedure was carried out in a flotation cell, which is a cylindrical tube of 1.5 cm inner diameter and 29 cm length with a stopcock at the bottom[27]. The stirring of solutions was performed with a magnetic stirrer model VEHP, Sientifica, Italy. The pH was measured using Jeanway 3310 pH meter.

Procedure

To study the various parameters affecting the sorption-flotation process, a 20 ml aliquot of a suspension containing 20.0 $mg\cdot l^{-1}$ Pb^{2+} ions and 100 $mg\cdot l^{-1}$ sorbent (PACI) 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 PACI. Then 3 cm^3 of 3×10^{-3} $mol\cdot l^{-1}$ HOL was added. The cell was again inverted upside down 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 by flame atomic absorption spectrometry at a wavelength of 217.0 nm (also, it was determined by EDTA titration at high concentrations). The removal percentage of Pb^{2+} ions, Re (%), was calculated from the relationship:

$$\mathbf{Re} = (1 - C_f / C_i) \times 100\ \%$$

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

To study the flotation of PACI alone, the previous procedural steps were conducted in the absence of Pb^{2+} ions. After complete flotation, the PACI-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°C. The floatability percentage of PACI, F (%), was calculated from:

$$\mathbf{F} = C_f / C_i \times 100\ \%$$

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

Another series of experiments was conducted on 1 l suspension (placed in a 2 l glass beaker) containing 2.0 or 4.0 mg of Pb^{2+} ions, 200 $mg{\cdot}l^{-1}$ PACI and 10 ml of 3×10^{-3} $mol{\cdot}l^{-1}$ HOL with an initial pH 7. The suspension was stirred magnetically for 10 min at 200 rpm where it was noted that the Pb-PACI-HOL system was self-floatable without a stream of air bubbles being necessary.

RESULTS AND DISCUSSION

Floatability of powdered activated carbon

The removal of fine particles of carbon sorbents from aqueous solutions (particularly those that passed through a filtration medium) was an obvious economic measure for the undertaken studies. A preliminary series of experiments was conducted to float different concentrations of PACI (namely 4 and 8 $g{\cdot}l^{-1}$) over a wide range of pH values using 3×10^{-3} $mol{\cdot}l^{-1}$ HOL. The obtained results are depicted in figure 1, from which it is clear that a maximum flotation (~100 %) for 4 $g{\cdot}l^{-1}$ of PACI was attained over a wide pH range 1-10. Furthermore, the separation process was more efficient in acidic, neutral and alkaline media.

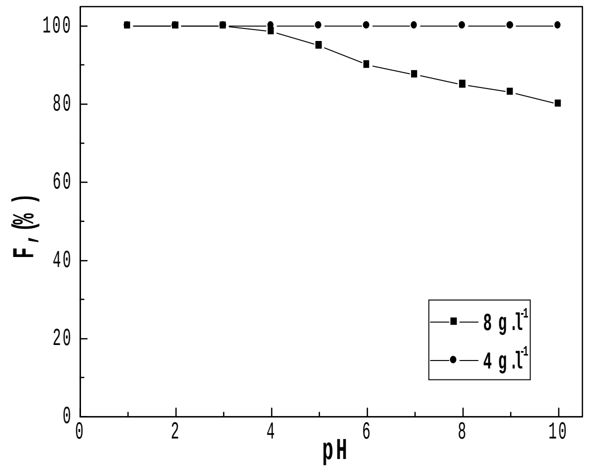

Figure 1: Floatability of PACI sorbent as a function of the pH using 3×10^{-3} $mol{\cdot}l^{-1}$ of HOL

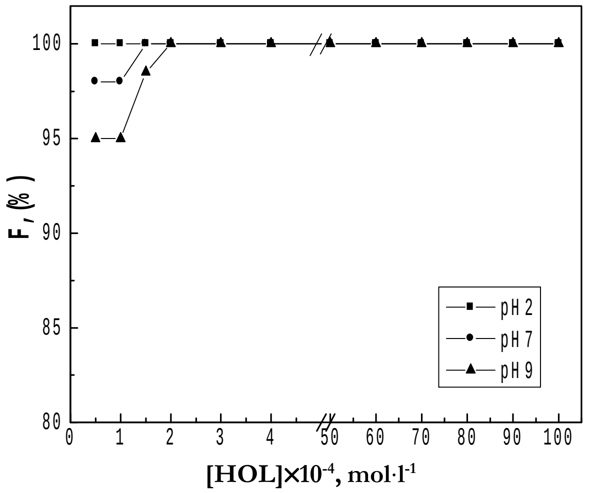

Figure 2: Floatability of 4 $g{\cdot}l^{-1}$ of PACI versus [HOL] at different pH values

The separation of the powdered activated carbon using different concentrations of oleic acid (HOL) surfactant at pH values of 2, 7 and 9 is presented in figure 2. The results proved that oleic acid is an effective surfactant for a quantitative removal of the sorbent at all the pHs investigated when applied within the concentration range of 2×10^{-4} to 1×10^{-2} $mol{\cdot}l^{-1}$. However, at lower surfactant concentrations, HOL gave better results at pH values of 2 and 7 rather than at pH 9. In general, it was found that for the studies undertaken the recommended HOL concentration range was 1×10^{-3}-1×10^{-2} $mol{\cdot}l^{-1}$.

Another series of experiments was carried out to float different concentrations of PACI samples using 3×0^{-3} $mol{\cdot}l^{-1}$ HOL at pH values of 2,7 and 9. As can be seen from the data recorded in figure 3, quantitative separation of the sorbent was attained over a wide concentration range at pH 2. Hence, for each experiment a definite concentration of PACI may be recommended for a given pH value and concentration of HOL.

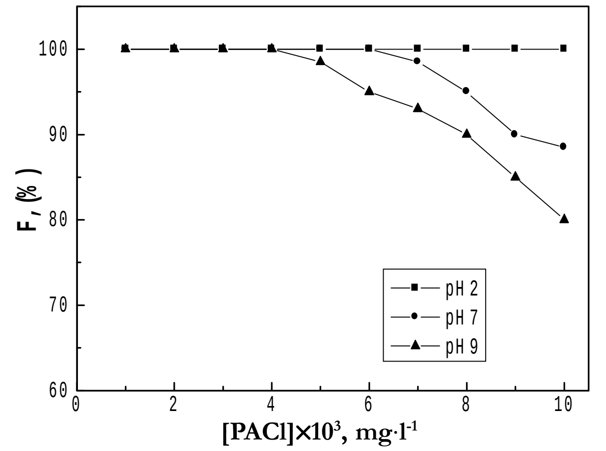

Figure 3: Floatability of different concentrations of PACI using 3×10^{-3} mol·l^{-1} HOL at different pH values

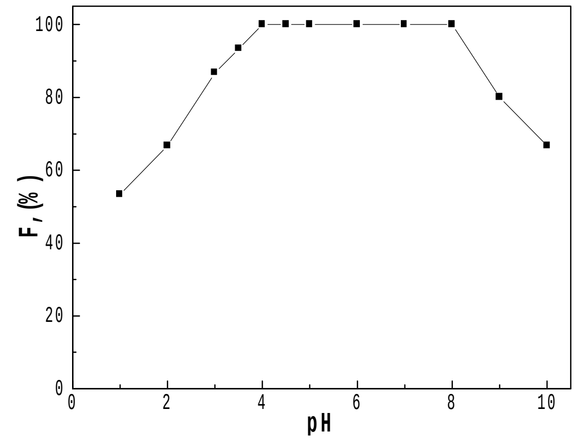

Figure 4: Floatability of 20 mg.l^{-1} Pb^{2+} at different pH values using 100 mg·l^{-1} PACI and 3×10^{-3} mol·l^{-1} HOL

Removal of lead ions

Effect of pH

The concentrating tendency of hydroxyl ion in the float is sensitive to variations in solution 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[3,28], 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.

In order to find the optimal pH value for the sorptive-flotation process, the removal efficiency of Pb^{2+} ions over the pH range 1-10 was studied. Figure 4 illustrates the influence of pH on the combined process of sorption and flotation for the removal of 20.0 mg·l^{-1} Pb^{2+} ions using 100 mg·l^{-1} of PACI and 3×10^{-3} mol·l^{-1} of HOL. It should be noted that the removal of Pb^{2+} ions was diminished at pH < 1.0 which may be attributed to the fact that the oxo groups (C_xO and C_xO_2) formed on the carbon surface during activation react with water according to:

$$C_xO_2 + H_2O = C_xO^{2+} + 2OH^-$$

to form positively charged surface group[21], thereby hindering the adsorption of Pb^{2+} ions. At pH >1, the removal of Pb^{2+} ions increases gradually which may be due to the chemical combination of Pb^{2+} ions with carboxylic group of activated carbon, or with sulfur (obtained from per-sulfate that used in the modification of activated carbon surface) or via co-precipitation of its colloidal insoluble sulfides. However, over the pH range 4-8, in addition to the above mechanisms the removal of Pb^{2+} ions may proceed via adsorption of its hydrolytic species, $Pb(OH)^+$. The decrease in the removal rate at high pH values (>8) may be attributed to the fact that oleate anions are not capable of combination with the negative surface of PACI. Therefore, pH 7 was recommended throughout all other experiments.

Effect of sorbent and metal ion concentrations

Two parallel series of experiments were performed to study the influence of powdered activated carbon dose (Figure 5) and changing lead concentrations (Figure 6) on the removal percentage of Pb^{2+} ions from aqueous solutions at pH 7 using 3×10^{-3} mol·l^{-1} of HOL. As can be seen from figure 5, the removal percentage of Pb^{2+} ions was increased as the PACI dose increased while it decreased as the concentration of the metal ion increased (Figure 6). The reason for attaining a maximum removal of Pb^{2+} ions (~ 100 %) at higher PACI dose may be due to an increase in the number of binding sites on the adsorbent available to Pb^{2+} ions. Hence, 100 mg·l^{-1} of PAC may be a suitable dose for the removal of Pb^{2+} ions having a concentration of ≤ 20 mg·l^{-1}.

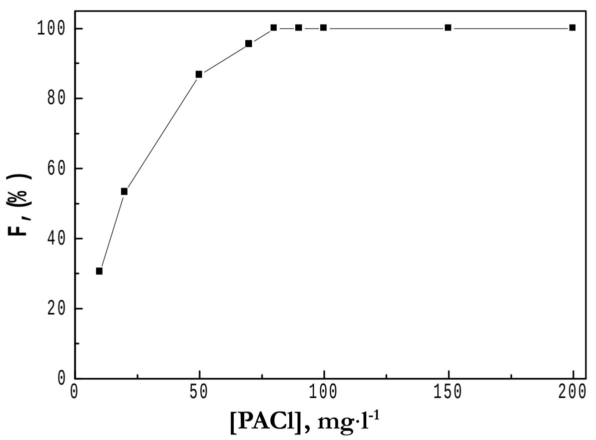

Figure 5: Floatability of 20 mg·l^{-1} Pb^{2+} ions using different concentrations of PACl and 3×10^{-3} mol·l^{-1} HOL at pH 7

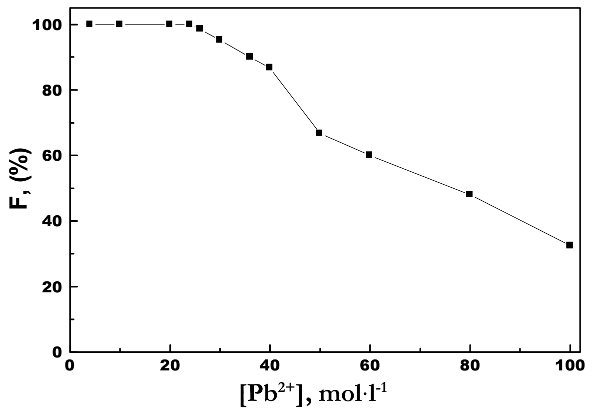

Figure 6: Floatability of different concentrations of Pb^{2+} ions using 100 mg·l^{-1} PACl and 3×10^{-3} mol·l^{-1} HOL at pH 7

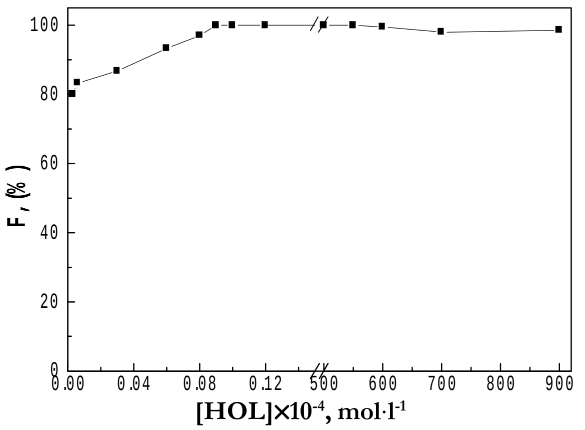

Figure 7: Floatability of 20 mg·l^{-1} Pb^{2+} ions using 100 mg·l^{-1} PACl and different concentrations of HOL at pH 7

Effect of surfactant concentration

A series of experiments was undertaken to float 20 mg·l^{-1} of Pb^{2+} ions from aqueous solutions at pH 7, in the presence of 100 mg·l^{-1} of PACl sorbent, using different concentrations of HOL. The obtained results (Figure 7) showed that a complete removal of Pb^{2+} ions (~100%) was attained over the HOL concentration range of 1.0×10^{-5} to 4.5×10^{-2} mol·l^{-1}. The removal of Pb^{2+} ions decreased at concentrations above this range, a phenomenon which may be attributed to the formation on the air bubble surface of a stable, hydrated envelop of surfactant or alternatively to the formation of a hydrated micellar coating on the solid surface. In either case, the hydrophobocity of the surface would then not be satisfactory for flotation[29,30]. Consequently, the concentration of HOL was fixed at 3×10^{-3} mol·l^{-1} throughout.

Effect of shaking time

The variation in the percentage removal of Pb^{2+} ions with shaking time was also studied using 20 mg·l^{-1} of Pb^{2+} ions, 100 mg·l^{-1} of PACl and 3×10^{-3} mol·l^{-1} of HOL at pH 7. The shaking time was varied from 1 min to 25 min. The obtained results showed that the percentage removal increased to its maximum value (~100%) after 3 min for 20 mg·l^{-1} of Pb^{2+} ions. Therefore, 5 min of shaking was considered to be sufficient for the adsorption and flotation of Pb^{2+} ions having a concentration of 20 mg·l^{-1}.

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 20 or 40 mg·l^{-1} of Pb^{2+} ions and 100 mg·l^{-1} of PACl and a second solution containing 3×10^{-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 fiberglass insulation. The mixture was then floated using the previously described process.

The obtained results (Figure 8) indicated that the removal percentage of Pb^{2+} ions increased as the temperature increased. Such data propose that the ad-

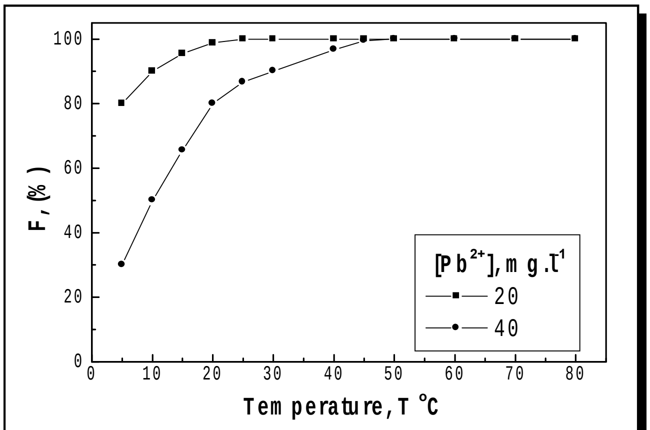

Figure 8: Effect of temperature on the floatability of different lead concentrations using 100 mg·l^{-1} of PACI and 3×10^{-3} mol·l^{-1} of HOL at pH7

sorption of Pb^{2+} ions may proceed through chemical bond formation which is in good agreement with literature data[31]. Moreover, a comparison with previous data (i.e. Figure 6) revealed that an increase of temperature to ~45°C resulted in an increase of the removed Pb^{2+} ions from 20 to 40 mg·l^{-1} for the same dose of PACI sorbent, viz. 100 mg·l^{-1}. Such results suggest the creation of new active sites on PACI surface available for Pb^{2+} ions adsorption[32].

Effect of ionic strength

TABLE 2 shows the effect of ionic strength on the floatability of 20 mg·l^{-1} of Pb^{2+} ions using 100 mg·l^{-1} of PACI and 3×10^{-3} mol·l^{-1} of HOL at pH 7. The cations and anions nearly present in natural waters were taken into consideration. As can be seen, all the salts added to the floating medium have no effect on the percentage removal of Al^{3+} ions. Therefore, this simple sorptive-flotation procedure may find its application for the recovery of Pb^{2+} ions from sea-water samples.

TABLE 2: Effect of the ionic strength on the percentage removal, Re (%), of 20 mg·l^{-1} of Pb^{2+} ions from aqueous solutions using 3×10^{-3} mol·l^{-1} of HOL and 100 mg·l^{-1} of PACI at pH 7

Salt	Concentration/mol.l^{-1}	Re, %
NaCl	0.1	99.9
	0.5	99.1
KCl	0.1	99.9
	0.5	99.8
Na_2SO_4	0.1	100.0
	0.5	99.7
$MgCl_2$	0.1	99.9
	0.5	99.0
$CaCl_2$	0.1	100.0
	0.5	99.1

TABLE 3: Effect of various ions on the percentage removal, Re (%), of 1.35mg dm^{-3} of 20 mg·l^{-1} of Pb^{2+} ions from aqueous solutions using 3×10^{-3} mol·l^{-1} of HOL and 100 mg·l^{-1} of PACI at pH 7

Cation	Tolerence limit/×10^3, mg·l^{-1}	Re, (%)	Anion	Tolerence limit/×10^3, mg·l^{-1}	Re, (%)
K^+	19.6	100.0	SO_4^{2-}	48.0	100.0
Na^+	11.5	100.0	NO_3^-	31.0	100.0
NH_4^+	9.0	100.0	CH_3COO^-	29.5	100.0
Ca^{2+}	8.2	100.0	$HCOO^-$	29.3	100.0
Mg^{2+}	7.1	100.0	$C_2O_4^{2-}$	22.0	99.8
Ba^{2+}	6.90	100.0	Cl^-	17.7	100.0
Se^{4+}	6.8	99.9	$H_2PO_4^-$	12.1	99.9
Mn^{2+}	6.5	99.8	$S_2O_3^{2-}$	5.6	100.0
Sr^{2+}	6.05	99.9	CN^-	0.3	100.0
Hg^{2+}	4.2	100.0	$B_4O_7^{2-}$	0.2	99.8
$A1^{3+}$	3.4	99.9	-	-	-
Co^{2+}	2.95	99.7	-	-	-
$N1^{2+}$	2.93	99.9	-	-	-
Fe^{3+}	2.8	100.0	-	-	-
Cr^{6+}	1.4	99.7	-	-	-
Zn^{2+}	0.6	99.8	-	-	-
Cd^{2+}	0.5	99.8	-	-	-
Ag^+	0.2	99.5	-	-	-
Cu^{2+}	0.0004	99.3	-	-	-

Effect of various other ions

Under the optimized conditions determined for this investigation, the percentage removal of 20 mg·l^{-1} of Pb^{2+} ions from a solution of pH 7 containing 100 mg·l^{-1} of PACI sorbent and 3×10^{-3} mol·l^{-1} of HOL was studied in the presence of high concentrations of various cations and anions, usually present in some water samples. The corresponding results obtained are listed in TABLE 3. All the cations were used as their nitrates, whereas the anions were used as the corresponding sodium or potassium salts. Inspection of the data in TABLE 3 indicates that the investigated foreign ions did not in the removal of Pb^{2+} ions and the process was quantitative in all cases. However, it should be noted that higher concentrations of Cu^{2+} ions could have harmful effect on the removal process. This may be due to a competition between this cation and Pb^{2+} ions for adsorption onto the active sites of PACI. This problem could be overcome by increasing the dose of PACI sorbent.

Recovery of Pb^{2+} ions added to some water samples

To investigate the applicability of the recommended procedure, a series of experiments was performed to recover 2.0 and 4.0 mg of Pb^{2+} ions added to aqueous and some natural water samples. The sorptive-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, quantitative (~100%) and with a relative standard deviation (RSD %) does not exceed 2.0.

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 onto solid phases via co-precipitation of their insoluble hydroxides; (ii) flocculation by adsorption of hydrolytic products or (iii) complexation with specific surface sites, provided the appropriate conditions prevail[34,35].

(2) As a function of solution pH[3,28], 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.

(3) Most activated carbon surfaces are negatively charged[27] and are characterized by the presence of oxo groups[21] C_xO and C_xO_2 which react in aqueous suspensions as organic carboxylic and phenolic groups[36].

(4) Experimental characterization of the surfaces of carbon samples under investigation has been carried out using surface area measurements employing the conventional BET equation, by the measurement of their base neutralization capacities and by IR analyses. The results obtained are listed in TABLE 1 and reveal that (i) Surface area was 249.1 m^2/g; (ii) carboxylic, lactone and phenolic functional groups were present on the surfaces of the carbon samples as determined by the method reported[20], with free carboxylic groups comprising ca. 25%, lactone groups amounting to 55% while phenolic groups amounting to 20%; (iii) the decrease in the solution pH observed after stirring the PACI sorbent with distilled water for 4 h may be attributed to adsorption of OH^- ions from solution or desorption of H^+ ions from the sorbent surface; (iv) modification of powdered activated carbon gave sulfur containing active sites and (v) the presence of carboxylic and phenolic groups on carbon surfaces was confirmed by the appearance of characteristic bands at 1401 cm^{-1} and 3420 cm^{-1}, respectively, in IR spectra. In addition, new bands were observed in the regions of 1712, 2922 and 3428 cm^{-1} characteristic of ν(COOH), ν(C-H) and ν(OH) of un-dissociated oleic acid[37]

TABLE 4: Recovery of Pb^{2+} ions added to 1 l of various water samples using 10 cm^3 of 3×10^{-3} mol·l^{-1} of HOL and 100 mg mg.l^{-1} of PACI at pH 7

Sample (location)	Pb^{2+} added/ (mg)	Pb^{2+} found/ (mg)[a]	Re, %	RSD,[b] %
Double distilled Water	-	ND[c]	-	-
	2.150	2.148	99.9	1.2
	4.250	4.250	100.0	1.6
Tap water (our laboratory)	-	0.6±0.1[d]	-	-
	2.150	2.146	99.8	1.5
	4.250	2.241	99.8	2.0
Nile water (Mansoura City)	-	10.4±0.1[d]	-	-
	2.150	2.144	99.7	1.8
	4.250	2.241	99.8	1.7
Sea water (Ras El-Barr)	-	5.2±0.1[d]	-	-
	2.150	2.144	99.7	1.8
	4.250	2.241	99.8	1.9
Lake water (Manzalah)	-	53.5±0.1[d]	-	-
	2.150	1.146	99.8	1.7
	4.250	4.233	99.6	1.8
Underground water(Cinbillaween City)	-	-	-	-
	2.150	2.146	100.0	2.0
	4.250	4.241	99.8	2.0

a: The mean of five replicate analyses and the values are calculated for the only added Pb^{2+} ions. b: Calculated for five replicate analyses. c. ND means not detectable. d. Analysis has been carried out by AAS after preconcentration as reported elsewhere[33] and the values are in ppb

which appeared after flotation of carbon samples with HOL surfactant.

(5) Oleic acid (HOL) surfactant begins to dissociate at pH ^{3} 5.2[29].

Therefore, the proposed mechanism may occur as follows:

At pH < 1.0 the removal of Pb^{2+} ions was diminished which may be attributed to the fact that the oxo groups (C_xO and C_xO_2) formed on the carbon surface during activation react with water according to:

$$\mathbf{C_xO_2 + H_2O = C_xO^{2+} + 2OH^-}$$

to form positively charged surface group[21] thereby hindering the adsorption of Pb^{2+} ions.

At pH > 1, the removal of Pb^{2+} ions increases gradually which may be due to the chemical combination of Pb^{2+} ions with carboxylic groups of activated carbon, or with sulfur (obtained from per-sulfate that used in the modification of activated carbon surface) or via co-precipitation of its colloidal insoluble sulfides. The adsorbent-adsorbate system is made hydrophobic by combination with un-dissociated oleic acid molecules. Such combination may occur through hydrogen bonding of the carboxylic group of HOL as confirmed by the appearance of an absorption band at 1712 cm^{-1} during IR spectral analysis of PACI-HOL system.

Over the pH range 4-8, where the maximal removal of Pb^{2+} ions occurred (~100%) and in addition to the above mechanisms, the removal of Pb^{2+} ions may proceed via adsorption of its hydrolytic species, $Pb(OH)^+$. The aggregates of PACI- Pb^{2+} precipitate 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.

The decrease in the removal rate at high pH values (>8) may be attributed to the fact that oleate anions are not capable of combination with the negative surface of PACI.

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