

Full Length Research Paper

Sorption of lead from aqueous solution by modified activated carbon prepared from olive stones

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Accepted 2 April, 2007

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 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 and rapid procedure for lead (II) removal. Laboratory-scale adsorption experiments were conducted aiming to remove lead from water samples. 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 such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The main parameters (pH, sorbent, lead concentrations, stirring times and temperature) influencing the sorption process in addition to the effect of some foreign ions were investigated. The results obtained indicated that the sorption of Pb^{2+} ions onto PACI is well described by the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption models over the concentration range studied. Under the optimum experimental conditions employed, the removal of ca. 100% of Pb^{2+} ions was attained. The procedure was successfully applied to the removal of lead from aqueous and different natural water samples.

Key words: Sorption, lead, activated carbon, kinetics and water.

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 (Meunier et al., 2003; Yan and Viraraghavan, 2003). 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 and can damage the nervous system, kidneys, and reproductive system, particularly in children (Sheng et al., 2004). Also, lead is known to have a toxic effect on the neuronal system and the function of the brain cells (Ho et al., 2001; Freedman et al., 1990; Goldstein 1990). The health hazards of lead in waters have been reported in many journals (Grocetti et al., 1990; Aldrich et al., 1993). The U.S. Environmental Protection Agency (EPA) requires lead not to exceed 0.015 mg.l^{-1} in drinking water (ATSDR, 1999). 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 (van den Brandt et al., 2002; Brach-Papa et al., 2002). Numerous techniques are

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available in this concern and have been reported (Leyden and Wegscheider, 1981; Mizuike, 1986; Ghazy et al., 2004; Zouboulis et al., 1994). 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.

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 (Ghazy et al., 2001; Allen and Brown, 1995; Ho and McKay, 1998; Samra, 2000). They find their wide applications in the removal of color, odor, taste and other undesirable organic and inorganic impurities from different aqueous media (Zouboulis et al., 1994; Sharma and Forster, 1996). They are being increasingly used in the field of hydrometallurgy for the recovery of gold, silver, other in-organics and as catalyst support (Abd El-Rahiem, 1996). Their use in medicine to combat certain types of bacterial ailment is also well known (Abd El-Rahiem, 1996). Moreover, they are usually considered to be the adsorbents against which others are assessed (Sharma and Forster, 1996).

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 (Sharma and Forster, 1996). 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) under the recommended conditions.

MATERIALS AND METHODS

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 (NH₄)₂S₂O₈. 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. While 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 µm 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 m²/g (employing the conventional BET equation), its ash content was 5.7% and its suspension pH after 4 h stirring (water pH = 6.8) were 8.2. The base neutralization capacities (m equiv/g) for NaHCO₃, Na₂CO₃ and NaOH were 0.05,

Table 1. Characterization of modified activated carbon sample (PACI).

Type of characterization	PACI
Ash content (%)	5.7
Surface area (m ² /g) by BET equation	249.1
Suspension pH after 4 h stirring	8.2
Base neutralization capacities (mg equiv/g)	
NaHCO ₃	0.05
Na ₂ CO ₃	0.16
NaOH	0.20
IR bands (cm ⁻¹)	
v(COOH)	1401
v(OH)	3420

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 v (COOH) and v (OH), respectively.

Reagents

All the solutions were prepared from certified reagent-grade chemicals. Lead stock solution (1 mg/ml) was prepared from Pb(NO₃)₂ (BDH Ltd, Poole, England) by dissolving the calculated amount in doubly distilled water containing 1 ml of concentrated HNO₃, and diluting to 1 L. Aqueous solutions of HNO₃ 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. The stirring of solutions was performed with a magnetic stirrer Model VEHP, Scientifica, Italy. The pH was measured using Jeanway 3310 pH meter.

Procedure

Unless stated otherwise, all batch sorption experiments were conducted at room temperature (ca. 25°C). Known volumes of lead solutions with concentrations ranging from 5 to 40 mg.l⁻¹ were pipetted into quick-fit glass bottles containing 0.1 g.l⁻¹ of PACI sorbent in 100 ml aqueous solution of pH 7. The resulting solutions were then stirred with a magnetic stirrer at 250 rpm and the samples were taken at fixed time periods (1, 2, 3, 5, 7, 10, 15, 20, 25, 30, 40, 50, and 60 min) in order to study the kinetics of the adsorption process. Preliminary experiments showed that this time length was sufficient for adsorption of Pb²⁺ ions onto PACI. The samples were subsequently filtered off and the residual Pb²⁺ ion concentrations in the filtrate were analyzed using AAS at 217.0 nm. The percentage adsorption of Pb²⁺ ions from the solution was calculated from the relationship:

$$\% \text{ Adsorption} = (C_i - C_f) / C_i \times 100 \quad (1)$$

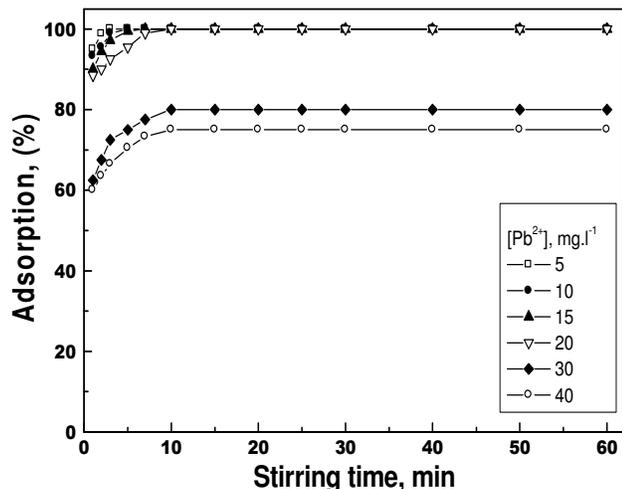


Figure 1. Influence of stirring time on the adsorption of different Pb^{2+} ion concentrations onto 100 mg.l^{-1} PACI at pH 7.

where C_i corresponds to the initial concentration of Pb^{2+} ions and C_r is the residual concentration after equilibration. The metal uptake q (mg/g) was calculated as:

$$q = [(C_i - C_r) / m] \cdot V \quad (2)$$

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

To assess the applicability of the procedure, another series of experiments was conducted on 1 L suspension of clear and pre-filtered natural water samples with an initial pH adjusted to 7.0. These suspensions were placed in 2 L glass beakers containing 10 or 20 mg of Pb^{2+} ions and 100 mg.l^{-1} of PACI at 25°C and stirred magnetically for 20 min at 250 rpm.

RESULTS AND DISCUSSION

Kinetics of the adsorption process

Figure 1 shows the variation in the percentage adsorption (removal) of lead ions onto PACI sorbent with stirring time using various initial metal ion concentrations at pH 7. The data depicted in this figure indicated that the adsorption of lead ions is quite rapid at the first stage of the process which may suggest that adsorption occurred mainly at the surface of the solid sorbent and to some extent by the internal macro-pores, transitional pores and micro-pores (Yubin et al., 1998; Al-Asheh and Banat, 2001). However, with the passage of time the rate of adsorption decreased and ultimately reached a constant value (equilibrium time). This slow adsorption during the second stage may be due to the decrease of lead diffusion into the pores of solid sorbent (Akhtar and Qadeer, 1997). The time necessary to reach such adsorption equilibrium was found to be 3, 5 and 7 min for initial concentrations of 5, 10 and 15 mg.l^{-1} Pb^{2+} ions, respec-

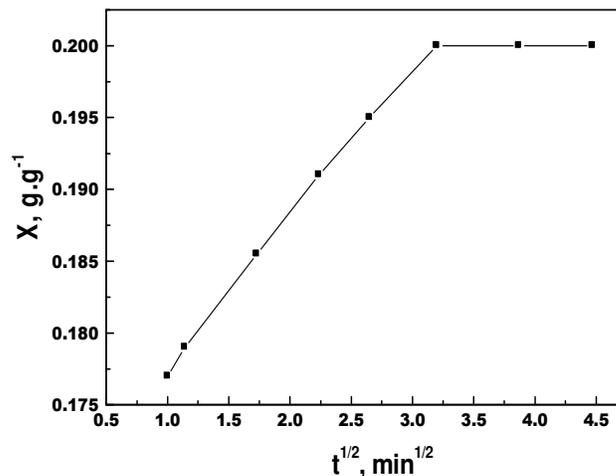


Figure 2. Plot of the amount of Pb^{2+} ions adsorbed onto 100 mg.l^{-1} PACI versus square root of time at pH 7.

tively and 10 min for those of 20, 30 and 40 mg.l^{-1} Pb^{2+} ions. Hence, to ensure that adsorption had reached equilibrium in all cases, a stirring time of 20 min was selected for all samples studied. The results also indicated that the percentage adsorption of the metal ion from the solution decreases with increasing initial metal ion concentration. This can be explained by a decrease in the number of adsorption sites having an affinity towards Pb^{2+} ions.

An interesting series of experiments was carried out to evaluate the effect of soaking time (that is, without stirring) on the removal rate of 15 and 20 mg.l^{-1} of Pb^{2+} ions using 100 mg.l^{-1} of PACI sorbent. The results obtained revealed that a maximum removal rate of Pb^{2+} ions (ca. 100%) was attained after soaking for a time ≥ 60 min. These results may be useful from an economic viewpoint of industrial wastewater treatment.

When the results depicted in Figure 1 were re-plotted against the square root of the stirring time, linear correlations were obtained as shown in Figure 2, which may verify the Morris-Weber equation (Weber and Morris, 1963):

$$X = K_d (t)^{1/2} \quad (3)$$

where X is the amount of Pb^{2+} ions adsorbed (g.g^{-1}). This indicates that an intrapore diffusion mechanism was involved in adsorption of Pb^{2+} ions by PACI (Figure 1). Figure 2 shows that two distinct regions were observed: an initial linear portion which is due to the boundary layer diffusion effect (Crank, 1965) and a second portion which is due to the intraparticle diffusion effect (McKay et al., 1980). However, the fact that the line depicted in Figure 2 does not pass through the origin indicates that intrapore

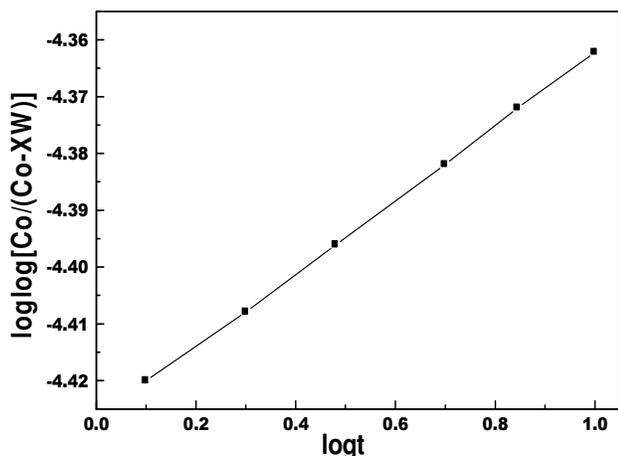


Figure 3. Plot of log log [C₀ / (C₀ - XW)] versus log t for the adsorption of Pb²⁺ ions by 100 mg.l⁻¹ PACI at pH 7.

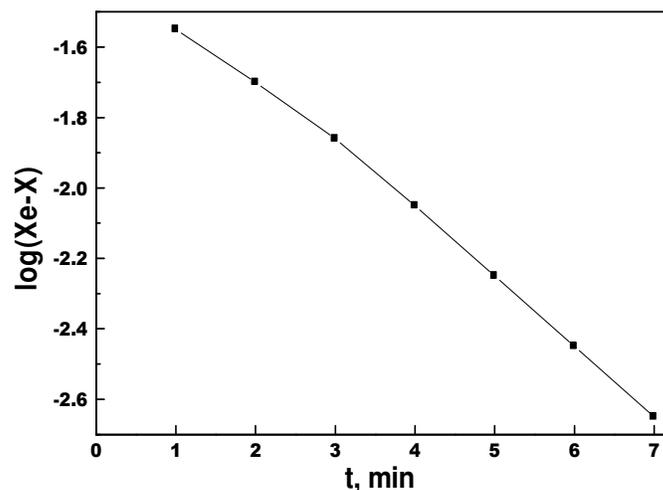


Figure 4. Plot of log (X_e - X) versus stirring time for Pb²⁺ ions adsorption onto 100 mg.l⁻¹ PACI.

diffusion is not the controlling step in sorption of Pb²⁺ ions by PACI (Al-Asheh and Banat, 2001; Weber and Morris, 1963). These data agree with those of Juang et al. (2000) who proposed that the first sharp portion of the curve should be attributed to an adsorption on the external surface of the sorbent while the second gradual portion should be attributed to intrapore diffusion. The calculated value of the rate constant for intrapore diffusion K_d is 1.05 × 10⁻² (g/g min^{1/2}) which give an indication about the mobility of the Pb²⁺ ions towards the PACI surface.

Again the kinetic data depicted in Figure 1 for the adsorption of Pb²⁺ ions onto PACI was checked via the Bangham equation (1924):

$$\text{Log log } [C_0 / (C_0 - XW)] = \text{log}(K_0W / 2.303V) + \alpha \text{ log } t \quad (4)$$

where X and V have been defined above, C₀ is the initial concentration of Pb²⁺ ions (mg.l⁻¹), W is the amount of PACI (g), t is the time (min), α is the Bangham equation constant (its value being usually < 1) and K₀ is a proportionality constant. Plot of log log [C₀ / (C₀ - XW)] versus log t gave straight line as shown in Figure 3. These results show that the diffusion of Pb²⁺ ions into the pores of PACI played a role in the adsorption process. These results were similar to those described elsewhere (Qadeer and Hanif, 1994; Akhtar and Qadeer, 1997). The calculated values of α and K₀ are 0.065 and 0.862, respectively.

The kinetic data depicted in Figure 1 for Pb²⁺ ions adsorption by PACI were tested using Lagergren equation, as cited by Gupta and Shukla (1996):

$$\text{Log } (X_e - X) - \text{log } X_e = -K_{\text{ads}} t / 2.303 \quad (5)$$

where X_e is the amount of Pb²⁺ ions adsorbed at equi-

librium (g/g), K_{ads} is the first-order rate constant for Pb²⁺ ions adsorption onto PACI (min⁻¹), X and t have been defined previously. The linear plot of log (X_e - X) versus t obtained in Figure 4 shows the appropriateness of the above equation and consequently the first-order nature of the process involved. The value calculated of K_{ads} is 0.127 min⁻¹.

Effect of pH

It is well documented that solution pH is an important parameter that affects the metal-solution, adsorbent-surface and hence the sorption of heavy metal ions (Sheng et al., 2004; Bradl, 2004). It should be noted that the removal of divalent lead by PACI sorbent is influenced by the surface properties of PACI and lead species present in aqueous solution. As a function of solution pH, Pb²⁺ is the dominant species below pH 5.5. Between pH 6 and 8, 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 (Sheng et al., 2004; Bradl, 2004).

In order to find the optimal pH value for the sorption process, the influence of variation of pH values and time on Pb²⁺ ions adsorption by PACI was investigated over the pH range 1 - 9 and time up to 30 min using 20.0 mg.l⁻¹ Pb²⁺ ions and 100 mg.l⁻¹ of PACI (Figure 5). The data show that the sorption of Pb²⁺ ions increased as the time and the pH of the suspension increased. It should be noted that the sorption of Pb²⁺ ions was diminished at pH < 1.0 which may be attributed to the fact that the oxo groups (C_xO and C_xO₂) formed on the carbon surface during activation react with water according to:

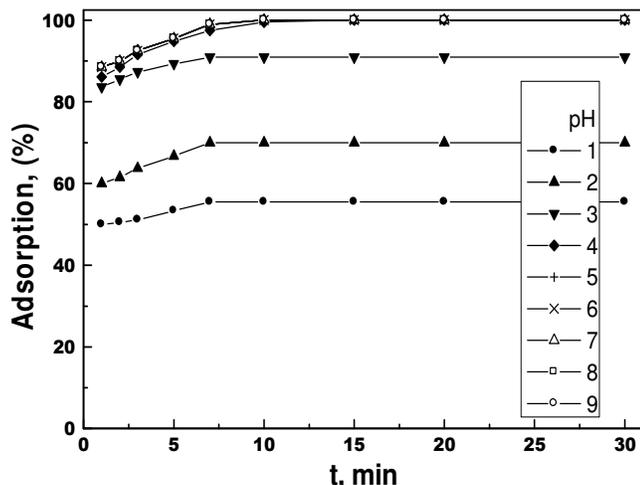


Figure 5. Adsorption of 20 mg.l⁻¹ Pb²⁺ ions by 100 mg.l⁻¹ PACI versus stirring time and pH.

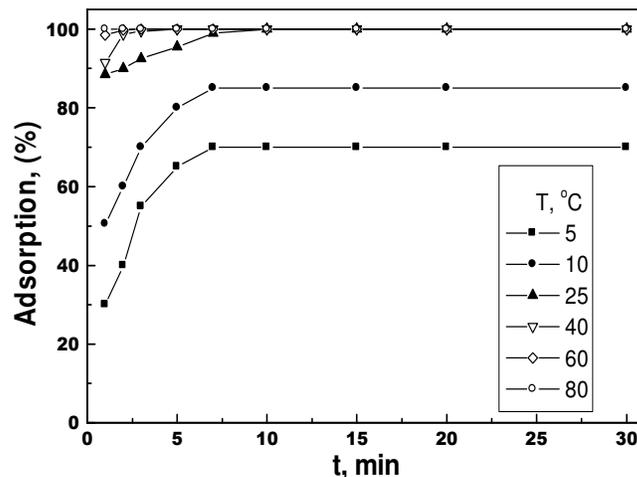
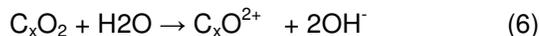


Figure 6. Adsorption of 20 mg.l⁻¹ of Pb²⁺ ions by 100 mg.l⁻¹ PACI at different temperatures and varying stirring times at pH 7.



forming positively charged groups (Sharma and Forster, 1996); thereby hindering the adsorption of Pb²⁺ ions. Therefore, the removal of Pb²⁺ ions is relatively small < 90% and increased to about 90% at pH 3.

Since PACI is alkaline in nature, (the pH of its suspension was always raised after its stirring for some time when the system was not buffered) 100% removal of Pb²⁺ ions occurred in the pH range 4 – 9, after stirring for 10 min, via adsorption of hydrolytic species, chemical interaction with the carboxylic groups of active carbon and sulfide group obtained from modification with (NH₄)₂S₂O₈, and/or precipitation of Pb(OH)₂ (s).

In alkaline medium, at pH > 10, the removal of Pb²⁺ ions decreased which may be attributed to the incapability of adsorption of the negative species, Pb(OH)₃⁻ and Pb(OH)₄²⁻, on the negative surface of PACI sorbent. Therefore, pH 7 was recommended throughout all other experiments.

Effect of the sorbent and lead amounts

The amount of PACI employed as the sorbent also influenced the efficiency of adsorption of 20.0 mg.l⁻¹ Pb²⁺ ions from aqueous solution at pH 7. The results obtained showed that the adsorption efficiency increased as the amount of PACI in the system increased to reach a maximum value (ca. 100%) at ≥ 60 mg.l⁻¹ of PACI. The reason for such behavior may be attributed to an increase in the number of binding sites on the sorbent surface available to the metal ions. For this reason, 100 mg.l⁻¹ of PACI were used in all subsequent experiments.

Another parallel series of experiments were conducted

to study the effect lead ion concentration on the adsorption process under the optimized conditions. The results obtained indicated that the adsorption of Pb²⁺ ions was virtually constant (ca. 100%) up to 25 mg.l⁻¹ of lead, beyond which the adsorption decreased. This may be explained in terms of the relatively smaller number of active sites available for higher Pb²⁺ ion concentrations.

Effect of temperature

The effect of varying the temperature on the adsorption efficiency of 20 mg.l⁻¹ Pb²⁺ ions at different stirring times is shown in Figure 6. Close inspection of the figure showed that increasing of temperature from 5 to 80°C plays two important functions. It increased both the efficiency of the adsorption and the amount of metal ions adsorbed on the same dose of sorbent. Such results may be attributed to an acceleration of some of the originally slow adsorption steps or to the creation of some new active sites on the adsorbent. In addition, the mobility of Pb²⁺ ions from the bulk solution towards the adsorbent surface may be enhanced (Khalid et al., 1998). Such results could suggest that the adsorption of Pb²⁺ ions may involve chemical bond formation (Yubin et al., 1998). Accordingly, chelate formation may occur between Pb²⁺ ions and carboxylic groups and/or sulfur atoms on modified PACI surface. Since most industrial effluents are usually hot, the simple adsorption procedure presented here may find application in industrial wastewater treatment for the removal of Pb²⁺ ions.

Adsorption isotherms

To determine the capacity of PACI as a sorbent for Pb²⁺

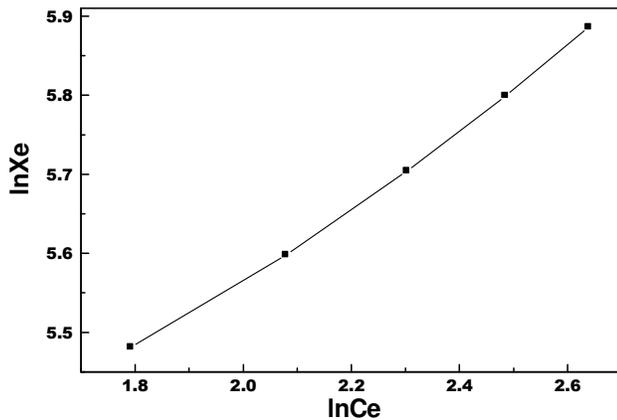


Figure 7. Freundlich plot for Pb²⁺ ion adsorption onto PACI.

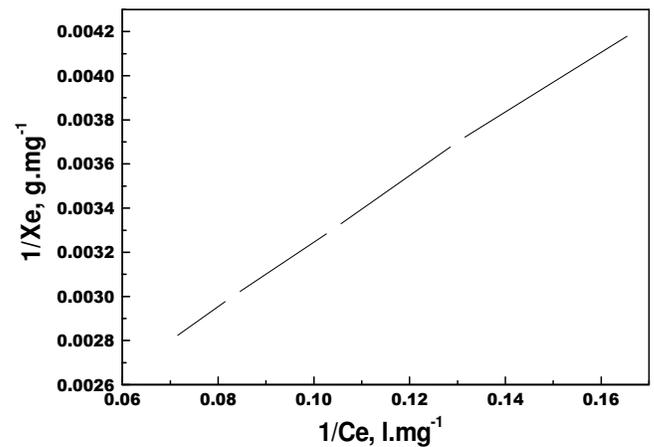


Figure 8. Langmuir plot for Pb²⁺ ions adsorption onto PACI.

ions, three isotherm equations, i.e. the Freundlich, Langmuir and Dubinin-Radushkevich, were employed. The linearized form of the Freundlich equation may be written as:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (7)$$

Where q_e (mg/g) is the amount of Pb²⁺ ion adsorbed at equilibrium, C_e (mg.l⁻¹) is its final equilibrium concentration and n and K_F are the Freundlich equation parameters. This equation was applied to the experimental data depicted in Figure 1 with a linear plot being obtained when $\ln q_e$ was plotted against $\ln C_e$ (Figure 7). This demonstrates the applicability of the Freundlich model to Pb²⁺ ion adsorption onto PACI. The parameters K_F and n for Pb²⁺ ions adsorption have been calculated from the intercept and slope of the plot depicted in Figure 7 giving values of 100.94 l/g and 2.09, respectively with a correlation coefficient (r) of 0.9979. Favorable adsorption of Pb²⁺ ions by PACI was demonstrated by the fact that the value of n was greater than unity (Nassar et al., 1996; Akhtar and Qadeer, 1997).

The linear form of the Langmuir equation applied to the lead ion adsorption data in Figure 1 was:

$$1/q_e = 1/K_L + (1/K_L b) \cdot 1/C_e \quad (8)$$

where K_L (mg/g) is the monolayer adsorption capacity and b (ml/mg) is the Langmuir constant. This also demonstrated that monolayer coverage of lead ions occurred on the outer surface of PACI (Panday et al., 1984; Akhtar and Qadeer, 1997). The values of K_L , b and the correlation coefficient (r) are 549.45 mg/g, 0.12656 ml/mg and 0.9997, respectively.

The Gibbs free energy change, ΔG (kJ/mol), for adsorption of Pb²⁺ ions by PACI can be calculated using the following thermodynamic equation (Panday et al.,

1985):

$$\ln(1/b) = -\Delta G / RT \quad (9)$$

where T is the absolute temperature (K) and R is a constant (8.3143 J / K.mol). The value of ΔG calculated at 298°K was found to be $-5.1212 \text{ kJ.mol}^{-1}$. The negative sign of ΔG indicates the spontaneous nature of Pb²⁺ ions adsorption onto PACI.

The Dubinin-Radushkevich (D-R) isotherm equation was also tested in its linearized form:

$$\ln X = \ln X_m - \beta \epsilon^2 \quad (10)$$

and

$$\epsilon = RT \ln (1 + 1/C) \quad (11)$$

Where C is the liquid-phase concentration of Pb²⁺ ions ($\mu\text{g/l}$), X_m is the monolayer capacity (g/g), ϵ is the Polanyi potential and β is the parameter of D-R isotherm with X , T and R having the same meaning as above. The value of X_m [Equation (10)] can be obtained from the slope of the plot of Figure 9 of another Langmuir equation:

$$C / X = 1 / K_L X_m + C / X_m \quad (12)$$

The isotherm expressed in equation (10) is more general than the Langmuir equation since it does not assume a homogeneous surface or a constant adsorption potential. Plotting of $\ln X$ versus ϵ^2 gave a straight line (Figure 10) thereby indicating the applicability of the D-R equation for Pb²⁺ ions adsorption onto PACI. From the slope and intercept of this plot, values of $\beta = -8.32 \times 10^{-3} \text{ mol}^2/\text{KJ}^2$ and $X_m = 0.903 \text{ g/g}$ were obtained for lead adsorption. The corresponding value of the correlation coefficient (r)

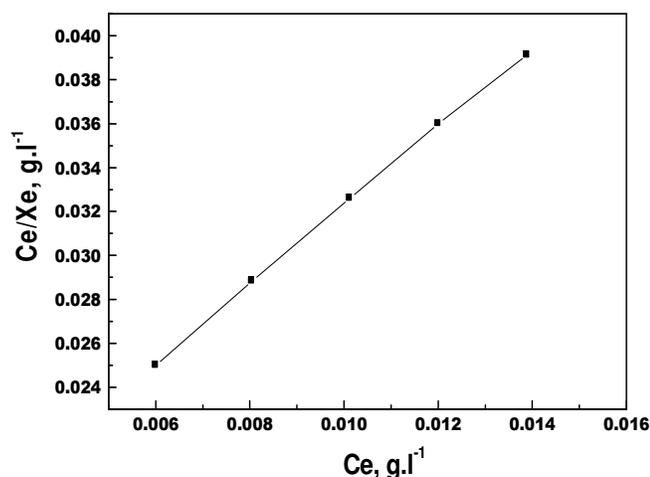


Figure 9. Second Langmuir plot for Pb²⁺ ions onto 100 mg.l⁻¹ of PACI.

is 0.9997. The value of the adsorption energy (E) was obtained from the relationship (Reichenberg, 1953; Akhtar and Qadeer, 1997):

$$E = (-2\beta)^{-1/2} \quad (13)$$

and found to be 7.752 kJ/mol, indicating that the adsorption of some of the Pb²⁺ ions onto PACI may be physical in nature. This may be attributed to the formation of weak bonding between lead and the active sites of PACI present as a suspension.

Application

To investigate the applicability of the recommended procedure, a series of experiments was performed to recover 10 and 20 mg of Pb²⁺ ions added to aqueous and some natural water samples. The adsorption experiments were carried out using 1L of clear, filtered, uncontaminated sample solutions after adjusting their pH values to 7.0. The results obtained are listed in Table 2 and show that the recovery was satisfactory and quantitative (ca. 100%).

Adsorption mechanism

Although adsorption from solution by solids is of great practical importance and a vast number of papers have been published, it has been only over the last three decades a fundamental understanding has been developed. However, sharp limits between the different adsorption mechanisms are not clear. Before discussing the adsorption mechanism involved, the following points need to be taken into consideration:

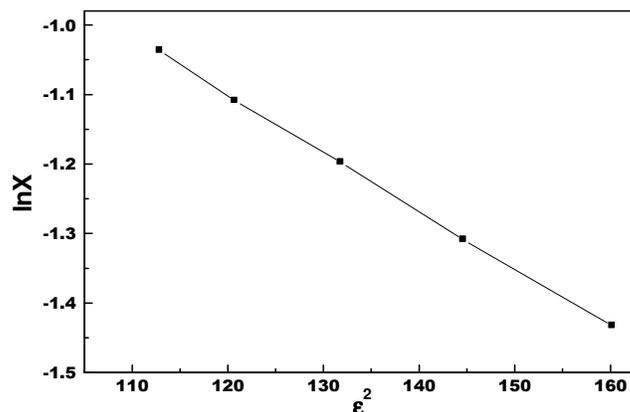


Figure 10. Dubinin-Radushkevich (D-R) plot for Pb²⁺ ions adsorption on to PACI.

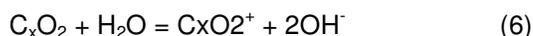
- Most metal cations are removed by: i) Adsorption on solid phases via precipitation of their insoluble hydroxides. ii) Ion exchange. iii) Flocculation by adsorption of hydrolytic species. iv) Complexation with specific surface sites provided the appropriate conditions prevail (Zouboulis et al., 1995; Apak et al., 1998).
- As a function of solution pH (Sheng et al., 2004; Bradl, 2004), lead species may exist as soluble Pb²⁺ and hydroxo-species [Pb(OH)⁺, Pb(OH)₃⁻ and Pb(OH)₄²⁻] in addition to the insoluble lead hydroxide Pb(OH)₂.
- Most activated carbon surfaces are negatively charged and are characterized by the presence of oxo groups C_xO and C_xO₂ which react in aqueous suspensions as organic carboxylic and phenolic groups (Ghazy and Moustafa, 2001).
- 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 m²/g. (ii) Carboxylic, lactone and phenolic functional groups were present on the surfaces of the carbon samples as determined by the method reported (Samra 2000), with free carboxylic groups comprising ca. 25%, lactone groups amounting to 55% while phenolic groups amounting to 20%. (iii) The increase in the solution pH observed after stirring the PACI sorbent with distilled water for 4 h may be attributed to adsorption of H⁺ ions from solution or de-sorption of OH⁻ ions from the sorbent surface. (iv) Modification of powdered activated carbon gave sulfur containing active sites. (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.

Table 2. Recovery (%) of Pb²⁺ ions spiked to 1 L of various water samples using 100 mg of PACI at pH ~ 7 and stirring for 10 min at 200 rpm.

Sample (location)	Pb ²⁺ added (mg)	Pb ²⁺ found (mg)	Recovery (%)
Distilled water	10	10	100.0
	20	19.98	99.9
Tap water (our laboratory)	10	9.93	99.3
	20	19.94	99.7
Nile water (Mansoura City)	10	9.93	99.3
	20	19.95	99.8
Sea water (Gamasah)	10	10	100.0
	20	19.98	99.9
(Ras El-Barr)	10	9.98	99.8
	20	19.96	99.8
(Alexandria)	10	9.98	99.8
	20	20	100.0
Lake water (Manzalah)	10	9.96	99.6
	20	19.96	99.8
Underground water (Cinbillaween City)	10	10	100.0
	20	19.98	99.8

Therefore, the proposed mechanism may occur as follows:

a) At pH < 1.0 the removal of Pb²⁺ ions was diminished which may be attributed to the fact that the oxo groups (C_xO and C_xO₂) formed on the carbon surface during activation react with water according to



to form positively charged surface groups (Sharma and Forster, 1996); thereby hindering the adsorption of Pb²⁺ ions.

b) At pH > 1, the sorption of Pb²⁺ ions increases gradually which may be due to the chemical combination of Pb²⁺ ions with carboxylic groups of activated carbon, or with sulfur (obtained from per-sulfate that was used in the modification of activated carbon surface) or via co-precipitation of its colloidal insoluble sulfides.

c) Over the pH range 4 - 8, where the maximal sorption of Pb²⁺ ions occurred (~100%) and in addition to the above mechanisms, the removal of Pb²⁺ ions may proceed via adsorption of its hydrolytic species, Pb(OH)⁺.

d) The decrease in the sorption rate at high pH values (> 10) may be attributed to the fact that the negative species of lead such as Pb(OH)₃⁻ and Pb(OH)₄²⁻ are not capable of sorption onto negative surface of PACI.

Conclusion

Powdered modified activated carbon has been investigated as cheap and effective organic sorbent for the

removal of Pb²⁺ ions from aqueous solutions. The experimental results revealed the following:

(i) The adsorption process was endothermic and followed first-order kinetics.

(ii) It occurred mainly at the surface of the solid waste and to some extent by the internal pores.

(iii) It was well described by the Langmuir and Freundlich models.

(iv) It could occur through adsorption of hydrolytic species and/or precipitation of lead hydroxide and sulfide onto sorbent.

(v) The procedure was successfully applied for the removal of Pb²⁺ ions from drinking and natural waters.

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