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### Equilibrium Sorption Isotherm And Kinetics For Lead (II) Onto Activated Carbon Development From Doum-Palm Seed

*Corresponding Author*

Ola Abdelwahab  
 Environmental Division,  
 National Institute of Oceanography and Fisheries,  
 Kayet Bay, El-Anfushy, Alexandria (EGYPT)  
 Tel: +203- 4953632; Fax: +203-4950086  
 E-mail: olaabdelwahab53@hotmail.com

*Co-Author*

Nevine K.Amin  
 Chemical Engineering Department,  
 Faculty of Engineering, Alexandria University,  
 Alexandria (EGYPT)

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#### ABSTRACT

Three new sorbents for removing of lead (II) ion from aqueous solutions have been investigated. The new sorbents are the crushed doum-palm seed coat (RD) and two activated carbons developed from RD by physical activation at 300°C (DAC1) and by chemical activation with H<sub>3</sub>PO<sub>4</sub> followed by carbonization at 300°C (DAC2). The effect of the adsorption capacity of the three adsorbents was studied using different pH (1 to 9), initial lead (II) concentration (10 to 60 mg l<sup>-1</sup>), dose of adsorbent (1 to 10 g l<sup>-1</sup>) and contact time (5 to 180 min). The maximum removal of lead (II) was obtained at pH 5.0 (97%) using DAC2 adsorbent. The isotherm equilibrium data were fitted well by Freundlich adsorption isotherm to obtain the characteristic parameters of the model. The adsorption of lead ions follows the pseudo-second order rate kinetic equation. Adsorption capacity of lead (II) was 18.9 mg per gram of adsorbent at pH 5. © 2006 Trade Science Inc. - INDIA

#### KEYWORDS

Lead;  
 Activated carbon;  
 Adsorption;  
 Agricultural waste.

#### INTRODUCTION

The prime concern of environmental engineer is the removal of small concentrations of toxic substances from wastewater. Lead, which is widely used

as an industrial raw material for storage battery manufacture, photographic material, matches manufacturing<sup>[1]</sup>, is one of these toxic substances. Its toxicity to humans and the environment has been well documented, where it can cause severe dysfunction in

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the kidneys, reproductive system, liver, brain and central nervous system so cause sickness or death. For this reason, it is essential to remove  $Pb^{++}$  ions from industrial wastewater before being discharged. It is generally used the advanced treatment processes such as chemical reduction, ion exchange, reverse osmosis, electro-dialysis and activated carbon adsorption<sup>[2]</sup>.

Since the cost of these processes is rather expensive the uses of agricultural residues or industrial by-products having biological activities have been received with considerable attention<sup>[3]</sup>. Thus, many materials have been examined. In recent years, a number of agricultural material such as wheat bran shell<sup>[4,5]</sup>, moss peat<sup>[6]</sup>, coconut husk<sup>[7,8,9]</sup>, chitosan<sup>[10,11,12,13]</sup>, peanut hulls<sup>[14,15]</sup>, and almond husk<sup>[16,17]</sup>, have been reported for the removal of toxic metals from aqueous solutions.

The doum-palm (*hyphaenethebaica*) is an african plant has been cultivated since time immemorial in Egypt. Doum seed-coat is readily available in great abundance in upper Egypt and generally discarded as waste.

The aim of study was to investigate the possibility of using doum-palm seed-coat and two developed activated carbons from doum seed-coat as new adsorbents for the removal of  $Pb^{++}$  from aqueous solution. The isotherm, kinetics and reaction rate of the adsorption of lead ions from aqueous solution, were also investigated. This paper reported also the effect of adsorption parameters such as pH, adsorbent concentration, contact time and initial concentration of lead (II) on metal adsorption with doum seed-coat activated carbon and doum seed-coat as a raw adsorbent.

## EXPERIMENTAL

### Materials and equipment

All reagents were of AR grade chemicals. A stock solution of lead ( $1000 \text{ mg l}^{-1}$ ) was prepared in double distilled water using lead acetate. All other solutions were prepared by diluting stock solution. The pH measurements were made using pH meter (Model 744, metrohm) and the pH test solutions were adjusted using 0.1N NaOH or 0.1N HCl solutions.

Lead ions concentrations were determined with an atomic absorption spectrophotometer (Perkin Elmer 2380).

### Preparation of adsorbent

The doum seed-coats were collected locally from Upper Egypt. They were first freed of the doum kernels by filling. Then, they were washed with distilled water and dried in an oven at  $105^{\circ}\text{C}$  over night and used for adsorption without activation. The dried seed-coats were crushed and sieved to a particle size ranging from 1-2 mm. Activated carbons have been prepared from the above material by application of physical activation only, and by application of both chemical and physical activation. First treatment was carried out by carbonization of the raw material in the stainless steel covered tube at  $300^{\circ}\text{C}$  in a muffle furnace for 1 hour in the absence of air. The carbon obtained by this treatment is termed "Doum Activated Carbon-1 or DAC1". In the second treatment the raw material was soaked in 28%  $\text{H}_3\text{PO}_4$  for 24 h, and then it was filtered and carbonized in a stainless steel covered tube in the absence of air at  $300^{\circ}\text{C}$  in a muffle furnace. This activated carbon was then neutralized with ammonia solution and washed several time until it reached neutralization. The adsorbent obtained by this treatment is termed as "Doum Activated Carbon-2, DAC2".

### Adsorption experiments

Adsorption experiments were conducted to investigate the influence of adsorption parameters such as pH, adsorbent concentration, contact time and initial concentration of lead ions uptake by using the three adsorbents (RD, DAC1 and DAC2).

Batch adsorption experiments were carried out in a 250 ml stopper conical flask by adding 0.1-1.0 g of adsorbent and 100 ml of lead acetate solution of specific concentration. The concentration of  $Pb^{++}$  solution was varied from 10-60  $\text{mg l}^{-1}$ . All experiments were done at room temperature. The samples were shaken in a mechanical shaker for a contact time ranging from 5-180 min. The pH of the solutions was ranged from 1-9. After each experiment the contents were filtered through a Whattmann filter paper N.44 neglecting the first 5 ml of the filtrate in order to saturate the filter paper with lead acetate

solution. Concentrations of lead ions in the filtrate were then determined by atomic absorption spectrophotometer. The amount of lead ions adsorbed was calculated based on the difference between the lead ion concentration in aqueous solutions before and after adsorption.

## RESULTS AND DISCUSSION

### Investigation of sorption parameters

The results obtained from the present investigation revealed the ability of treatment of waste streams containing  $Pb^{++}$  ions. Effect of the following parameters on the removal of  $Pb^{++}$  was monitored as follows:

#### 1. Effect of pH

It is well known that adsorption of heavy metal ions depends on pH of the aqueous solution. Figure 1 presents the effect of initial pH (1.0 to 9.0) on the removal of  $Pb^{++}$  by RD, DAC1 and DAC2. The percentage adsorption of metal ions increased with the increase in pH value up to a certain value (pH ~5.5) and then decreased with further increase in pH value. It is clear that activated carbon prepared by phosphoric acid activation prior to carbonization (DAC2) was effective for the quantitative removal of lead ions at pH 5.5. The maximum adsorption of 97%, 81% and 77% took place by DAC2, DAC1 and RD, respectively at pH 5.5 from an initial concentration of 20 mg l<sup>-1</sup>.

#### 2. Effect of contact time

The effect of contact time on the adsorption of lead ions by RD, DAC1 and DAC2 are shown in figure 2. The percentage of  $Pb^{++}$  ions removal from aqueous solution increases with time and attains equilibrium at 90, 60 and 30 min for RD, DAC1 and DAC2, respectively, using initial  $Pb^{++}$  concentration of 20 mg l<sup>-1</sup> at pH 5.5, while the percentage removal was found to reach 77, 83 and 97, respectively.

#### 3. Effect of initial concentration

Figure 3 represented the effect of initial metal concentration on the adsorption of  $Pb^{++}$  by RD, DAC1 and DAC2. When the initial  $Pb^{++}$  concentration of sample was increased from 10 to 60 mg l<sup>-1</sup>,

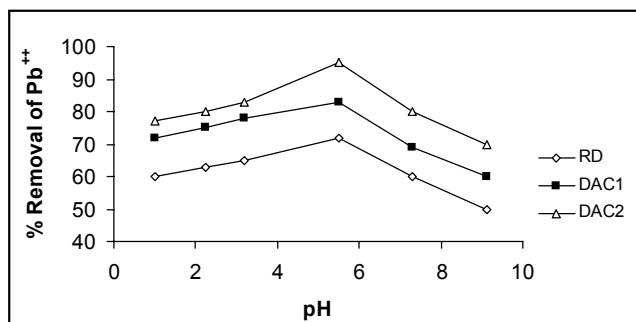


Figure 1: Effect of initial pH on the removal of  $Pb^{++}$  using different adsorbents, dose of adsorbent 5.0 g l<sup>-1</sup>, concentration of  $Pb^{++}$  solution is 20.0 g l<sup>-1</sup>, and time of agitation 2h

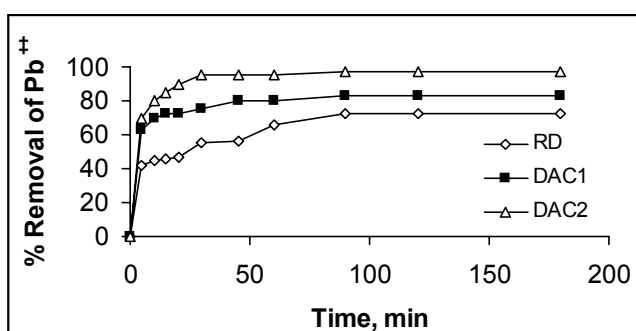


Figure 2: Effect of time on adsorption of  $Pb^{++}$  on different adsorbents at initial concentration 20 mg l<sup>-1</sup>, dose of adsorbent 5 g l<sup>-1</sup>, pH=5.5

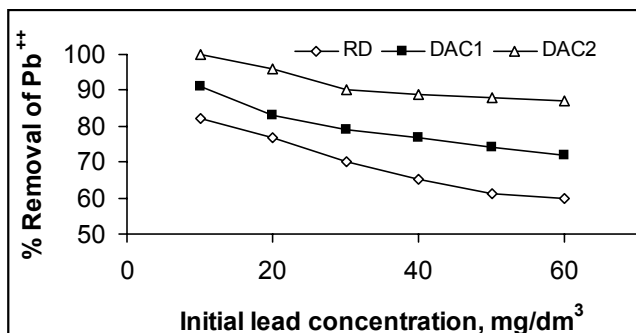


Figure 3: Adsorption of  $Pb^{++}$  as a function of  $Pb^{++}$  initial concentration for different adsorbents and contact time 2h, adsorbent dose 5.0 g l<sup>-1</sup>

the percentage removal decreased from 81 to 58, 90 to 75 and 97 to 88 for RD, DAC1 and DAC2, respectively, for an agitation time of 2 hours, pH 5.5 and adsorbent dose 5.0 g l<sup>-1</sup>. It is clear that the increase in initial  $Pb^{++}$  concentration decreased the percentage removal; this is because, at higher initial concentrations the ratio of initial number of moles of

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Pb<sup>++</sup> to the available surface area is high, and hence fractional adsorption becomes dependent on initial concentration. For fixed adsorbent dose, the total available adsorption sites are limited thereby adsorbing almost the same amount of sorbate thus resulting in a decrease in percentage removal of the adsorbate corresponding to an increase in initial sorbate concentration.

### 4. Effect of adsorbent dose

Figure 4 indicates the effect of adsorbent dose on Pb<sup>++</sup> uptake for RD, DAC1 and DAC2. It is clear that the percentage removal of lead ions increases with the increase in the dose of adsorbent until the dose reached 5 g l<sup>-1</sup>, after which the percentage removal becomes constant. This trend is expected because as the adsorbent increases the number of adsorbent particles increase. Hence, more Pb<sup>++</sup> ions attached to the active sites in adsorbent surface and same results were reported elsewhere<sup>[18-19]</sup>.

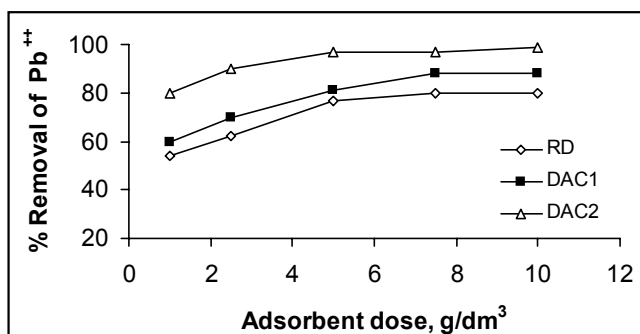


Figure 4: Effect of different sorbent dose on Pb<sup>++</sup> removal at solution pH=5.0, Initial concentration of Pb<sup>++</sup> solution is 20 mg l<sup>-1</sup> and contact time 2h

### Adsorption isotherms

The Langmuir isotherm model assumes that the uptake of metal ions occur on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. Langmuir equation can be determined from a linearised form of Eq. (1), represented by

$$\frac{C_e}{q_e} = \frac{1}{bC_1} + \frac{C_e}{C_1} \quad (1)$$

where  $C_e$  is the equilibrium concentration (mg l<sup>-1</sup>),  $q_e$  the amount adsorbed per specified amount of adsorbent (mg g<sup>-1</sup>) and  $b$  (l mg<sup>-1</sup>) and  $C_1$  (mg g<sup>-1</sup>) are

Langmuir constants related to the energy and capacity of adsorption respectively.

The Freundlich model assumes that the uptake of metal ions occur on a heterogeneous surface by monolayer adsorption. It is frequently found that the data on adsorption from a liquid phase are fitted better by the Freundlich isotherm equation

$$q_e = k_f C_e^n \quad (2)$$

or

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

The common terms in equations (1) and (2) are described above and  $k_f$  and  $n$  are Freundlich constants, where  $k_f$  is the measure of adsorption capacity (mg g<sup>-1</sup>) and  $n$  is a measure of adsorption intensity.

The linear plot of  $C_e/q_e$  Vs  $C_e$  at different adsorbents (Langmuir isotherm) is shown in figure 5. The values of  $b$  and  $C_1$  for the removal of Pb<sup>++</sup> ions by the different adsorbents were determined from the slopes and intercepts of these lines. The essential characteristic of Langmuir isotherm can be expressed in terms of a separation factor,  $R_L$ , which is defined by the following equation<sup>[20]</sup>:

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where  $b$  is the Langmuir constant;  $C_0$  is the initial concentration. The values of separation factor  $R_L$  at different conditions were found to be in the range from 0.1 to 0.71, i.e., between 0 and 1, indicating the favorable adsorption of Pb<sup>++</sup> on doumpalm seed-coat.

Plots of  $\log(q_e)$  against  $\log(C_e)$  are linear as shown in figure 6. This shows the applicability of

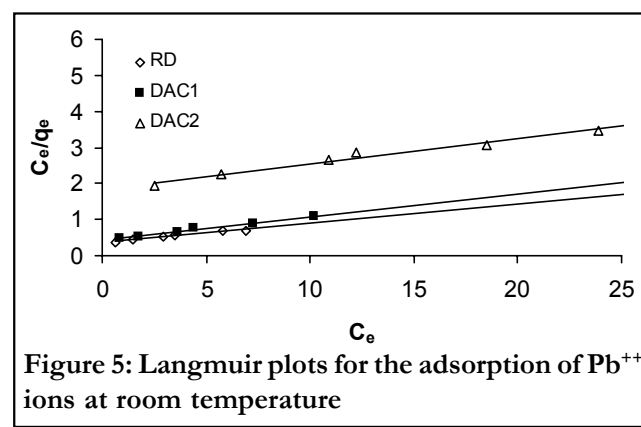


Figure 5: Langmuir plots for the adsorption of Pb<sup>++</sup> ions at room temperature

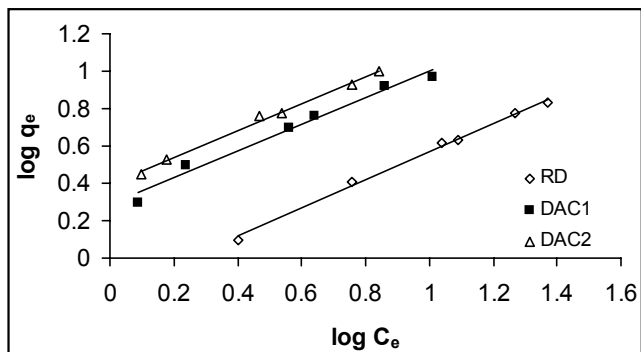


Figure 6: Freundlich plots for adsorption of Pb<sup>++</sup> ions at room temperature

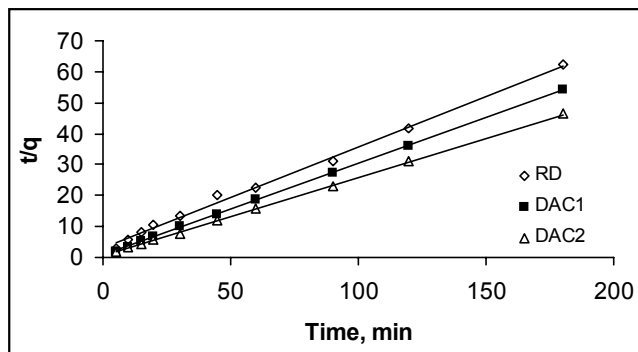


Figure 7: Pseudo-second order sorption kinetics of lead onto various adsorbents

applying Freundlich isotherm. The values of  $k_f$  and  $n$  for the uptake of Pb<sup>++</sup> ions by RD, DAC1 and DAC2 were determined from the slopes and intercepts of these lines, and are given in TABLE 1. Values of  $1 < n < 10$  show favorable adsorption of Pb<sup>++</sup> on the three adsorbents<sup>[21]</sup>. The Langmuir correlation coefficient ( $r^2$ ) obtained from figure 5 was 0.97 for the three adsorbents, while the Freundlich correlation coefficients were found to be approximately 0.99 for them. According to these results, the data fitted reasonably well the Freundlich isotherm with different three adsorbents. This leads to the conclusion that the surfaces of RD, DAC1 and DAC2 prepared from doum seed-coats are made up of small homogeneous and heterogeneous batches.

**Adsorption kinetics**

Kinetics of adsorption, in terms of solute uptake rate, which governs the residence time, is one of the important characteristics defining the efficiency of adsorption. The reaction order was examined using pseudo first order kinetic equation

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \tag{5}$$

where,  $q_e$  is the amount adsorbed at equilibrium

TABLE 1: Adsorption constants for adsorption of Pb<sup>++</sup> ions on different activated carbons prepared from doum palm-seed coat

Adsorbent	Langmuir constants			Freundlich constants		
	C <sub>i</sub> (mg/g)	b(l/mg)	r <sup>2</sup>	k <sub>f</sub> (mg/g)	n	r <sup>2</sup>
RD	14.3	0.04	0.95	2.50	1.38	0.995
DAC1	15.6	0.15	0.98	1.93	1.39	0.980
DAC2	18.9	0.15	0.97	0.65	1.33	0.996

TABLE 2: The adsorption kinetic model rate constants for RD, DAC1 and DAC2

Adsorbent	Pseudo first-order		Pseudo second-order	
	k <sub>1</sub>	r <sup>2</sup>	k	r <sup>2</sup>
RD	0.026	0.892	0.039	0.996
DAC1	0.035	0.933	0.118	1.000
DAC2	0.050	0.801	0.143	1.000

(mg g<sup>-1</sup>),  $q$  is the amount adsorbed at time  $t$  (mg g<sup>-1</sup>) and  $k_1$  is the rate constant of pseudo first order (l min<sup>-1</sup>). The values of  $\log (q_e - q)$  Vs  $t$  were plotted for different adsorbents. The data were fitted with a poor correlation coefficient (TABLE 2). As a result, the rate constant of the adsorption of Pb<sup>++</sup> ions on the adsorbents was determined using the following pseudo second-order adsorption kinetic rate equation:

$$\frac{t}{q} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{6}$$

where,  $k$  is the rate constant of pseudo second order (g mg<sup>-1</sup> min<sup>-1</sup>). The kinetic plots of  $t/q$  Vs  $t$  for Pb<sup>++</sup> removal at different adsorbents are presented in figure 7. The relationship shows a good compliance with the pseudo second-order equation. The correlation coefficient  $r^2$  for the linear plot (TABLE 2) suggests a strong relationship between the parameters and also explains that the process of adsorption follows pseudo second order kinetics.

**CONCLUSIONS**

The agriculture waste, doum palm seed-coats, was used for the removal of lead ions from aqueous

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solution. DAC2 was the most effective sorbent, for which the removal reached 97% of Pb<sup>++</sup> ions at pH 5.5 and dose of adsorbent 5.0 g l<sup>-1</sup>. Adsorption of Pb<sup>++</sup> was dependent on pH and the maximum adsorption was attained at pH 5.5. Pb<sup>++</sup> removal was increased with adsorbent dose then reached a plateau at 5 g l<sup>-1</sup> adsorbent. Contact time was found to increase the percentage removal of Pb<sup>++</sup> ions in the first 30 min. While, the efficiency decreased with increasing Pb<sup>++</sup> ions concentration. The removal followed Langmuir and Freundlich isotherms. The order of reaction of sorption of lead on different sorbents prepared from doum-palm seed-coat followed a pseudo- second order rate expression.

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