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Adsorption of Lead from Aqueous Solution onto Untreated Orange Barks

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Waste materials with no further treatment such as orange barks from commercial oranges may act as adsorbent for the removal of Pb^{2+}. Batch kinetic and equilibrium experiments were conducted to study the effects of contact time, initial pH, adsorbent dose and initial concentration of lead. The results show that the equilibrium was achieved less than 30 min of contact time. Three adsorption isotherm models namely, Langmuir, Freundlich and Dubinin-Radushkevich were used to analyse the equilibrium data. The Langmuir isotherm which provided the best correlation for Pb^{2+} adsorption onto orange barks reveals that the adsorption was favourable and the maximum adsorption capacity found was equal to 112,36 $mg.g^{-1}$. The results of the present study suggest that orange barks will be used as an effective and economical adsorbent for Pb^{2+} removal.

1. Introduction

The excessive release of heavy metals into the environment is a major concern worldwide. Lead contamination in drinking water is a major source of concern due to its detrimental effect on human health when ingested, its pollution results from textile dyeing, ceramic and glass industries, petroleum refining, battery manufacture and mining operations. Various processes of heavy metals elimination, in particular lead, are used, we can cite: precipitation, electro precipitation, electro coagulation, cementing and separation by membrane, the solvent extraction and the exchange of ions on resins. Strict environmental protection legislation and public environmental concerns lead the search for novel techniques to remove heavy metals from industrial wastewater. Adsorption is considered quite attractive in terms of its efficiency of removal from dilute solutions. Many adsorbents have been used for removal of lead ions (Ibrahim et al., 2010; Teoh et al., 2013). These adsorbents were used in raw state (Lalhruaitluanga et al, 2010; Liao et al., 2011) or with modified surface (Depci et al, 2012; Mouni et al., 2011). Thus, there is a growing demand to find relatively efficient, low cost and easily available adsorbents for the adsorption of lead, particularly if the adsorbents are the wastes (Anirudhan et al., 2011). The present study was carried out to show the potential of lead adsorption on a vegetable material: orange barks, coming from commercial orange and which constitute a waste. The aim of this research, were to evaluate the adsorption behavior of Pb^{2+} onto orange barks and to compare its performance with those of other adsorbents. The influence of experimental conditions, contact time, pH solution, adsorbent dose and initial Pb^{2+} concentration on the adsorption behavior was investigated.

2. Materials and methods

2.1 Preparation of the adsorbent

The orange barks coming from commercial oranges was first dried at ambient air and then grounded. After this, the adsorbent was washed with water, dried at 105°C and sieved by applying the TAYLOR norm.

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2.2 Preparation of the metal solution

The Lead solution is prepared by dissolving lead nitrate ($PbNO_3$) in distilled water. The initial concentration varies from 10 to 600 mgL^{-1}. The initial pH of the solution is adjusted by using a solution of HNO_3 or NaOH.

2.3 Metal adsorption experiments

The adsorption experiments were carried out in batch system at room temperature (25 °C). A given mass of adsorbent was added to lead solution and the entirety was agitated during a certain time in a magnetic stirrer at 430 rpm. The samples were carried out at quite time intervals, filtered through filter paper (Double Boxing rings 102). Pb^{2+} analysis was realized by atomic absorption spectrophotometer (PERKIN ELMER, A 800) with a wavelength of 228.8 nm, a slit of 0.5 and one flame of the air–C_2H_2 type. The quantity of metal adsorbed at equilibrium was calculated by the following expression:

$$q_e = (C_o - C_e)V/m \quad (1)$$

where m is the mass of adsorbent (g), V is the volume of the solution (L), C_o is the initial concentration of metal (mg L^{-1}), C_e is the equilibrium metal concentration (mg.L^{-1}) and q_e is the metal quantity adsorbed at equilibrium (mg of Pb^{2+}/g of adsorbent).

For the calculation of the yield of cadmium adsorption (R_e), we used the following expression:

$$R_e(\%) = (C_o\text{-}Cr).100/C_o \quad (2)$$

where Cr is the residual concentration of lead in the solution (mg L^{-1}).

2.4 Calculation of adsorption isotherms parameters

The tests concerning the study of the adsorption equilibrium were carried out for metal concentrations of 10 mg.L^{-1} to 600 mg.L^{-1} using for each experiment, one liter of lead solution. During adsorption, a rapid equilibrium is established between the quantity of metal adsorbed on the adsorbent (q_e) and metal remaining in solution (C_e). The isotherms data were characterized by the Langmuir (3) and Freundlich (4) equations:

$$q_e = q_{max}\, bC_e / (1+bC_e) \quad (3)$$

$$q_e = K_F\, C_e^{\,n} \quad (4)$$

where (b, q_{max}) and (K_F, n) are empirical constants of Langmuir and Freundlich isotherms, respectively, that will be calculated from the linear forms of the equations (3) and (4) :

$$1/q_e = (1/q_{max}b).1/C_e + 1/q_{max} \quad (5)$$

$$\ln q_e = \ln K_F + n \ln C_e \quad (6)$$

Dubinin-Radushkevih (D-R) model is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant sorption potential. The D-R equation is:

$$q_e = q_{max} \exp([-B[RT]\, Ln(1+1/C_e)]^2)] \quad (7)$$

where B is a constant related to the adsorption energy, R (8.314 J.mol^{-1}.K^{-1}) is the gas constant, and T (K) is the absolute temperature. The constant B (mol^2 .kJ^{-2}) gives the mean free energy E (kJ.mol^{-1}) of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship:

$$E = 1/(2.B)^{0,5} \quad (8)$$

This parameter gives information about chemical or physical adsorption. The magnitude of E between 8 and 16 KJ.mol^{-1} indicates that the biosorption process follows chemical ion-exchange, while for the values of E< 8 KJ.mol^{-1}, the biosorption process is of a physical nature. The linear form of this model is expressed by :

$$Lnq_e = lnq_{max} - B.\varepsilon^2 \quad (9)$$

Where

$\varepsilon = RT\ Ln(1+1/C_e)$ (10)

3. Results and discussions

3.1 Effect of operating parameters

3.1.1 Effect of contact time

The effect of contact time was studied for an initial lead concentration of 100 $mg.L^{-1}$ and for different adsorbent mass 4, 5, and 6 g. The figure 1 shows a rapid initial adsorption rate of lead at the beginning until 20 min of contact time, thereafter, the adsorption rate became practically constant. The variation in the extent of adsorption may be due to the fact that initially all sites on the adsorbent surface were vacant and the solute concentration gradient was relatively high.

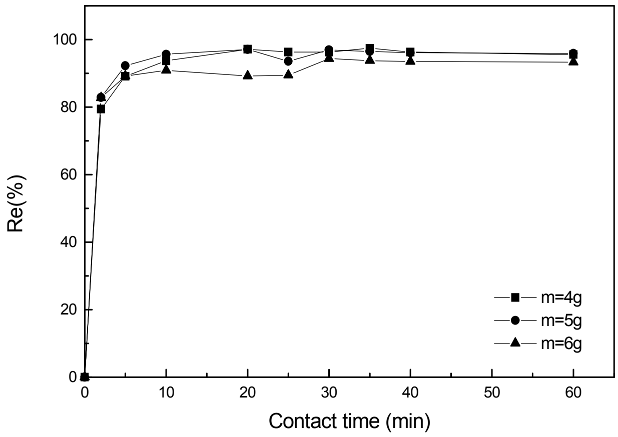

Figure 1: Effect of contact time on adsorption rate of Lead onto orange barks. [Pb]o = 100 $mg.L^{-1}$, Adsorbent dose = 4, 5, 6 g, pH = 4,6, T= 25 °C,

3.1.2 Effect of initial pH

Aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the sorbent, It has been identified as the most important variable affecting metal adsorption onto adsorbent, this partly because hydrogen ions themselves are strongly competing with adsorbate. Adsorption experiments were carried out in pH range of 1 to 4,6 keeping all other parameters constant (adsorbent mass = 4 g, $[Pb]_0$ = 100 $mg.L^{-1}$ and T = 25 °C). The lead removal efficiency of orange barks at different pH values are shown in figure 2. It can be observed optimal pH values around 3 - 4,6. The increase in metal removal with increase in pH values can be explained on the basis of a decrease in competition between proton and the metal cations for the same functional groups and by the decrease in positive charge of the adsorbent which results in a lower electrostatic repulsion between the metal cations and the surface.

3.1.3 Effect of adsorbent dose

The adsorbent dose in solution will affect the metal adsorption capacity. Several other investigators have also reported the same trend of adsorbent concentration effect on lead adsorption (Mouni et al., 2011). It can be shown in figure 3, that the adsorption rate of Pb(II) increased with increasing orange barks until 3 g, this can be explained as adsorbent dose increased, more and more surface area will be available which exposed more active sites for binding of metal ions. For a given initial concentration of lead, further increase of the adsorbent mass don’t have practically any effect on the adsorption rate of lead.

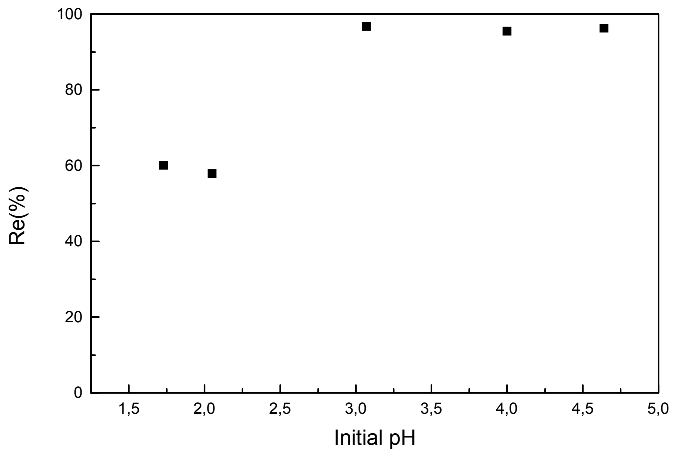

Figure 2: Effect of initial pH on adsorption rate of Lead onto orange barks. $[Pb]_0$ = 100 mg.L^{-1}, Adsorbent dose = 4 g, T= 25 °C,

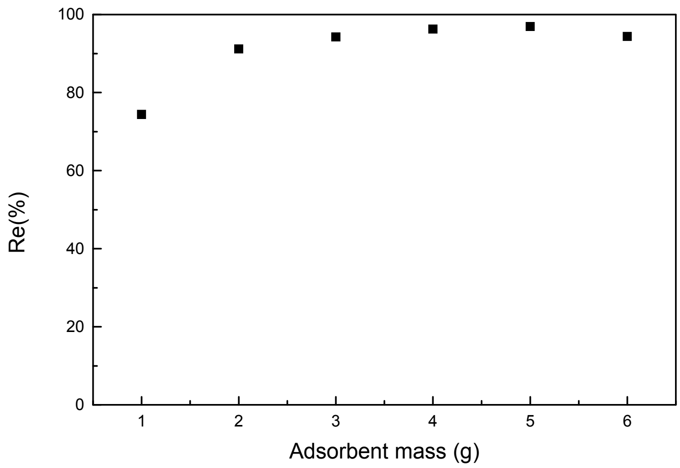

Figure 3 Effect of adsorbent dose on adsorption rate of Lead onto orange barks. $[Pb]_0$ = 100 mg.L^{-1}, pH = 4,6, T= 25 °C,

3.1.4 Effect of initial lead concentration

Adsorption of metals by any adsorbent is highly dependent on the initial concentration of metal ion. The adsorption of lead was carried out at different initial Pb^{2+} ion concentrations ranging from 10 mg.L^{-1} to 600 mg.L^{-1}. The results presented in figure 4, show that the percentage of removal decreases with increasing initial lead concentration. This can be explained that all the biosorbents has a limited number of active sites, which become saturated at a certain concentration.

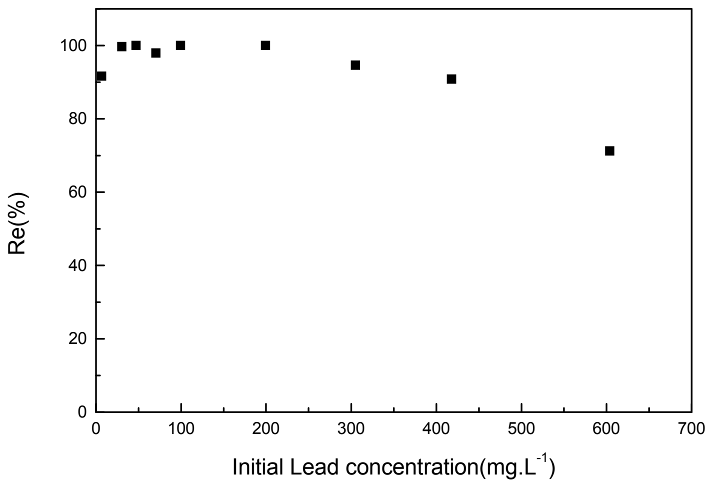

Figure 4 : Effect of initial lead concentration on adsorption rate of Lead onto orange barks. Adsorbent dose = 4g,, pH = 4,6, T= 25°C,

3.2 Adsorption isotherms

Adsorption isotherm plays a crucial role in the predictive modelling procedures for the analysis and design of an adsorption system. Therefore, in this study, the adsorption data of Pb^{2+} were tested with Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models within metal ion concentration range 10 to 600 mg.L^{-1}. The various constants of the three models were calculated and are collected in Table 1.

Table 1. Isotherm constants for lead adsorption onto orange barks

Langmuir			Freundlich			Dubinin-Radushkevich			
q_{max} (mg.g^{-1})	B (L.mg^{-1})	R^2	K_F	n	R^2	q_{max} (mg.g^{-1})	B (mol^2.J^{-2})	E (kJ.mol^{-1})	R^2
112,36	0,1234	0,95	11,20	0,493	0,71	82,40	6,8.10^{-7}	0,855	0,98

By comparing the correlation coefficients, it can be concluded that both Langmuir and Dubinin-Radushkevich isotherm models provide good models for the sorption system. Experimental and calculated data are displayed in figure 5 and showed that experimental results were accurately described by Langmuir isotherm model.

The maximum adsorption capacity estimated by means of the Langmuir model, was 112,36 mg.g^{-1} namely higher than the maximum adsorption capacities reported for some other adsorbents in the available literature and collected in Table 2.

Table2. Maximum capacity of cadmium adsorption on some adsorbents

	qmax (mg.g-1)	References
AC from waste coconut buttons	92,72	(Anirudhan et al, 2011)
Bamboo	53,76	(Lalhruaitluanga et al., 2010)
AC from apricot stones	21,36	(Mouni et al., 2011)
Lemna perpusilla Torr.	86,96	(Tang et al., 2013)
Mercapto functionalized sepiolite	97	(Liang et al., 2013)
Orange barks	112,36	Present study

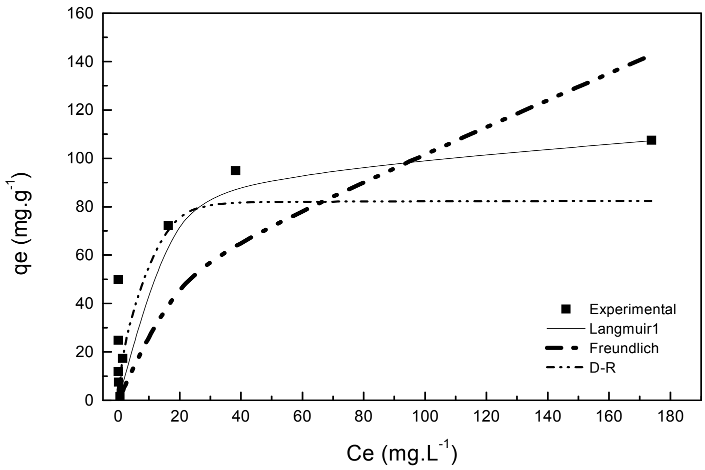

Figure 5 : Experimental and adjusted isotherms for adsorption of Lead onto orange barks. Adsorbent dose = 4 g, pH = 4,6 T= 25°C,

4. Conclusion

The present investigation shows that the orange barks can be employed as a potentially low cost sorbent for the removal of Pb^{2+} ions from industrial wastewaters. The Pb^{2+} adsorption is found to be greatly dependent on the initial pH of the solution, its concentration and adsorbent mass. The maximum biosorption of Pb^{2+} was found at pH values between 3 and 4,6. The kinetic experiments show that the adsorption was rapid and the adsorption equilibrium was achieved in 20 min of contact time The equilibrium data are well described by the Langmuir isotherm model and the maximum adsorption capacity of Pb^{2+} on orange barks was 112,36 $mg.g^{-1}$. These results show that adsorbents which have a very low economical value may be used effectively for removal of Pb^{2+} ions from aqueous systems for environmental protection purpose.

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