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Adsorption isotherms and kinetics Studies for the removal of Pb(II) from Aqueous Solutions using Low-cost adsorbent

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Abstract. In this present work, the ability to remove Pb(II) from aqueous solutions was studied using waste almond shells (AS) as adsorbent. Activated carbon was prepared from agricultural waste (AS) by chemical activation with H_2SO_4 as an activating agent at 180 ^oC. Adsorption isotherms were expressed by Langmuir and Freundlich adsorption models. Results were analyzed at different temperatures and determined the characteristic parameters for each adsorption isotherm. The maximum sorption capacity q_m was found to be almost 133.3, 125.0 and 111.1, by using Langmuir isotherms at 25ºC, 45ºC and 60 ºC, respectively. The kinetic data were analyzed using pseudo-first-order and pseudo-second-order kinetic models. The kinetic uptake data were best interpreted by a pseudo second-order kinetic model with values of rate constants of adsorption of 1.24 x 10^{-2} (g $mg^{-1}\cdot min^{-1}$).The results of this study show that the (AS) is an efficient adsorbent for the removal of Pb(II) from aqueous solutions.

Keywords: Adsorption isotherm, Kinetics, aqueous solutions , almond shells, Pb(II)

1. Introduction

Toxic heavy metals are released into the environment through industrial activities Their presence in the environment can be detrimental to people, plants and animals. They can accumulate in water, soil, plants and living tissues, thus becoming concentrated throughout the food chain (Cimino, et al, 2000). The important toxic metals are Cd, Zn, Pb and Ni. Lead causes many serious disorders like, anemia, kidney disease, nervous disorders, and even death, it heads the toxic element list of 2008 (Karthika, et al, 2010). Among different heavy metal removal methods, membrane filtration (reverse osmosis), chemical precipitation, electro dialysis, electrolytic processes, biological sorption and adsorption could be mentioned. In recent years adsorption techniques for wastewater treatment have become more popular with regard to their efficiency in the removal of pollutants, especially heavy metal ions. Adsorption has advantages over other methods for remediation of heavy metals from wastewater because its design is simple and it is sludge-free and can be of low capital intensive. In the present adsorption of dissolved Pb(II) on to almond shells has been investigated.

2. Experimental

2.1. Materials and methods

Almond shells (As) was obtained from regions of Arak-Iran. (AS) was first washed several times with deionized water to remove the impurities, and then dried in an oven at 105 ^0C for 24 h. The adsorbent materials was impregnated with concentrated H_2SO_4. Then it was activated in a hot air oven at 180 ^0C for 24

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h. The carbonized material was washed with distilled water to remove the free acid and the activated carbon was then soaked in 1% $NaHCO_3$ solution to remove any remaining acid. Then it was washed with distilled water until the pH of the activated carbon reached 6.5, dried at 105 ^{0}C,and sieved to the particle size 120µm. All the reagents used where of analytical reagent grade and doubly distilled deionized water was used in sample preparation. Stock solution of Pb(II) was prepared by dissolving $Pb(NO_3)_2$ in distilled deionized water. Further working solutions were prepared by diluting this stock solution. Initial pH was adjusted using 0.1N HNO_3 or 0.1N NaOH.

2.2. Batch mode adsorption studies

Adsorption experiments were carried out in 100 mL Erlenmeyer flasks containing 0.1gr of carbon prepared previously and 20 mL solution with known concentration, pH value and temperature. The flasks were stirred , the agitator stirring speed was 200 rpm. After a preset contact time, the samples were separated from the solution by filtration through the filter paper. The exact concentration of the residual metal ion in the filtrate was analyzed by an atomic absorption spectrometer (Shimdzu AA-680, Japan).The equilibrium adsorption amount (q_e) is calculated according to Eq. (1):

$$q_e = \left(\frac{C_o - C_e}{m}\right)V \qquad (1)$$

Where q_e is the amount of P (II) adsorbed (mg g^{-1} carbon) at equilibrium contact time, C_o is the initial Pb(II) concentration (mgL^{-1}), *Ce* is the Pb(II) concentration at equilibrium time in the solution(mgL^{-1}), *V* is the volume of the Pb(II) solution (L), and *m* is the weight of carbon added into the solution (g).

3. Equilibrium sorption study

3.1. Langmuir isotherm model

The Langmuir model was expressed in Eq. (2) (Langmuir, 1916):

$$q_e = \frac{q_m k_l C_e}{1 + k_l C_e} \qquad (2)$$

Where Ce is concentration of Pb (II) ions at equilibrium (mgL^{-1}), qe is amount of Pb (II) ions adsorbed at equilibrium (mgg^{-1}), K_L is Langmuir isotherm constant related to free energy of adsorption (Lmg^{-1}), q_m is maximum adsorption capacity (mgg^{-1}).

Equation (2) could be linearised into:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m k_l} \qquad (3)$$

The plot of C_e/q_e against C_e gave a straight line with slope of $1/q_m$ and intercept of $1/q_mK_L$. Figure (1) showed the Langmuir plot of Pb(II) ions adsorption by (AS) with a correlation coefficient of 0.9989, which was very close to unity (25^{o}C), thus indicating that the data conform well to the Langmuir isotherm model. According to the Langmuir equation, the maximum uptake capacity for Pb (II) ions was 133.33 mgg^{-1}.

3.2. Freundlich isotherm model

The Freundlich isotherm assumes a heterogeneous surface with a non-uniform distribution of heat of biosorption over the surface and a multilayer biosorption can be expressed Freundlich, (1906). The Freundlich model was expressed as:

$$q_e = K_f C_e^{\frac{1}{n}} \qquad (4)$$

Where K_f is Freundlich indicative of relative adsorption capacity of adsorbent,n is Freundlich indicative of the intensity of adsorption. Equation (4) could be linearised by taking logarithms as followed:

$$logq_e = \log K_f + \frac{1}{n} logC_e \quad (5)$$

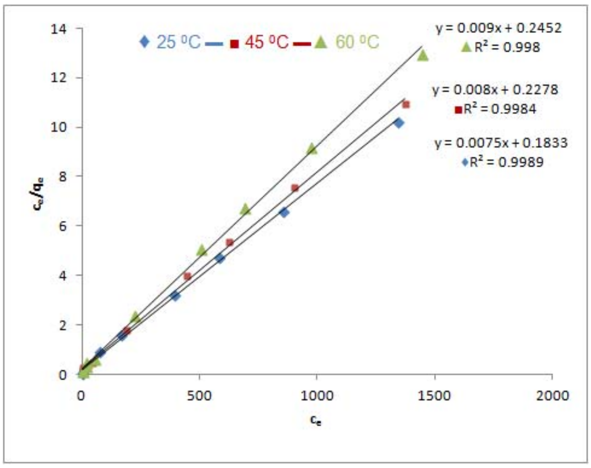

Fig. 1: Langmuir isotherm plot for the sorption of Pb(II) ions onto almond shells Condition: 0.1 g of carbon active (AS) in 20 mL of Pb(II) solution at 200 rpm for 14 hours.

The plot of log q_e against log C_e gave a straight line with slope of $1n$ and intercept of K_f. Figure (2) showed the Freundlich isotherm plot of Pb(II) ions adsorption (AS), with a correlation coefficient of 0.9617. The value of K_f and n obtained from the plot were 0.0857 and 0.3119 respectively. The n value of Freundlich equation could give an indication on the favourability of sorption. It is generally stated that values of n in the range of 2 to 10 is good, 1 to 2 as moderately difficult and less than 1 as poor sorption characteristic (Chen *et al*., 2010). The model parameters are listed in Table 1.

4. Adsorption kinetic study

The kinetics data obtained from adsorption of Pb(II) ions onto (AS) was studied by using two common kinetic models, which are the pseudo-first order kinetic model and pseudo-second order kinetic model. The best fit model was selected based on the linear regression correlation coefficient (R^2), which is a measure of how well the predicted values from a forecast model match with the experimental data.

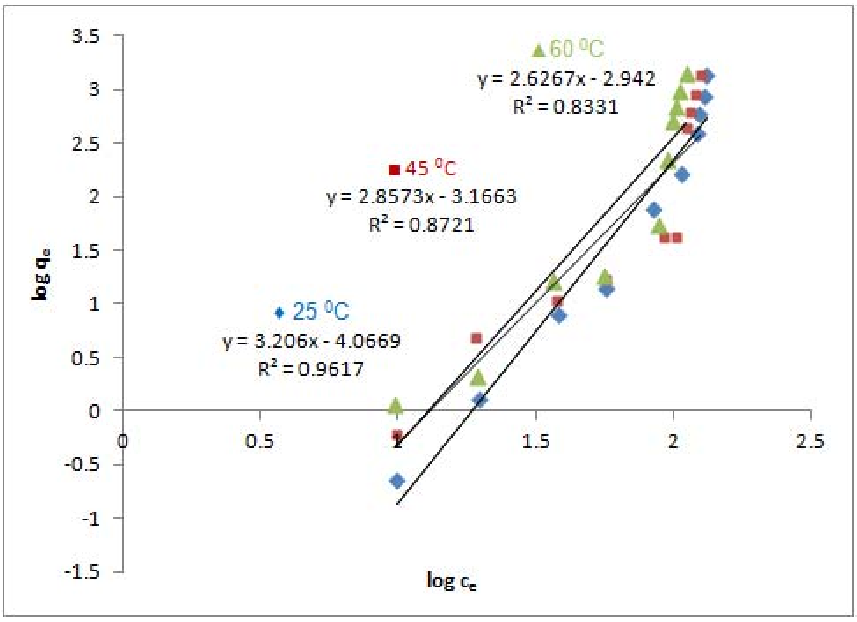

Fig 2 : Freundlich isotherm plot for the sorption of Pb(II) ions onto (AS) Condition: 0.1 g of (AS) in 20 mL of Pb(II) solution at 200 rpm for 14 hours.

4.1. pseudo-first order kinetic model

The pseudo-first order kinetic model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. The pseudo-first order equation in linear form was expressed in equation (6) (Lagergren, 1898):

$$\log\,(q_{e-}q_t) = \log q_e - \frac{k_1}{2.303}t \quad (6)$$

Where k_1 is the first order rate constant (min^{-1}).The plot of log (q_e-q_t) versus t gave the slope k_1 and intercept of log q_e.

Table 1: Isotherm model parameters and correlation coefficient

Isotherm model	Parameters	values		
		25 ^oC	45 ^oC	60 ^oC
Langmuir				
	q_{max} (mg g−1)	133.33	125.00	111.11
	K_L	0.0409	0.0351	0.0367
	R^2	0.9989	0.9984	0.9980
Freundlich				
	K_F □10^{-3}(mg.g^{-1})	0.0857	0.6818	1.1428
	n	0.3119	0.3499	0.3807
	R^2	0.9617	0.8721	0.8331

4.2. Pseudo-second order kinetic model

The pseudo second order is based on the assumption that the rate limiting step may be chemical sorption involving valence forces through sharing or exchange of electrons between heavy metal ions and adsorbent. Pseudo second order equation (Ho and McKay, 1998) can be given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (7)$$

Where k_2 is the rate constant of second order adsorption. This model is more likely to predict the behavior over the whole range of adsorption. The parameters obtained from these models, pseudo first order (Fig. 3) and pseudo second order (Fig. 4) plots for Pb(II) were compared in Tables 2.

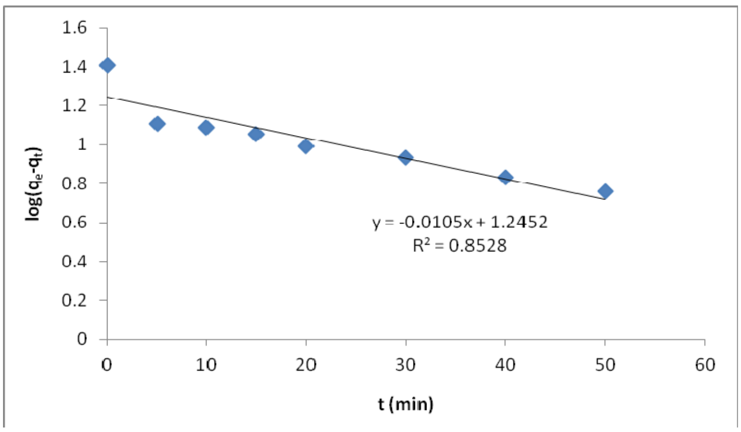

Fig. 3: Pseudo first order Kinetics for adsorption of Pb(II) by activated carbon (AS).

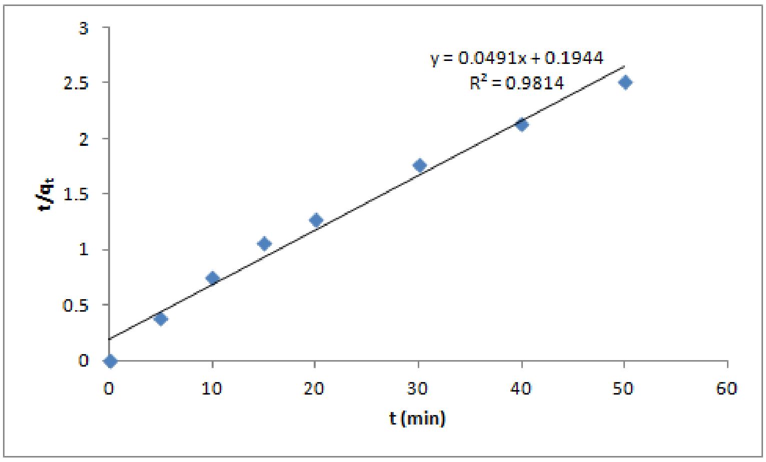

Fig. 4 : Pseudo second order Kinetics for adsorption of Pb(II) by activated carbon (AS).

5. Conclusion

The results from the experiments described in this study show that nickel ions can be absorb efficiently on activated carbon (AS). Results were analyzed by the Langmuir and Freundlich equation and determined the characteristic parameters for each adsorption isotherm. The adsorption equilibrium data were best represented by Langmuir adsorption isotherm. Pseudo second order gave better R^2 values confirming chemisorptions onto the surface. The result indicates that, (AS) is environmentally friendly and promising material which can be used successfully for separation of Pb(II) from aqueous solution.

Table 2: The kinetic parameters evaluated for Pb (II) ion adsorption.

Kinetic model	Parameter	Pb(II) Concentration (100 $mg.L^{-1}$)
Pseudo-first order	K_1 (min^{-1})	0.0242
	q_e ($mg.g^{-1}$)	17.587
	R^2	0.8528
Pseudo-second order	K_2 ($g.mg^{-1}.min^{-1}$)	0.0124
	q_e ($mg.g^{-1}$)	20.367
	R^2	0.9814

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