Mycopath (2014) 12(2): 87-93 **Research Article**

Biosorption of lead(II) ions from aqueous solution by Egyptian peach stones activated carbon

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Abstract

The potential of Peach Stones Activated Carbon (PSAC) waste as a low-cost biosorbent was investigated for removal of lead ions from aqueous solution. Various physico-chemical parameters were studied such as solution pH, biosorbent dose, metal ion concentration and contact time. The experimental results show that the percentage of biosorption increases with an increase in the biosorbent dose at optimum pH 5. 0. The adsorption equilibrium was achieved after 100 min. Generally the maximum percent removal of Pb(II) ion was 99.56% The equilibrium adsorption data were fitted to Langmuir, Freundlich and Dubinin–Radushkevich (D-R) adsorption isotherm models and the model parameters were evaluated. All three models adequately describe adsorption data on to biomass of PSAC. Kinetic data were best described by the pseudo-second order model with high correlation coefficient (R^2, 0.99). These results demonstrated that the PSAC could be used as a natural biosorbent for removal of lead ions from aqueous solution.

Keywords:

Biosorption , Pb(II), Peach stones, activated carbon, Adsorption, Isotherms, Kinetic

Introduction

The presence of heavy metals in wastewater and surface water is becoming a severe environmental and public health problem. Lead or Pb(II) is a particularly hazardous heavy metal because once it gets into human body; it disperses throughout the body immediately and causes harmful effects. For example, it can damage the red blood cells and limit their ability to carry oxygen to the organs and tissues. It can affect the nervous system, kidneys and hearing as well (Zhu *et al*., 2008). In particular unborn babies and young children are at risk of health problems from lead poisoning because their smaller bodies make them more susceptible to absorbing lead ions. Lead compounds are known as metabolic poisons and enzyme inhibitor (King *et al*., 2007).

Many industrial activities such as battery manufacturing, metal plating and oil refining are the major sources of lead pollution. Lead is taken into the body via inhalation, ingestion, and skin adsorption. The world health organization (WHO) recommended the maximum acceptable concentration of lead in drinking water as 0.1-0.05 mg L^{-1} (Zhang *et al*., 2004). It is, thus, important to remove lead and other toxic heavy metal ions from waters and wastewaters before they are released to the environment. Many physicochemical methods such as extraction, ion exchange, chemical precipitation, membrane filtration, adsorption, and electrodialysis have been developed for the removal of heavy metals from aqueous solutions, but most of these methods have significant disadvantages. They have a relatively high cost and low feasibility for use in small scale industries (Witek *et al*., 2011; Wang *et al*., 2010). In contrast, biosorption is cheaper and more effective than conventional technologies (precipitation, ion exchange and membrane), so it has become one of the most preferred methods for the removal of heavy metals in recent years (Seyda *et al*., 2014). Researchers have investigated the production of activated carbon from many agricultural wastes including apricot stone, novel agricultural waste and Egyptian Banana Peel (Somaia, 2013; Ghasemi *et al.*, 2014; Mahmoud *et al.*, 2014). In this regard, besides the raw natural fruits, peaches are utilized in the form of products such as juices, pulp and nectar. Peach is one of the most important deciduous fruit trees in Egypt. The harvested area in Egypt reached 33017 ha produced 273256 Tons (FAO, 2010). Peach's cultivation spreads in many areas in Egypt especially in the newly reclaimed lands which include many types of soil. Peach stones are agricultural by-products that are

currently exhibits no economic value, and have a hard lignocellulosic material shell that gives them the potential to be used as raw materials for production of activated carbon. The main objective of this research was to evaluate the feasibility of using peach stones activated carbon (PSAC) as a biosorbent for the removal of Pb(II) from the aqueous solution. The effects of different parameters including solution pH, biosorbent dose, different concentrations and contact time were studied. Additionally, the isotherm and kinetic parameters were explored to describe the experimental data.

Materials and Methods

Preparation of metal ions solutions

Metal ion solution was prepared from analytical grade chemical (Merck Ltd). Stock solution of 1000 mg L^{-1} of Pb(II) was prepared from $Pb(NO_3)_2$ in double distilled water. The working solutions were prepared from the stock solutions by diluting it to appropriate volumes. The initial pH of the working solution was adjusted to 5.0 by adding 0.1 N HNO3 or 0.1 N NaOH solutions and was measured using a JENWAY pH-Meter 3305. Atomic adsorption spectrometer (AAS Model HGA 850, USA) was used to measure the Pb(II) concentration.

Adsorbent (PSAC)

Peach stones were collected from a local market in Egypt. These were washed with distilled water to remove water-soluble impurities and dried to constant weight in an oven at 70 ºC for 2 days. The dried samples were ground and sieved by AS 200 Analytical Sieve Shakers, Retsch GmbH, Germany to particle size of 63 µm prior to activation. Chemical activation using H_2SO_4 at moderate temperatures produces a high surface area and high degree of microporosity (Demirbas, 2003). The materials were mixed in a 1:1 weight ratio with concentrated H_2SO_4, placed in an oven and heated to 200 ºC for 24 h. After this, the samples were allowed to cool to room temperature, washed with distilled water and soaked in 1% $NaHCO_3$ solution to remove any remaining acid. The samples were then washed with distilled water until pH of the activated carbon reached 6, dried at 105 ºC for 5 hours.

Biosorption experiments

Adsorption experiments were conducted at different contact time (5-120 min), pH (1-7), initial Pb(II) ion concentration (5-100 mg L^{-1}), and peach stones activated carbon (PSAC) dose (0.1-1 g 100 mL^{-1}). Batch adsorption experiments were carried out at room temperature (30 ± 1 °C) by taking 0.8 g of the adsorbent in 100mL of metal solution in in 250 mL conical flask and agitated on a mechanical shaker. The samples were filtered through Whatman 40 filter paper after completion of experiment and filtrate was analyzed for remaining metal concentration. .

The amount of metal ion adsorbed by the biosorbent at equilibrium ($q_{e,}$ mg/g) was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad \textbf{(1)}$$

Where V is the volume of solution treated in ml, C_o is the initial concentration of metal ion in mg L^{-1}, C_e is the equilibrium metal ion concentration in mg L^{-1} and m is the biomass in gram and W is the amount of adsorbent used (g).
The percent removal of metal ion was calculated using the following equation:

$$\text{Removal (\%)} = \frac{C0 - Ce}{C0} X100 \qquad \textbf{(2)}$$

Results and Discussion

Effect of pH

The pH value of aqueous solution is an important parameter in adsorption process because it affects the surface charge of the adsorbent, the degree of ionization and specification of the adsorbate (El-Ashtoukhy *et al*., 2008). In the present study, the effect of pH on biosorption of Pb(II) onto PSAC was studied in a range of 1-7. Results are shown in Fig. 1. It was observed that, the removal Pb(II) ions in the aqueous solution was low at low pH values and gradually increased with increasing pH of the solution up to pH 5.0. With further increase in pH, there was no significant increase in the amount of metal ion removed. Maximum removal was observed at pH 5.0. Hence, all further experiments were carried out at pH 5.0. At low pH values, concentration of H^+ ions far exceeds that of the metal ions and hence H^+ ions compete with Pb(II) ions for the surface of the adsorbent which would hinder the Pb(II) ions from reaching the binding sites of the adsorbent resulting in low adsorption amount of Pb(II). As the pH increases, there are fewer protons in the solution and consequently there is lesser competition with Pb(II) for binding sites.

Effect of biosorbent dose

The effect of biosorbent dose was investigated over the range of 0.1 to 1.0 g in 100 mL of solution (Fig. 2). The removal percentage of Pb(II) was increased from 97.15 % to 99.57 % for biosorbent dosage of 0.1 and 1.0 g, respectively. This is due to the availability of more binding sites as the dose of biosorbent increased. However, the amount of Pb adsorbed onto the sorbent, q (mg g^{-1}), was found to decrease from 19.43 to 1.990 mg g^{-1} with increasing biosorbent dose. It is due to the high number of unsaturated sorption sites during biosorption process.

Effect of contact time

The biosorption efficiency of Pb(II) ions was evaluated as a function of contact time. The initial concentration of Pb(II) ions was 20 ppm. The relationship of percentage Pb(II) ions removal by PSAC with contact time is shown in Fig. 3. Results showed that the % removal of metal was relatively rapid in the initial 10 minutes. Because the biosorption sites were vacant, and Pb(II) could easily interact with these sites, with 82.51% of the Pb(II) ions being biosorbed by that time. In addition, the biosorption efficiency increased with contact time and reached a maximum value (93.81%) after approximately 100 minutes. After 100 minutes, the biosorption efficiency was almost constant such that it could be considered the equilibrium time of the Pb(II) biosorption. To ensure that sufficient contact time was obtained, further biosorption experiments were carried out for 100 minutes.

Effect of initial metal concentration

The effect of initial metal concentration on the Pb(II)ions sorption was investigated in the ranges of 5-100 mg L^{-1}, while the rest of the parameters were kept same as optimized in the previous experiments, i.e., pH 5, equilibrium time of 2 hours using 0.8 g of biosorbent. The results are depicted in Fig. 4. It has been found that the biosorption capacity of the PSAC increased from 0.556 to 12.0 mg g^{-1} with increasing metal ion concentrations from 5 to 100 mg L^{-1}. The initial metal ion concentration provides an important driving force to overcome all the mass transfer resistance between the solution and solid phases.

Adsorption isotherms

Isotherm studies provide information on the capacity of sorbent, which is the most important parameter for a sorption system. Adsorption isotherms are characterized by certain constants and describe the mathematical relationship between the quantity of adsorbate and concentration of adsorbate remaining in the solution at equilibrium. There are several isotherm equations describing the equilibrium and the most common of them are Langmuir, Freundlich and Dubinin-Radushkevich (D–R) adsorption isotherm models were used to describe the obtained equilibrium data (Hussain *et al*., 2009).

Langmuir isotherm

The Langmuir model suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between the adsorbed molecules (Zainal, 2010). The linear form of Langmuir adsorption isotherm is given by the following equation;

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \qquad (3)$$

Where q_e is the equilibrium metal ion concentration on the biosorbent (mg g^{-1}), b is the Langmuir constant and q_m is the monolayer adsorption capacity. The plot of C_e/q_e versus C_e is employed to generate the intercept value of $1/bq_m$ and slope of $1/q_m$ (Fig. 5).

One of the essential characteristics of this model can be expressed in terms of the dimensionless separation factor for equilibrium parameter, R_L, s (Farooq *et al*., 2010).

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

The value of R_L indicates the irreversible (R_L=0) type of isotherm and it could be, favorable (0< R_L<1), linear (R_L=1) or unfavourable (R_L>1). The value of R_L in the present investigation was found to be 0.003 indicating that the adsorption of Pb(II) on PSAC is favorable.

Freundlich adsorption

The Freundlich adsorption model on the other hand deals with non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. It is expressed mathematically as Freundlich (1906).

$$\log q_e = \log K_f + 1/n \log C_e \qquad (5)$$

Where K_f is a constant related to adsorption capacity and n is an empirical parameter which reflects the intensity of adsorption that varies with the degree of heterogeneity, the larger these values, the higher the adsorption capacity The value of n obtained as a result of plotting of log C_e versus log q_e (Fig. 6), given in Table 1 shows that adsorption of Pb(II) is favorable for the prepared biomass.

It is found that both isotherm models fit very well according to the correlation coefficient values

given in Table 1. Thus, the results of the present study indicate that biosoroption adsorption of Pb(II) onto BPAC is homogeneous in nature.

The Dubinin-Radushkevich (D–R) isotherm

The Dubinin–Radushkevich model (Dubinin *et al*., 1947) was chosen to estimate the heterogeneity of the surface energies and also to determine the nature of biosorption processes as physical or chemical. The D–R sorption isotherm is more general than the Langmuir isotherm. The D–R isotherm dose not assumes a homogeneous surface or constant sorption potential and it has commonly been applied in the following form.

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (6)$$

Where q_m is the theoretical saturation capacity (mol g^{-1}), β is a constant related to the mean free energy of adsorption per mole of the adsorbate ($mol^2\ J^{-2}$), and ε is the polanyi potential given by the relation = RT (ln 1+1/ C_e),C_e is the equilibrium concentration of adsorbate in solution mol L^{-1}), R (J $mol^{-1}\ K^{-1}$) is the gas constant and T (K) is the absolute temperature. The D–R constants q_m and β were calculated from the linear plots of ln q_e versus ε^2 (Fig. 7) and are given in Table 1.

The constant β gives an idea about the mean free energy E (kJ mol^{-1}) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the relationship (Kundu and Gupta, 2006).

$$E = 1/\sqrt{-2\beta} \quad \textbf{(7)}$$

If the magnitude of E is between 8 and 16 kJ mol^{-1}, the adsorption process is supposed to proceed via chemisorption, while for values of E < 8 kJ mol^{-1}, the sorption process is of physical in nature. The values of E calculated is 6.88 kJ mol^{-1}, which indicating that the physico-sorption process plays the significant role in the adsorption of Pb(II) onto PSAC. These E values are in agreement with Sahar and Somaia (2014) for the adsorption of oxamyl onto Egyptian Apricot Stone.

Kinetic studies

For analyzing the adsorption kinetics of heavy metal ions, the pseudo-first- and pseudo-second-order models were applied to the experimental data. The first-order rate equation is one of the most widely used equations for the adsorption of a solute from an aqueous solution and is represented as:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}(t) \quad (8)$$

Where q_e and qt are the amount of metal ion adsorbed (mgg^{-1}) at equilibrium and time t, respectively. K_1 is the first-order reaction rate constant (min^{-1}). Examination of the data shows that the pseudo-first order kinetic model is not applicable to lead ions adsorption onto PSAC judged by low correlation coefficient (data not shown).

The pseudo-second-order

The pseudo-second-order equation based on adsorption equilibrium capacity may be expressed as follows:

$$\frac{t}{qt} = \frac{1}{K2qe2} + \frac{1}{qe}(t) \quad (9)$$

Where q_e is the equilibrium biosorption capacity and K_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}). A plot of (t/q_t) versus t gives a linear relationship for the applicability of the second-order kinetic model (Fig. 8).

The initial sorption rate can be calculated using the relation Koynucu (2008).

$$K_0 = K_2\ q_e^2 \quad (10)$$

High R^2, indicates that the pseudo-second order is predominant kinetic model for the Pb(II) adsorption by PSAC biosorbent. Similar kinetic result was reported for Pyracantha coccinea, rice husk and adsorption of oxamyl pesticide on different agricultural waste adsorbents (Akar *et al*., 2010; Safa and Bhatti, 2011; Somaia *et al*., 2014).

Conclusions

The adsorption of lead on activated carbon was found to be dependent on contact time, lead concentration, pH and adsorbent dose. Equilibrium data fitted well with the Langmuir, Freundlich and Dubinin–Radushkevich isotherm model. The kinetic data were best described by the pseudo-second order model. Activation energy found as 6.88 kJ mol^{-1} showed that lead sorption onto peach stones Activated Carbon was a physical sorption. The results indicated that the PSAC could be a promising biosorbent for removal of lead from aqueous solution.

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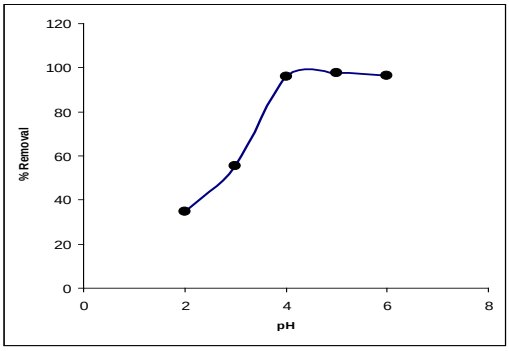

Fig. 1: Effect of pH on the adsorption of Pb(II) by peach stones activated carbon (PSAC).

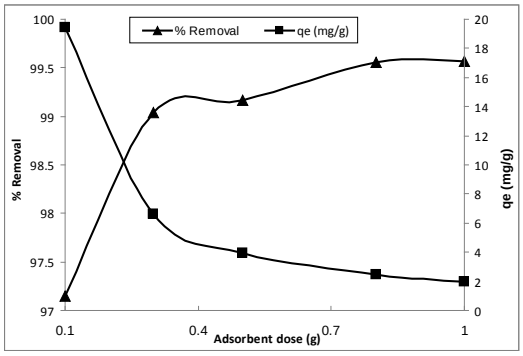

Fig. 2: The effect of biosorbent dose on Pb^{2+} sorption (pH 5 at 20 mg L^{-1}).

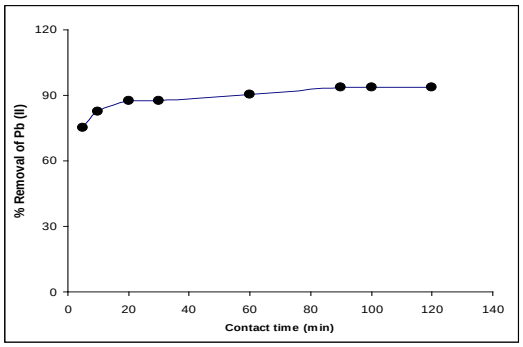

Fig. 3: Effect of contact time on Pb(II) adsorption on PSAC.

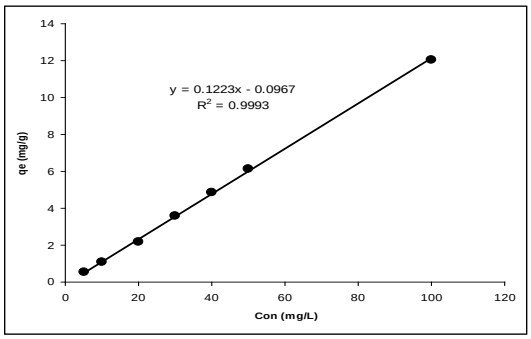

Fig. 4: Effect of initial metal ion concentrations of Pb(II) biosorption on PSAC**.**

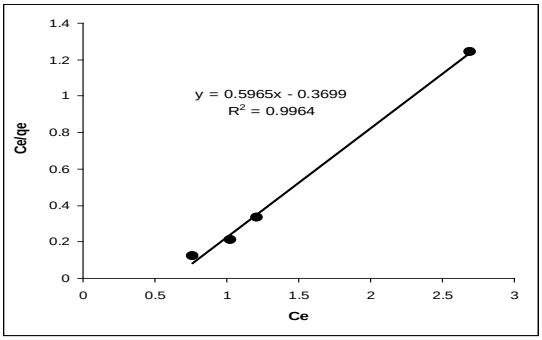

Fig. 5: Langmuir isotherm plot for adsorption of Pb(II) onto PSAC.

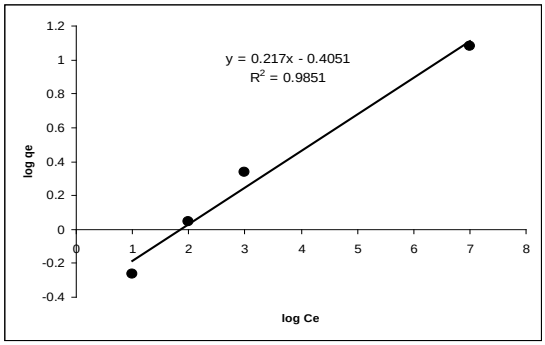

Fig. 6: Freundlich isotherm plot for adsorption of Pb(II) onto PSAC.

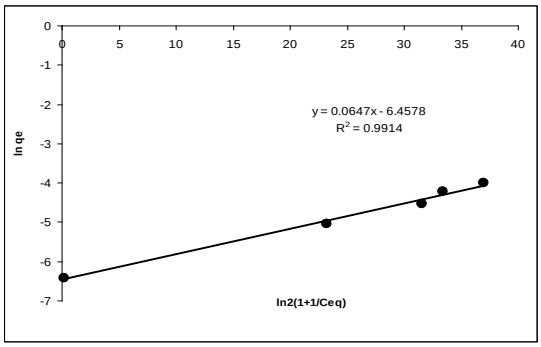

Fig. 7: D-R isotherm for Pb(II) adsorption onto PSAC.

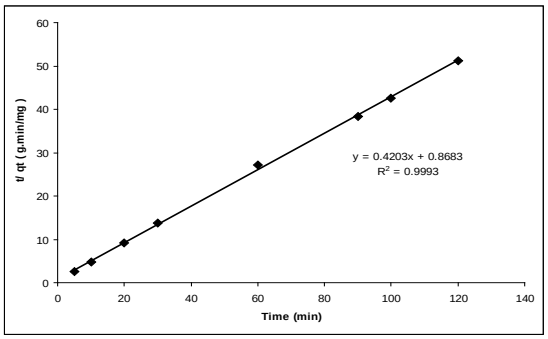

Fig. 8: Second order kinetic model for Pb(II) adsorption onto PSAC**.**

Table 1: Isotherm parameters for adsorption of Pb(II) onto PSAC.

Biosorbent	Langmuir isotherm parameters			Freundlich isotherm parameters			Dubinin-Radushkevich (D-R) isotherm parameters		
Peach Stones activated Carbon	q_m (mg g^{-1})	b (L mg^{-1})	R^2	K_F (mg g^{-1})(1 mg^{-1})$^{1/n}$	1/n	R^2	Q_e (mg g^{-1})	E (KJmol^{-1})	R^2
	1.67	1.61	0.99	2.54	0.22	0.99	2.54	0.227	0.99

Table 2: Pseudo-second order kinetic parameters for the removal of Pb(II) onto PSAC.

Parameter	Value
K_2 (g mg^{-1}min)	0.21
K_0 (g mg^{-1} min)	1.15
R^2	0.99
q_e (mg g^{-1})	2.4

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