Batch and Continuous Removal of Pb (Ⅱ) By Sonochemically Treated Phanerochaete Chrysosporium from Aqueous Solutions: Kinetics and Thermodynamics

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ABSTRACT: Biological adsorption of heavy metals is an effective process for removing heavy metals from aqueous solutions. In this study, the adsorption properties of non-viable Phanerochaete Chrysosporium biomass are studied for biological adsorption of lead ion in both continuous and batch systems. In the batch process, Langmuir, Freundlich and Dobbinin-Radushkevich isotherms are studied. The adsorption kinetics including pseudo-first order, pseudo-second order and intraparticle diffusion models are also investigated. The experimental equilibrium data follow Langmuir, Freundlich and Dobbinin-Radushkevich models. The kinetic data fit well to the pseudo-second order and intraparticle diffusion models. In the continuous system, by studying the Thomas and Yoon-Nelson models it can be concluded that particles of Phanerochaete Chrysosporium are very suitable adsorbents for the adsorption of heavy metal of lead with high efficiency. Increasing input flowrate causes earlier breakthrough point. Thermodynamic calculations also prove that the process is spontaneous and self-healing and positive ΔH indicate process is endothermic.

Introduction

Today, with the growth of technology and industrialization of the world as well as the increase in the population, exploitation of the environment has been tremendously increased. Therefore, environmental pollution is a major concern of human societies. Due to contamination of the water flows and the entry of sewage containing various pollutants (including heavy metals) into the environment and the absorption of these toxins by aquatic organisms, organisms and plants, biological status of the environmental is disrupted. Part of these creatures are used as sources of nutrition, and human beings

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are at risk of life-threatening illnesses. Among the heavy metals, lead can be one of the major pollutants. Lead is a toxic metal that can damage nerve system (especially children and adolescents) and cause brain malfunction and its effectiveness. Long-term contact with lead or its salts (especially soluble salts and strong oxidants such as PbO_2) can cause neoplasm and abdominal cramps.

In order to remove heavy metals from waste water some techniques have been used such as chemical precipitation (Ku and Jung, 2001), ion exchange (Kang et al., 2004), adsorption (Çoruh *et al.*, 2010; Ma *et al.*, 2009), electrochemical (Wang et al., 2007b), reverse osmosis (Shahalam *et al.*, 2002) and nanofiltration (Cheremisinoff, 2002).Through all these methods, adsorption has been recognized as an suitable treatment for removing heavy metals from aqueous solutions due to its simplicity and economic benefits.(Gerami, 2017; Biriaei, 2017).

Removal of heavy metals through biological adsorption procedures have been studied using different bio-adsorbents such as polyporous colour (Dilek, 2002), straw (Han 2006), Undaria pinnatifida alga (Zhen Chen, 2007), baking yeast (V. Padmavathy, 2007), Hydrilla Verticillata (Sushera Bunluesin, 2007), Undaria Pinnatifida (Zhen Chen, 2007).

In this study the credibility of non-living biomass of phanerochaete chrysosporium fungus in removing heavy metal from wastewater through a batch and continuous adsorption process is investigated focusing on pH variation in order to find the best performance of the adsorbent. In addition, experimental data is used to determine various equilibrium and kinetic parameters and to understand the probable mechanism of adsorption.

Materials and Methods

- Biomass Preparation

In order to produce fungus, 15.8 gr of sabaro-gluzacarugar with 3 g pf agar-agar was dissolved in 250 ml of distilled water and then it was autoclaved at 121 ℃ under 151 IBS of pressure. The resulting fungus specimen afterwards was placed in incubator at 30 ℃ for five days. In parallel to the above preparation, 30 g of sabaro-decroserase culture media was dissolved in 1000 ml of distilled water and then it was placed in autoclave. The produced culture media was then introduced into the fungal medium from the first operation and then it was placed in shaker-incubator for one week at 32 ℃ with 150 rpm to allow growing of fungus. The fungi were then passed through paper filters. In order to kill the fungus, it was boiled in 0.5 N Sodium Hydroxide solution for 30 min. The sample was then washed by distilled water until its pH value became neutral. Finally, the dried sample was turned into powder form. To reduce the particle size a satellite mill, homogenizer, ultrasonic bath, and liquid nitrogen were used.

- *Preparation of Metal Solution (Artificial Wastewater)*

The metal solution for Pb (II), with a concentration of 1000 mg / l was prepared with dissolution of specific amount of lead nitrate in 1000 ml of water. Exact concentration of solution was investigated using the atomic absorption device (GBS Plus932 model).

- *Adsorbent Characterization*

The morphology of nanoparticles was examined by the scanning electron microscope (SEM).

- *Evaluation of Adsorbent Performance*

Two methods i.e., continuous and batch systems were used for biological adsorption via the fungi. In batch system, a

series of 250 ml Erlenmeyer flasks of metal ions solutions with 100 mg/L initial concentration containing 0.1 g biomass were kept in a shaker with stirring for 60 min and pH value of 4.5 for Pb at 25ºC. After equilibration, the quantity of adsorbed metal was detected by atomic absorption spectrometer. In continuous system, a 2 cm diameter column with 70 cm height was used. This column is filled with calcium alginate biomass up to 50 cm in height. The flow rates of 2, 4 and 6 ml/min was chosen and every five minutes one sample was taken from the outflow. Then the quantity of adsorbed metal was detected by atomic absorption spectrometer. The amount of adsorption (Q_e) was calculated by the following equations (cheunget al., 2003; Huet al., 2006; laus and de Favere, 2011):

$$(1) \qquad Q_e = \frac{(Co - Ce)}{m} v$$

$$(2) \qquad \text{Removal} (\%) = \frac{(Co - Ce)}{Co} * 100$$

Where Q_e is the amount of metal ions absorbed (mg/g), C_o and C_e are the initial and equilibrium ions concentration (mg/L), m is the mass of adsorbent (g), and V is the volume of solution (L).

Results and Discussion
- SEM

SEM images of sample are demonstrated in Figure 1. It can be seen from Figure 1-a, irregular shape with average particle size of 1-10μm are obtained. Applying the satellite mill, homogenizer, Liquid nitrogen, and ultrasonic bath results in reducing the particle size (Figure 1b-1d).
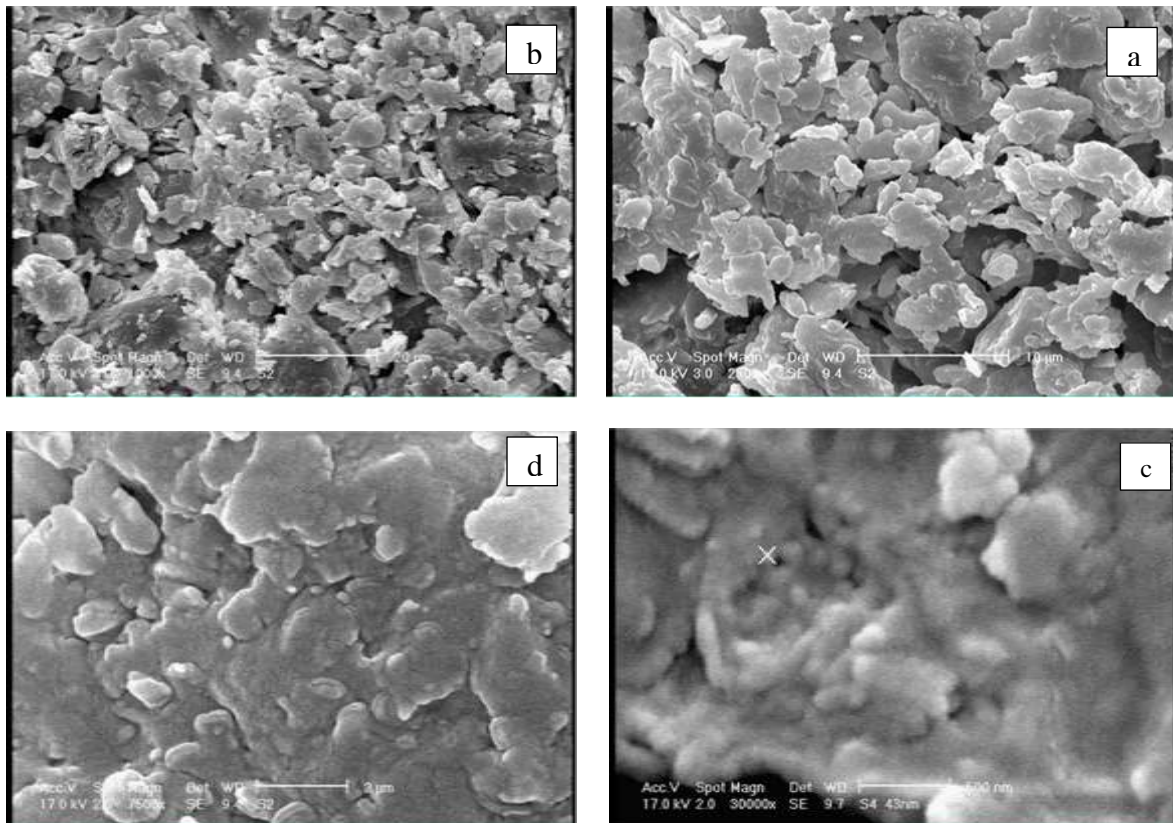
Fig. 1. SEM images of treated by phanerochaete chrysosporium after (a) satellite mill (b) homogenizer (c) ultrasonication (d) Liquid nitrogen

- Effect of pH

In order to investigate the effect of pH on the adsorption process, some experiments were carried out by varying pH value from 2 to 6. The metal ion concentration of 100 mg/g and volume of 100 ml have been used in which every sample contained 0.1 g biomass. As it can be seen from Figure 2, the adsorption efficiency increases by increasing pH and the maximum of adsorption happens at the pH value of 4.5. This can be explained by the high concentration of H^+ at pH values less than 4.5 which leads to a competition between heavy metal ions and hydronium ions for adsorption on the biomass surface. At higher pH values of 4.5, the adsorption efficiency of heavy metal ions starts to decrease, because of precipitation of metal ions.

- Evaluation of Adsorbent Performance

As illustrated in Figure 3, the rate of adsorption is dramatically high for 15 min as a results of high mass transfer driving force as well as more free active sites on the surface of adsorbent. It then become slow and finally constant after 210 minutes showing the adsorption process reaches to the equilibrium state. Table 1 shows the comparison of maximum adsorption capacity of some adsorbents for lead adsorption. The adsorption efficiency of phanerochaete chrysosporium is high and it can be considered as a promising adsorbent for lead ion removal from wastewater.
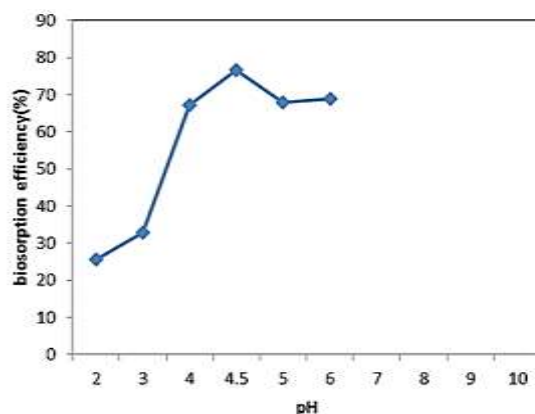

Fig. 2. Effect of pH on adsorption efficiency of metal ions by phanerochaete chrysosporium (adsorbent dosage =0.1 gr/100 ml, Co=100 mg/l, t=60 min, T=25 ℃)
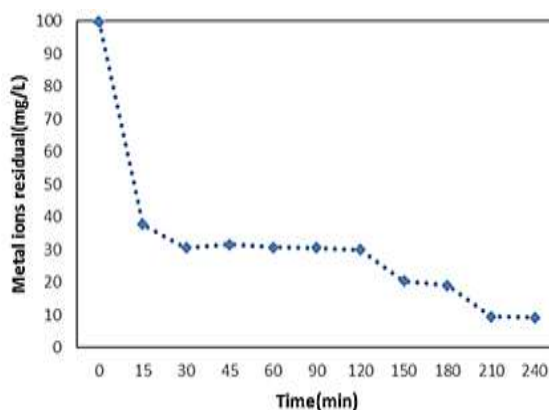

Fig. 3. The metal ions depletion rate by adsorption on adsorbent (pH=4.5, sorbent dosage=0.1gr/100ml, C0=100mg/l)

Table 1. Comparison of maximum adsorption capacity of some adsorbents for lead adsorption

Type of adsorbent	Adsorbent dose (g/L)	Temp. (°C)	pH	Contact time (min)	Maximum adsorption capacity (mg/g)	Ref
Lactobacillus plantarum	1	37	7	60	34.5	(Pakdel et al., 2019)
Cellulose-metallothionein-carbohydrate	10	25	9	10	39.02	(Mwandira et al., 2020)
Eggshell	4	-	6	60	90.90	(Putra et al., 2014)
Phanerochaete Chrysosporium	1	۲۵	4.5	15	55.4	This study

- Adsorption Kinetics

Experimental kinetic data gives important information to figure out how to model the adsorption process. One of the most general methods for describing the rate of adsorption in aqueous solution is Legergren equation. This model is represented by the following formulas. (Gerenteet al., 2007; Monieret al., 2012; Zhouet al., 2008):

$$(3) \qquad Ln\,(q_{eq} - q) = lnq_{eq} - k_1 t$$

$$(4) \qquad \frac{t}{q_{eq}} = \frac{1}{k_2 q_{eq}^2} - \frac{1}{q_{eq}}t$$

Where q_e and q_t are the amount of metal ions sorbed at equilibrium and time t respectively (mg/g). k_1 is the pseudo-first order(min^{-1}) and k_2 is the pseudo-second order constant(g/mg.min). By plotting ln $(q_e - q_t)$ and t/q_t versus time (Figures 4 &5), k_1 and k_2 are calculated respectively. Figure 4 shows pseudo-first order and Figure 5 shows pseudo-second order model. Kinetic data are also shown in Table 2. As it can be seen in these figures and Table 2 adsorption process with high values of k_2 and R^2, properly fits to pseudo-second order model showing chemisorption process of lead by Phanerochaete Chrysosporium. Through diffusion process, intraparticle mass transfer resistance can control the rate of adsorption process. To investigate the impact of intraparticle diffusion on a rate of the process, experimental data are fitted to equation (5) (Zhouet al., 2008).

$$(5) \qquad q_t = k_i t^{0.5}$$

Where k_i is the rate constant of diffusion (mg/g.min$^{0.5}$). Calculated data are provided in Table 2. As shown in Figure 6 the curve has two straight lines which indicates initial phase (before equilibrium) and final phase (after equilibrium). Because of the high value of R^2, the rate of adsorption also follows intraparticle diffusion model (Huanget al., 2008; tripathy and Raichur, 2008).

- Adsorption Isotherms

For studying the adsorption isotherms, a series of experiments by varying ion concentration from 100 to 500 mg/L with 0.1 gr of adsorbent were carried out at pH=4.5, temperature of 30 ℃ for 1h. Generally, to describe the adsorption mechanism at equilibrium state, applying data to the isotherm models can be helpful. Three common and widely used models, Freundlich, Langmuir and Dubbin-Radushkevich are studied in this work.

In Langmuir model there are some assumption which are importance and must be considered. Adsorption happens through monolayer coverage and all the surface sites are the same in order to absorbed atoms. However, Freundlich

model's best use is in the highly heterogenous surfaces with multilayer adsorption. (Ng *et al*., 2003) (VanLoon and Duffy, 2011). The Langmuir and Freundlich models are represented as equation 6 and 7 respectively:
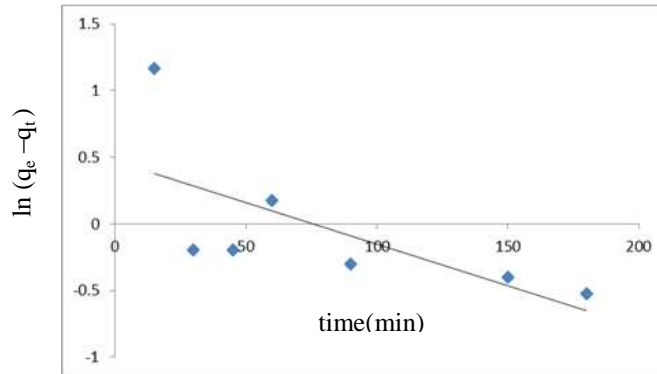

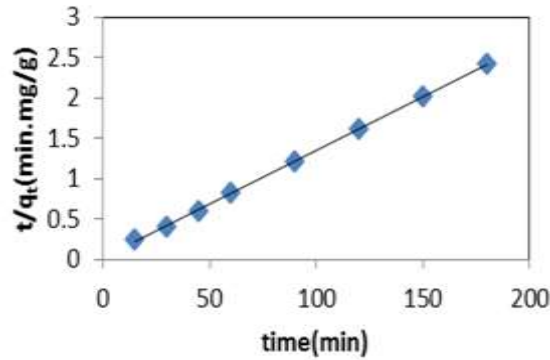**Fig. 4.** Pseudo-first order model plot (pH=4.5 for lead, sorbent dosage=0.1gr/100 ml, Co=100 mg/L).

Fig. 5. Pseudo- second order model plot, (pH=4.5 for lead, sorbent dosage=0.1gr/100 ml, Co=100 mg/L).
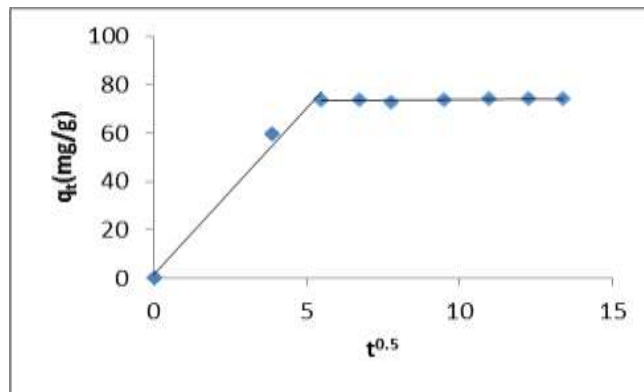

Fig. 6. The intra-particle model plot (pH=4.5, sorbent dosage =0.1gr/100ml, C0=100mg/l).

Table 2. Pseudo-Second Order and Intra-Particle Diffusion Model Parameters

Pseudo-Second Order				Intra-Particle Diffusion	
q_e (mg/g) Exprimental	Model	K_2 (g/mg.min)	R^2	K_i (mg/(gmin^{-1}))	R^2
74	75.2	0.008	0.997	13.85	0.988

(6)
$$q = q_m \frac{bc_e}{1+bc_e}$$

(7)
$$q = k_f C_e^{1/n}$$

Where C_e is the equilibrium concentration (mg/L), q is the amount of metal ions sorbed (mg/g), q_m is the amount of metal ion for a complete monolayer (mg g^{-1}) , b is a constant related to the affinity of the binding sites (L/mg), k_f is empirical Freundlich constant (Monieret al., 2012). The linear expression of these models represented as following formulas.

(8)
$$\frac{C_e}{q} = \frac{1}{q_m b} + \frac{C_e}{q_m}$$

(9)
$$\ln q = \ln k_F + \frac{1}{n}(\ln C_e)$$

For the sake of pursuing which of the two model describe the adsorption better, experimental equilibrium data are fitted to both models. By the correlating C_e versus C_e/q and ln C_e vs ln q (shown in Figure 7), the calculated values of R^2 in both cases are higher than 0.9 (Table 3). Therefore, the adsorption process fits well to both these models.

Dubbin-Radushkevich is generally used in cases with heterogeneous surfaces to describe the distribution of Gaussian energy onto a surface. This empirical model often suitable for intermediate range of adsorbate concentration. (Gunay, kaya and tosun, 2007; Dabrowski, 2001).

(10)
$$\ln q_e = \ln(q_m) - (\beta \varepsilon^2)$$

(11)
$$E_a = \frac{1}{\sqrt{2\beta}}$$

(12)
$$\varepsilon = RT \ln(1 + \frac{1}{C_e})$$

Where q_e and q_m are amount of metal ions sorbed at equilibrium and theoretical saturation capacity respectively (mg/g), β (mol2/kj2) and ε both are Dubinin-

Radushkevich isotherm constants. E_a is mean adsorption energy. T is absolute temperature (k), R represents the gas constant (8.314 j/mol.k) and Ce is the concentration of adsorbate at equilibrium. (Dubinin, 1960; Hobson, 1969)

The values of Dubbin-Radushkevich constants are calculated by plotting $\ln q_e$ against ε^2 (Figure 8). linear regression results in high values of R^2 showing the equilibrium data follow Dubbin-Radushkevich (Table 3).

- *Thomas and Yoon-nelson Models*

Considering continuous system, to describe the column performance, Thomas and Yoon-nelson models are investigated. In Thomas model it is assumed that its behavior follows Langmuir isotherm and second –order reversible reaction kinetics with no axial dispersion. (Thomas, 1944; Wu and Yu, 2008; Ayoob and Gupta, 2007; Rozada et al., 2007)

Yoon-Nelson model is much simpler, also needs no detail about properties of the system (Yoon and nelson, 1984). Thomas and Yoon-Nelson models both are represented below respectively:

(13)
$$\ln\left(\frac{C_o}{C} - 1\right) = \frac{k_{th} q_{oth} m}{Q} - k_{th} C_o t$$

(14)
$$\frac{C_t}{C_0 - C_t} = \exp(k_{YN} t - \tau k_{YN})$$

Where k_{th} (L/mg.min) is Thomas rate constant, Q is volumetric flow rate(L/min) ,m is the mass of sorbent(g), k_{YN}(1/min) is the rate constant and τ is the time required for 50% adsorbate breakthrough.

The linear form of Yoon-Nelson model is expressed as Equation 15:

(15)
$$\ln \frac{C_t}{C_0 - C_t} = k_{YN} t - k_{YN} \tau$$

By applying experimental data to both models, linear regression results in high

values of R^2 showing the adsorption process with biological adsorbent follows both models. Linear regression results, values of R^2 and models' parameters are provided in Figure 9, Figure 10 and Table 4.
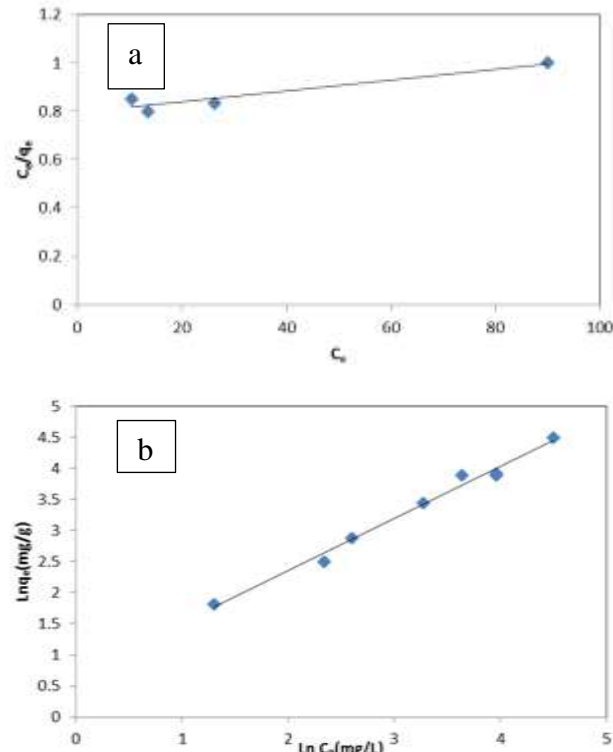

Fig. 7. Langmuir isotherm model plot (a), Freundlich isotherm model plot (b) (pH=4.5 for lead, sorbent dosage=0.1gr/100 ml, Co=100 mg/L).
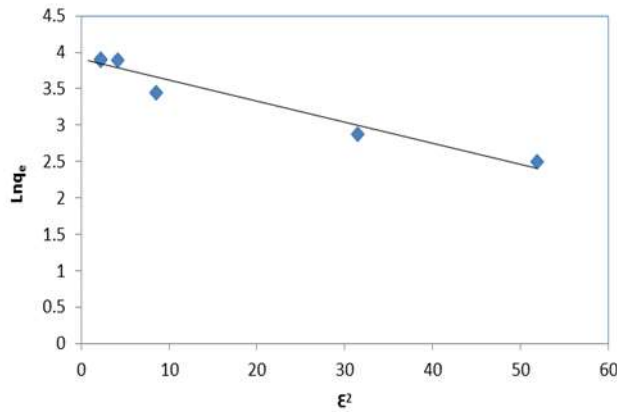

Fig. 8. Dubbin-Radushkevich isotherm model plot (pH=4.5 for lead, sorbent dosage=0.1gr/100 ml, Co=100 mg/L).

Table 3. Langmuir, Freundlich and Dubinin-Radushkevich Isotherm Model Parameters

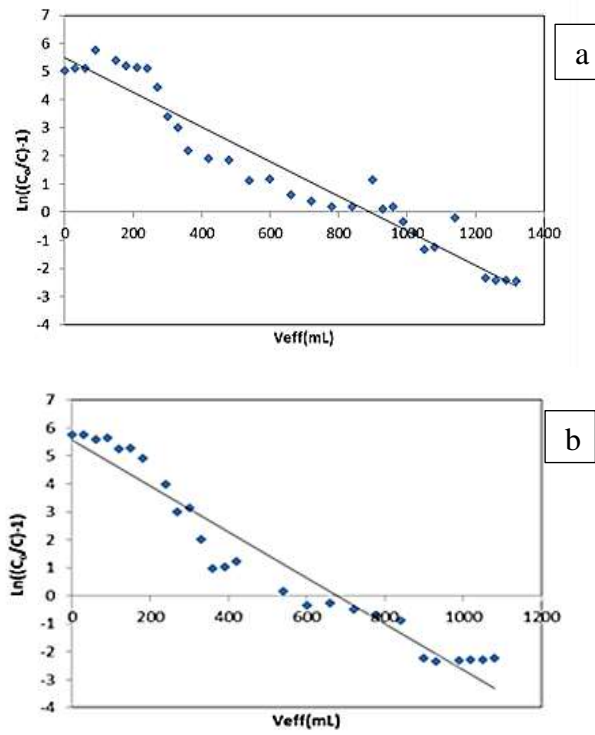| Langmuir		Freundlich			Dubinin-Radushkevich		
R^2	k_L	R^2	k_F	$1/n$	R^2	β	E_a
0.91	0.003	0.98	1.85	0.68	0.98	0.03	0.25
k_L(L/mg)		$k_F(mg/g)(L/mg)$			$\beta(mol^2/KJ^2)$		E_a(kJ/mol)

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Fig. 9. Thomas isotherm model plots: input flow rate =2 ml/min: (a) basic particle size, (b) finer particle size.
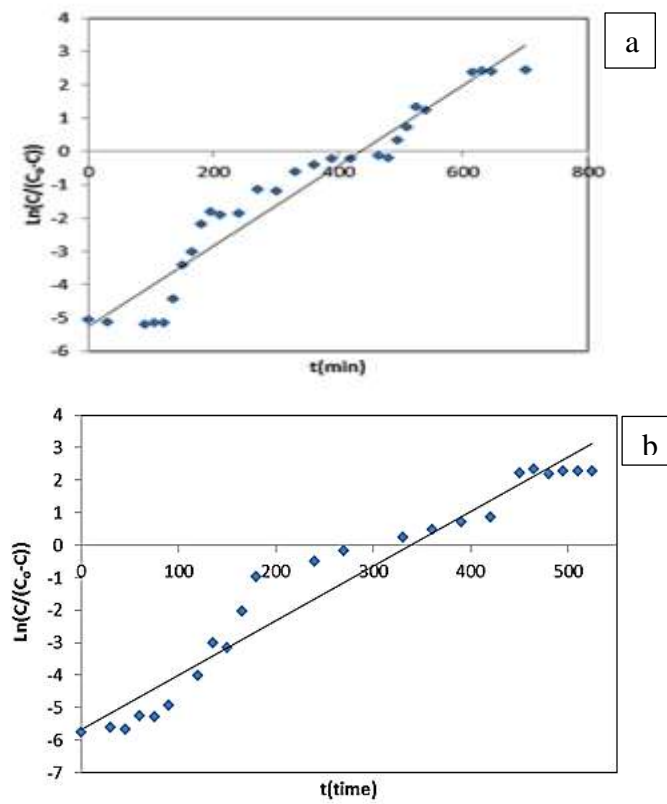
Fig. 10. Yoon-nelson model plots: (a) basic particle size, (b) finer particle size**.**

- *Effect of Input Flowrate on Breakthrough Curve*

Three different input flowrate, 2,4 and 6 ml/min, were applied for studying the effect of input flowrate. Accordingly, glass column with 2 cm diameter and 70 cm height was filled up to 50 cm with calcium alginate biomass and kept at pH value of 4.5. As shown in Figure 11, increasing input flowrate causes earlier breakthrough point (K. H. Chu, 2003; D. Kratochvil, B. Volesky, G. Demopoulos, 1997). Fast column saturation occurs due to smaller contact time when flowrate is high (E. M. Trujillo, T. H. Jeffers, C. Ferguson, H. Q. Stevenson, 1991). When adsorbent particle size becomes finer, the contact area is increased, speed of adsorption is also increased hence leads to lesser time consumption (Figure 12).

Table 4. Thomas Model and Yoon-nelson Model Parameters

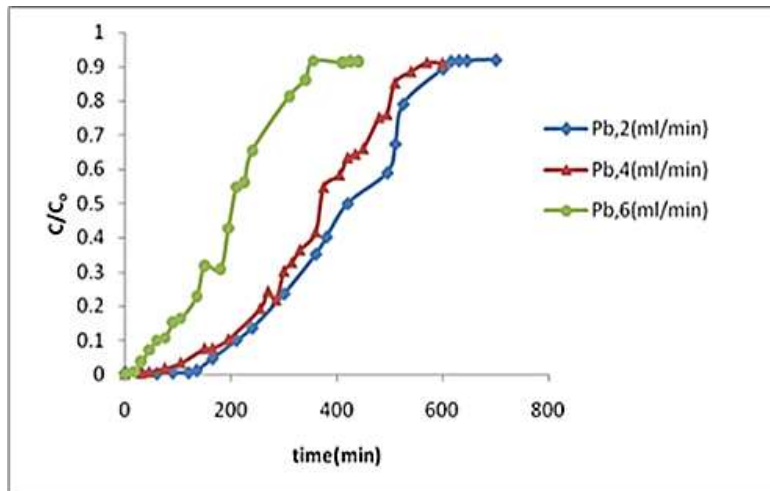| Particle size	Thomas			Yoon-nelson		
	q_o(mg/g)	k_{th}(L/mg.min)	R^2	k_{YN}(1/min)	τ (min)	R^2
Basic	70.5	0.026	0.935	0.012	437	0.935
small	51.8	0.036	0.939	0.017	335	0.95

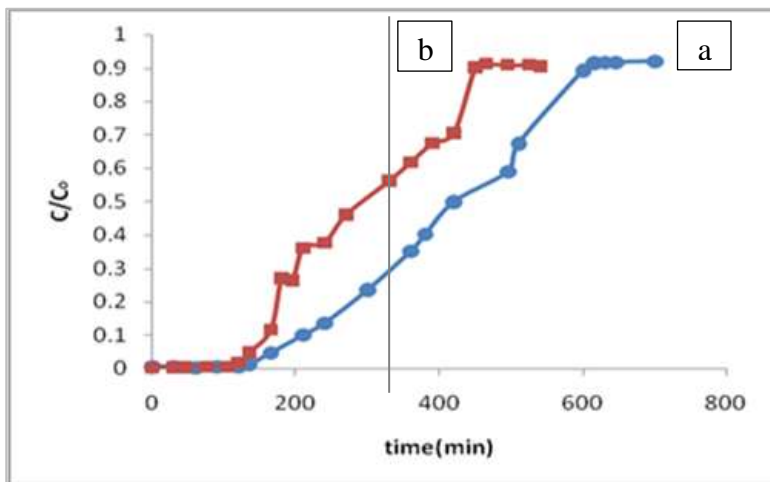**Fig 11-** Effect of different flowrate on breakthrough curve.

Fig. 12. Breakthrough curve (a) basic particle size, (b) finer particle size.

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- Thermodynamic Studies

Calculating Gibb's free energy change, $\Delta G°$, is very important to know if reactions occur spontaneously or not. Plotting $\ln K_L$ (langmuir parameter) versus $1/T$, gives values of ΔH (enthalpy changes) and ΔS (entropy changes) in adsorption process. These parameters calculated by the following equations:

$$\Delta G° = \Delta H° - T\Delta S° \tag{16}$$
$$\Delta G = -RTL\ln K_c \tag{17}$$

Where R and T are gas constant (8.314 J/mol.K) and absolute temperature (K) respectively. As shown in Table 5 negative values of ΔG show that the process is spontaneous and positive ΔH indicate process is endothermic.

Conclusion

In the present study, removal of heavy metal (Pb) by phanerochaete chrysosprium bio-adsorbent from aqueous solution in both batch and continuous systems, was investigated. In batch mode, the effect of varying pH was studied. It is found that the appropriate value of pH is 4.5. It is observed that 0.1 gr of adsorbent is enough for reducing the level of heavy metals in the solution. The adsorption process follows the pseudo-second order adsorption kinetics and intraparticle diffusion model also the equilibrium data show great agreement with Langmuir, Fruendlich and Dubinin-Radushkevich isotherm models. In the case of continuous system, process fits well to the Thomas and Yoon-Nelson models. The effect of input flowrate on breakthrough curve is determined. Increasing input flowrate causes earlier breakthrough point. Also, thermodynamic studies demonstrate that the process is spontaneous and endothermic. The result of this study illustrates that the using of Phanerocate chrysosporium as an adsorbent have a considerable potential to reduce the level of heavy metal ions in aqueous solutions.

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Table 5. thermodynamic parameters for adsorption of Lead

T(K)	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(kJ/mol.K)
300	-0.35		
303	-0.41	1.465	6.144
313	-0.47		
323	-0.51		

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