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Kinetic and equilibrium studies on the adsorption of lead by the chitin of pink shrimp (*Solenocera melantho*)

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ABSTRACT

The presence of metal ions in aqueous solutions represents a major environmental problem. These inorganic species are persistent and non-biodegradable pollutants that should be eliminated from water. In the recent years, Biosorption is emerging as a technique offering the use of economical alternate biological materials for the decontamination of polluted water. This paper presents a systematic characterization of new and commonly abundant low-cost biosorbents: chitin of pink shrimp (Solenocera melantho). Lead was chosen as a model sorbet. The effect of the most significant process parameters (pH, initial concentration of lead ions on kinetics, as well as pH) on biosorption equilibrium was studied. The equilibrium was reached within 0-200 minutes. Optimum conditions of pH, contact time, biosorption dosage and initial concentration of lead were determined to be 9, 0-200 minutes, 5gr/L and 7.99ppm respectively. The best efficiency biosorption was found to be 99.7%. The kinetics of the process in the case of both biomaterials was described with pseudo-second order equation and the equilibrium of biosorption by chitin produced by pink shrimp was described with the Freundlich equation and Langmuir model. These equations were chosen to achieve the best consistency of experimental data with the model results.

Key words: Chitin, Lead ion, Biosorption, Isotherm models, Kinetic models

INTRODUCTION

In recent years, heavy metal pollution has become one of the most serious environmental problems. Heavy metal ions have lethal effects on all forms of life and these enter the food chain through the disposal of wastes in water channels [1].

According to World Health Organization the metals of most immediate concern are lead, chromium, copper, iron, cadmium and zinc. Among heavy metals, Lead has been identified as one of the most toxic metals due to its detrimental effects on human nervous system, blood circulation system, kidneys and reproductive system. Lead in the environment commonly originated from various kinds of industrial activities such as mining, smelting and metal plating, battery manufacturing, ammunition production, paint production and paper and pulp processing. In order to solve the problems of heavy metal pollution in the environmental, it is important to bring pragmatic solutions to the issue [2, 3].

The traditional methods for removing heavy metals have several disadvantages. Chemical precipitation leads to the production of toxic sludge. Due to the economics of dealing with large volumes of liquids and of solvent losses, solvent extraction is limited to streams containing more than 1 g/l of the targeted heavy metal. Application of the ion-exchange process is rather expensive due to the cost of synthetic ion-exchange resins. Furthermore, they are not always selective enough to allow an effective recovery of heavy metals present in the waste [4].

Therefore, it is urgent to develop efficient and environmentally compatible means able to remove or detoxify heavy metals in an economical way. Among the physicochemical treatment processes for pollutant removal, adsorption is highly efficient, inexpensive and easy to adapt. Biosorption is becoming an important component in the integrated approach to the treatment of aqueous effluents [5].

The main objectives were to determine the possibilities for using the chitin of pink shrimp *(Solenocera melantho)* in biosorption of lead, which is one of the most frequent heavy metal found in waste and mining waters.

MATERIALS AND METHODS

Materials

Shells of pink shrimps (*Solenocera melantho*) were collected from a local fish market in bushehr, Iran. The shrimp shells were soaked in 0.5 N sodium hydroxide solutions for 6 hours at ambient temperature. They were then washed and flushed with distilled water at room temperature (20-25°C). This was conducted to remove the organic compounds or protein loosely associated on the surface of the shells. Sodium hydroxide; hydrochloric acid and nitrate were purchased from Merck (Germany). To prepare solutions containing lead, double-distilled water was used for this experiment.

Stock preparation

In order to prepare the lead stock solution, Lead nitrate was used. Stock metal solutions were prepared by dissolving 0.16 g of lead in 1000 ml of deionized water. Then different concentrations of lead (1-20ppm) were prepared. All chemicals used in this study were analytical grade (Merck). The pH was adjusted with 1 mol.L^{-1} solutions of HCl and NaOH.

Chitin preparation process

In order to produce chitin from pink shrimp (*Solenocera melantho*) Chang method [6] was used with some modifications. The shrimp shells were washed and flushed with double distilled water at room temperature (20-25 °C). This was conducted to remove the organic compounds or protein loosely associated on the surface of the shells. The remaining shells were sun-dried at 24 hours. The shells were then ground with a laboratory scale hammer mill (Moulinex) and screened to 60-80 mesh powder. The powder was prepared to serve as a single species, uniform-size stimulant of the commercial shrimp shell powder.

Then 20 g shrimp shells were treated with 200ml of 7% hydrochloric acid at 25 °C for 24 hours. After that, the samples were respectively filtered and neutralized with distilled water. The shrimp shells were soaked in sodium hydroxide solution for 6 hours at ambient temperature. Then the mixture was placed in an autoclave for 30 minutes. Subsequently, the samples were washed with distilled water and filtered again. For bleaching, the chitin was placed indirectly exposed to sunlight for 24 hours until white and dry.

Method

The study was carried out in vitro and discontinuous. The adsorption assays were performed using a standard volumetric flask with the volume of 250ml, including 100ml solution.

To investigate the effect of pH on the lead ion adsorption efficiency, the pH was adjusted in range of 2-10. In order to evaluate the effect of pH, the experiment was performed in optimum conditions of temperature, absorbent dosage, initial concentration of lead ion, Solution agitation speed and contact time that were determined to be 30°C, 3 gr/L, 10ppm,200rpm and 200minutes respectively. Before adding Biosorbent to an aqueous solution, the pH was adjusted with 1 mol.L^{-1} solutions of HCL and NaOH. Subsequently, the solution was filtered through Whatman filter paper and Biosorbent was removed. After determining the optimal pH, the Effect of initial concentration of lead ions on the removal of lead ions was studied. To determine the concentration of lead ions in aqueous solution on process efficiency, the initial concentration of Pb (1, 3, 5, 10, 15, 20 ppm) in laboratory conditions such as initial pH 9, adsorbent dose 5 gr /L, stirring speed 200 rpm, 0-200 minutes at different times and temperatures (30°C) were studied. After determining the pH and initial concentration of lead ions, the effect of absorbent dosage (1-6 gr /L) on the removal of lead was studied. To measure the concentration of lead ion, flame atomic absorption spectrometry SpectrAA-10 Plus models (Varian) was used in this experiment.

In all cases, the amount of lead adsorbed (R %) was expressed in equation (1).

$$\%R= (C_i\text{-}C_0/C_i) \times 100 \quad (1)$$

Where R = metal ion uptake at equilibrium (mg/L), C_i is the metal ion concentration remaining in solution at equilibrium, C_0 is the initial metal ion concentration.

RESULTS AND DISCUSSION

The effect of initial pH of aqueous solution on absorption efficiency of the lead ion

The initial pH of aqueous solution is one of the most important parameters in retrieval and removal process of heavy metal ion from the solutions. The initial pH of solution has some effects on the absorbent surface and also it is the reason of ionization of heavy metal ion in solutions [7].

In order to evaluate the optimum pH, the experiment was performed in optimum condition of initial concentration of lead ion in aqueous solution, absorbent dosage, solution agitation speed and temperature were determined to be 10 , 3 mg/L biosorption, 200rpm and 30°C respectively.

The absorption efficiency mostly depends on the concentration of H_2 in aqueous solution. The effect of pH on removal lead process efficiency is shown in Fig.1. It shows that initial pH of solution increased the absorption efficiency until initial pH become 9. By increasing the pH 9 to 10, lead ions deposited it and left a white deposit at the bottom of the container. This factor decrease the contact time with the adsorbent and therefore absorption of lead by absorbent decreased .The highest amount of removal lead ion was in pH 9 that is equals to 95.3 %.

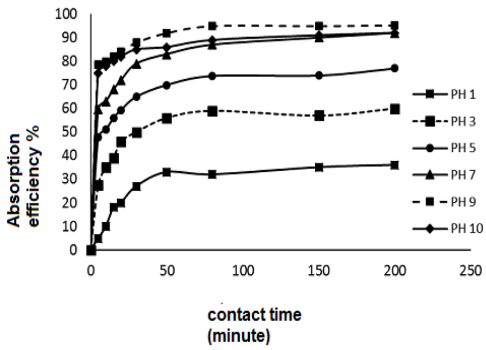

Fig.1. the effect of pH on the lead absorption efficiency by biosorption (T 30 °C, 3gr/L absorbent, 10 ppm initial lead ion, 200rpm stirring speed)

The effect of initial concentration of lead ion on absorption efficiency–study the kinetic behavior

The initial concentration of lead ions in the solution is an important parameter in adsorption process since the initial concentration of lead ions provide necessary energy for mass transferring between the aqueous solution and solid biosorption.

For determining the effect of lead ion concentration in aqueous solution on the processes efficiency some parameters need to consider such as different initial concentration of lead (3,1,5,10,15,20 ppm) , initial pH (pH 9) , dose of absorbent (5 gr/L), stirring speed(200 rpm) and time(0-200 minutes) at room temperature.

In this study, the effect of initial concentration of lead ion in aqueous solution was investigated (Fig.2). The results show that increases in lead ion concentration increased the absorption of lead ion by chitin biosorption.

According to the data, the highest amount of absorption and removal of lead ion by absorbent could be reached in initial time, because the slope of diagram rises quickly during this period due lead absorption by the active absorbent sites. After 50 minutes, the absorption decreased because the phenomenon of metal ions penetrates into the inner layers of biosorption and settled ions on the active sites.

The highest amount of absorption efficiency was obtained in 20 ppm initial concentration of lead ion after 200 minutes which is equal to 99.7 %.

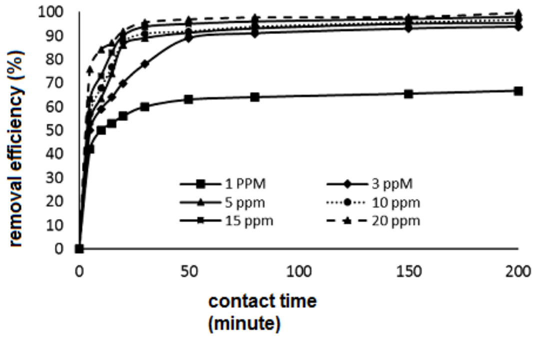

Fig.2. the effect of initial concentration of lead ion on the absorption efficiency
(30 °C temperature, 200 rpm stirring speed, 5 gr/L absorbent and pH 9)

The effect of adsorbent dosage on absorption efficiency of the lead ion

The amount of absorbent which is used in this study is an important parameter in absorption process because this parameter determines the absorption capability of absorbent in the standard concentration of absorbed material [8, 9]. In order to explore the effect of absorbent dose on absorption efficiency of lead ion by produced chitin from white shrimp , the absorbent dose was used in a range of 1-6gr/L .The experiment were conducted at a condition with pH (pH 9) , initial concentration of lead ion (200 ppm), contact time(200minutes) at 30°C and integrate speed (200rpm). It was found that an increase of adsorbent dosage resulted in absorption efficiency of lead ion concentration. Adsorbent dosage has a great influence on the biosorption process and determines the potential of biosorbent through the number of binding sites available to remove metal ions at a specified initial concentration. The highest amount of lead ion efficiency was 99.7% at 5 gr/L Adsorbent dosage. By increasing the amount of bio absorbent no significant changes observed in the absorption of lead ions. It is due to the saturate the active sites of absorbent. The effect of bio-absorbent dose on the lead ion absorption efficiency in aqueous solution is indicated in Fig. 3.

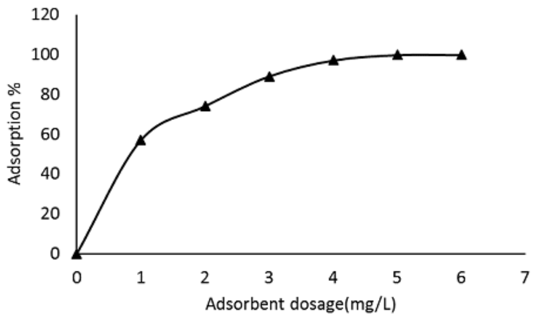

Fig.3. The effect of bio-absorbent dose on lead ion absorption efficiency
(30°C temperature, 200rpm stirring speed of solution , 20ppm initial concentration of lead ion, 200 min contact time and pH 9)

Kinetic Study

The absorption kinetic is used for determining controlling mechanisms of adsorption. The processes mechanism depends on physical and chemical properties of absorbent. In batch systems, adsorption kinetics is described by a number of models based on adsorption equilibrium such as the pseudo-first- order and the pseudo-second-order kinetic models. Pseudo-first and second models used for showing the quantity of absorption kinetic. Pseudo-second model illustrated that chemical absorption decreases the speed of process and control the adsorption and it basis on solid phase absorption. The pseudo-first-order and pseudo-second-order were applied to the kinetic study as shown in Eqs. (2) and (3) respectively [10] .For adjusting laboratory data with kinetic models the correlation coefficient (R^2) was used. The R^2 is determining by drawing a diagram of data with excel software.

$$Ln(q_e - q_t) = Lnq_e - K_1 t \quad (2)$$

$$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^2}\right) + \frac{1}{q_e(t)} \quad (3)$$

The initial absorption rate was determined according to:

$$H = Kq_e^2$$

Where K_1 is the Lagergren rate constant of the biosorption (min^{-1}); K_2 is the pseudo-second-order rate constant ($g.mg^{-1}.min^{-1}$); q_e and q_t are the amounts of metal ions sorbet ($mg.g^{-1}$) at equilibrium and at time t, respectively. For calculating absorption rate constant (K_1), we can draw Ln (q_e-q_t) against t [10, 11]. The pseudo-second-order model suggests that the biosorption process follows a pseudo second order mechanism. Therefore, the rate of occupation of biosorption sites is proportional to the square of the number of unoccupied sites [12, 13]. The plots of Pseudo-first (a) and second- order (b) for the biosorption of lead ion by the chitin of pink shrimp are shown in Fig.4.

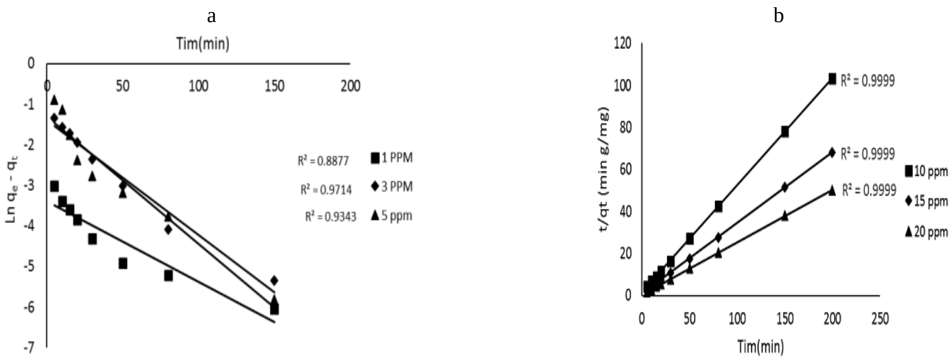

Fig.4. Pseudo-first (a) and second- order (b) plot for the biosorption of lead ion by the chitin of pink shrimp (*Solenocera melantho*) (Conditions: pH 9 ; absorbent dose, 5 gr/L; stirring speed, 200rpm; temperature, 30°C)

The correlation coefficient and other constants of pseudo first and second models is presented in Table 1. According to the determined data for R^2 in different concentrations of lead, it is clear that the laboratory data are following the second grade kinetic model, and this model is more capable for characterizing equilibrium data of mentioned absorbent in different concentrations of initial lead ion.

Table1. Pseudo first and second-order adsorption rate constants and coefficients at different initial concentrations

kinetic	The initial concentration of lead ions concentrations					
	1 ppm	3 ppm	5 ppm	10 ppm	15 ppm	20 pmm
pseudo-first kinetic						
$q_{e\ cal}$	0.0333	0.2457	0.2727	0.418	0.5224	0.5492
K1	0.0197	0.0282	0.0314	0.0221	0.023	0.0191
$q_{e\ exp}$	0.1334	0.5628	0.953	1.938	2.94	3.988
R2	0.8887	0.9714	0.9343	0.8396	0.7849	0.7806
psedue-second kinetic						
$q_{e.cal}$	0.135	0.5818	0.972	1.9646	2.9744	4.0128
$q_{e.exp}$	0.1334	0.5628	0.953	1.938	2.94	3.988
H	0.03515	0.0923	0.2671	0.6144	1.1589	2.0595
R^2	1.929	0.2727	0.2827	0.1592	0.131	0.1279
K^2	0.9999	0.9997	0.9999	0.9999	0.9999	0.9999

Biosorption isotherm models

Biosorption isotherm models usually are used for characterizing absorption process and its mechanism [14]. For optimization of the biosorption design, it is necessary to develop an equation that can be used to compare different biosorbents under different operational conditions. Various sorption isotherm models are used for fitting data in order to examine the relationship between sorption and aqueous concentration at equilibrium. In this investigation, the relationship between metal biosorption capacity and metal ion concentration at equilibrium has been described by two-parameter isotherm models: Langmuir and Freundlich models. Langmuir & Freundlich are two isotherms which are used in a widespread surface [15].

The Langmuir isotherm model is expressed as follows:

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{max}}\right) 1/c_e + \frac{1}{q_{max}}$$

Where q_{max} is the maximum metal biosorption and K_L (L/mg) is the Langmuir constant. These constants are related to monolayer adsorption capacity and energy of adsorption [14]. C_e is metal ion concentration in counterweight; q_e is the absorbed metal ion in counterweight for per gram of absorbent. R_L is one of the most important parameters that present basic features of languir equation. Amount of R_L shows the manner of isotherm model. If $0<R_L<1$ and $R_L=0$, RL>1, the process in order is undesirable, irreversible, linear and desirable [16, 17]. R_L is expressed as below:

$$R_L = \frac{1}{1} + K_L C_0$$

Where C_0 (mg/l) is the initial concentration of lead ion in a solution. Freundlich model is an empirical model and it can characterize that organic and inorganic compounds are absorbed by the different types of absorbent. The non-linear form of Freundlich isotherm model is expressed as follows:

$$q_e = K_f C_e^{\frac{1}{n}}$$

And the linear form is expressed as follows:

$$Lnq_e = Lnk_f + \frac{1}{n} LnC_e$$

Where q_e represent the absorption capacity of balance (mg/g), C_e is equilibrium concentration of cadmium ions in solution (mg/L), and K_f and n are constants of Freundlich model that are showing the relation between absorption capacity and absorption intensity. For determining 1/n and K_f values, Lnq_e was drawn in front of LnC_e for obtaining line slope that shows 1/n and K_f is the intercept. In other examinations, the extent of "n" has reported from 1 to 10. If Values of *n* greater than 1 it can conclude that there are much interplay between metal ion and absorbent, but if n equals 1, it shows the linear absorption for all the active absorbent sites [18]. For determining the optimum equilibrium model for characterizing the equilibrium data, the correlation coefficient (R^2) was used. If R^2 become 1, it shows that this model is very capable for characterizing the equilibrium behavior of absorbent. The Langmuir and Freundlich adsorption isotherm plots are presented in Fig.5.

a b

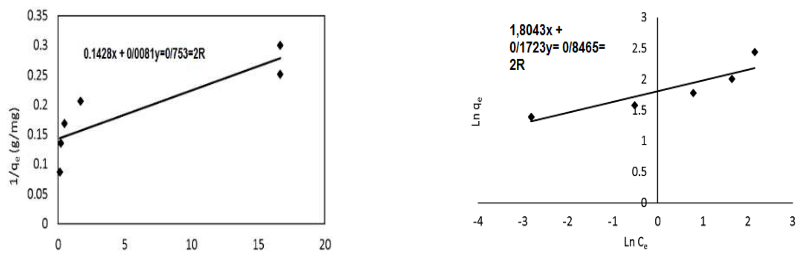

Fig.5. Langmuir (a) and Freundlich (b) adsorption isotherm plots for the adsorption of metal iron

The constants and correlation coefficient (R^2) of the both models are given in Table 2.

Table.2. Isotherm models parameters and theirs constants

Isotherm models / *Parameters*	**Langmuir**	**Friendlich**
R^2	0.753	0.8465
R_1	0.0028	-
K_1	17.64	-
q_{max}	7.003	-
n	-	5.804
K_F	-	6.07

The maximum capacity of lead ion absorption (q_{max}) by produced chitin was 7.003. The capacity of R_L value for the process determined 0.0028 which showed that the lead ion absorption by chitin absorbent is a desirable process. For comparing the capability of characterizing equilibrium data by two models the Langmuir isotherm model are more capable for characterizing data than the other model.

CONCLUSION

This study investigated the feasibility of chitin produced by chemical methods from the skin of white Hindi shrimp used as a low-cost adsorbent for the removal of lead from aqueous solution. Chitin is a kind of polysaccharide that can be finding in the skin of some crustacean such as crabs and shrimp. In this study, we considered some parameters such as initial pH and biosorption dose and initial concentration of lead ion in solution. Optimum conditions of pH, contact time, biosorption dosage and initial concentration of lead were determined to be 9, 0-200 minutes, 5gr/L and 7.99ppm respectively. The best efficiency biosorption was found to be 99.7%. The kinetic of the process in the case of both biomaterials was described with pseudo first and second order equation and the equilibrium of biosorption by chitin produced from pink shrimp was described with the Freundlich and Langmuir model. According to the correlation coefficient (R^2), the pseudo-first-order kinetic model is more capable for characterizing the kinetic behavior of process than the second one, as well as the Freundlich model is more capable than the Langmuir model, for characterizing the equilibrium behavior of biosorption. By considering the absorption efficiency of lead by using produced chitin of white Hindi shrimp`s skin since it is biocompatible, biodegradable and renewable so we can recommend this new biosorption for removal the lead from solutions.

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