



The Study of Kinetic and Biosorption of Pb Ion by Rice Husk from Wastewater

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Abstract

An agricultural waste i.e. rice husk has been used as a cheap adsorbent for the removal of lead as a harmful heavy metal from contaminated water via adsorption. The adsorption capacity of rice husk was calculated by equilibrium models. The results showed that the adsorption process has the best accordance with Langmuir model. The kinetics of the adsorption was also investigated and obtained that the experimental data has the best fit with pseudo-second kinetic model. In this study, the effect of the adsorbent amount as well as pH value on the results was also investigated.

Keyword: Adsorption; Rice husk; Pb removal

1. Introduction

The industrial activities represent an important pollutant source nowadays, mainly concerning the addition of heavy metals in soil. This is contributed to a significant increase on the concentration of metal ions in water, representing an important source of contamination of the aquatic bodies, especially when it is considered that such ions can be disseminated through the food chain [1].

Heavy metal contamination of water is a serious threat to the global ecosystem [2]. Water and wastewaters contaminated by heavy metals have an adverse impact on public health and economy; and their exposure to heavy metals, even at trace levels, is believed to be a risk for human beings [3]. Also strict

environmental regulations on the discharge of heavy metals and rising demands for clean water with extremely low levels of heavy metals make it greatly important to develop various efficient technologies for heavy metal removal from environment [4] and their detection or determination in trace levels.

Different alternatives for treating effluents are described in literature, including chemical precipitation, carbon adsorption, ion exchange and membrane separation process [5]. The most common of these various methods is the chemical precipitation. However, some limitations in this process can be pointed out such as its cost, low efficiency, labor-intensive operation and lack of selectivity of the precipitation process [6]. New approaches for removing metals based on biosorption using algae or bacteria have also been reported [7].

According to EPA's National Priorities List

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(NPL) lead has been ranked third, among all the other contaminants, in terms of frequency of detection on the sites [8]. The most widespread uses, which have led to environmental and health problems, have been the use of lead in gasoline antiknock products and paint pigments. Lead is recognized as a heavy metal poison; it acts by made complex with oxo-groups in enzymes and obstruct hem synthesis and porphyrin metabolism. It also inhibits acetylcholineesterase, acid phosphotase, ATPase, etc., and inhibits protein synthesis probably by modifying tRNA. Typically, symptoms of lead poisoning are headaches, convulsions, chronic nephritis of the kidneys, and central nervous system disorders [5, 6]. Therefore, development of a reliable method for the removal and determination of heavy metals at trace levels are highly desired. Atomic absorption spectrometry (AAS) is the often used as an appropriate technique for the determination of heavy metals because of simplicity and low running cost.

In this work, rice husk a by-product of rice processing, has been used for the removal of lead as a harmful heavy metal from contaminated water via adsorption. Rice husk acts as a cheap adsorbent via lead ion. The adsorption capacity of rice husk has been calculated by equilibrium models and the kinetics of the adsorption was also investigated. In this study, the effect of the adsorbent amount as well as pH value on the results has also been investigated.

2. Experimental

2.1. Materials and methods

All reagents were of analytical grade and distilled water obtained from a Hamilton system (Hamilton, UK) was used throughout. All chemicals and reagents were of analytical grade. Lead Nitrate, phosphoric acid (85% m/m), ammonia solution (25% m/m), hydrochloric acid (37% m/m), acetic acid (99.9% m/m), ethylenediamine(EDA) (99.8%) were purchased from Merck (Darmstadt, Germany). Acetate buffer solutions (pH 5) were prepared by adding appropriate amounts

of 1.0M sodium hydroxide solution into a mixture of 0.1M of phosphoric acid. The Pb(II) solutions, at 1000 mg l⁻¹ concentrations were prepared in distilled water using Pb(NO₃)₂. The concentration of Pb in each aqueous solution was measured with an AAS (Perkin Elmer model AA800) by measuring the absorbance of all samples at λ_{\max} of 283.3 nm. The experimental solutions were obtained by diluting the stock solution in accurate proportions to different initial concentrations. The wastewater used was obtained from an analytical chemistry laboratory. It was made up of residues from sample preparation processes (different mineral acids and oxidant agents), organic compounds used for extraction of different metals in biological samples, slurry samples (in general from biological samples) and, finally, solutions of metals used for calibration procedures in atomic absorption spectrometry.

2.2. Adsorbent: rice husk

The rice husk was obtained from a farm near Marvdasht city, Fars state, Iran. To prepare the powdered husks, they were initially ground and homogenized using a food blender with steel blades (Kenwood, China) for 15 min. Particle sizes $\leq 300\mu\text{m}$ were obtained by passing the milled material through a steel sieve. Then, the powder rice husks were stored in polyethylene bottles and used the rice husk was washed three times with distilled water and dried in room temperature. For more investigation on the effect of materials such as HCl, H₂SO₄, CH₃COOH and EDA on the adsorption efficiency of adsorbent, the rice husk was washed with these chemicals.

2.3. Batch equilibrium and kinetic studies

Adsorption experiments were carried out by adding a fixed amount of rice husk to a series of conical flasks filled with 25ml diluted solutions. The conical flasks were then sealed and placed in a water-bath shaker and shaken at 235 rpm with a required time at room temperature. The flasks were then removed from the shaker, and the final concentration

of Pb^{2+} in the solution was measured at maximum wavelength of 283.3nm using AAS. The amount of Pb^{2+} adsorption at equilibrium q_e (mg/g) was calculated from the following equation:

$$q_e = (C_0 - C_e) * \frac{V}{W} \quad (1)$$

Where C_0 and C_e (mg/L) are the liquid phase concentrations of Pb^{2+} at initial and at the equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of adsorbent.

The procedure of kinetic tests was basically identical to those of equilibrium tests. The aqueous samples were taken to preset time intervals and the concentrations of Pb^{2+} were similarly measured. The effect of initial concentration of Pb^{2+} , contact time, pH, temperature, the amount of solution as well as the amount of adsorbent were investigated.

3. Results and discussion:

3.1. Characterization of the adsorbent

FTIR spectroscopy was used for the characterization of rice husk. The FTIR spectrum (Fig. 1) indicated a broad band at 3390 cm^{-1} representing the bonded -OH groups (Kamath and Proctor, 1998). The stretching of the OH groups bound to methyl radicals presented a signal between 2940 and 2820 cm^{-1} . These groups are present on the lignin structure (Lopez Pasquali and Herrera, 1997). The peaks around 1070 cm^{-1} correspond to the Si-O asymmetric stretch. The bands observed at about 800 cm^{-1} could be assigned to the

Si-O symmetric stretching bond (Socrates et al. 1994) (Fig. 1). This adsorbent, Silica Group is responsible for the absorption of lead ions.

3.2. Effect of adsorbent amount

For the selection of the optimized adsorbent amount, by fixing the other parameters such as pH (5.0) and Pb^{2+} concentration (250 mg L^{-1}), the amount of rice husk was changed systematically. The results showed that up to 0.2 g of rice husk, the adsorption efficiency increases with increase in adsorbent amount (Fig. 2). After 0.2 g of the adsorbent, there was no change in the adsorption efficiency. So, 0.2 g of the adsorbent was chosen as an optimum amount. Results were shown in Fig. 2.

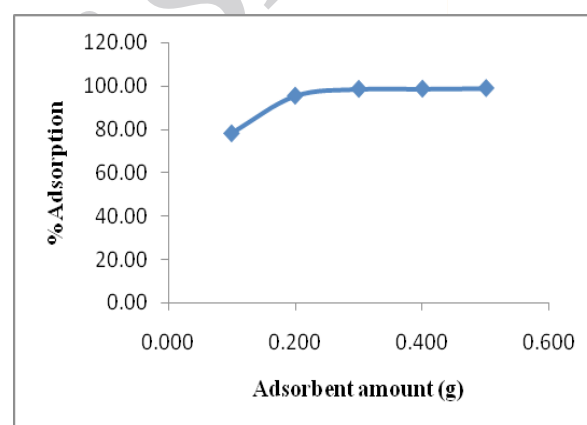


Fig. 2: Effect of adsorbent amount in sorption of MB by rice husk. pH 5.0, 50cc volume equation solution, Pb^{2+} concentration (250 mg L^{-1}), Temperature 25°C , contact time 60 min.

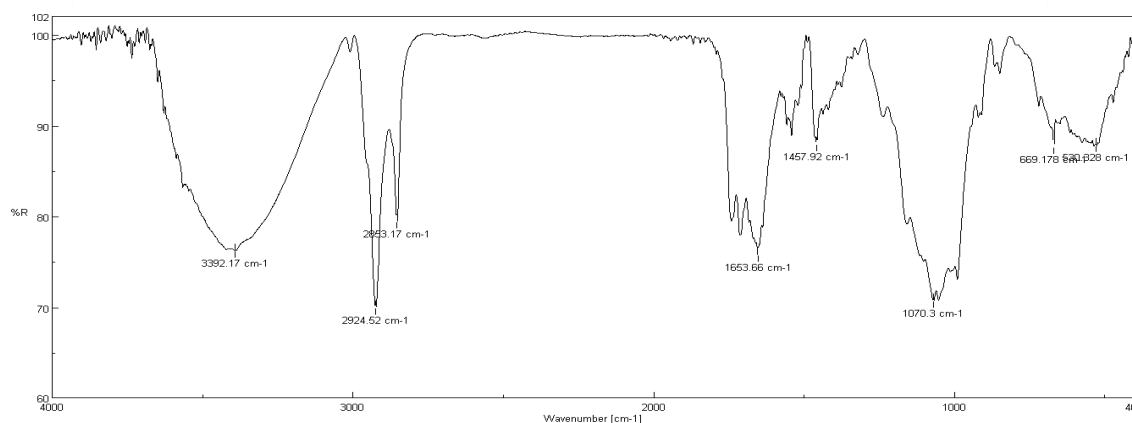


Fig. 1: FT-IR spectrum of rice husk

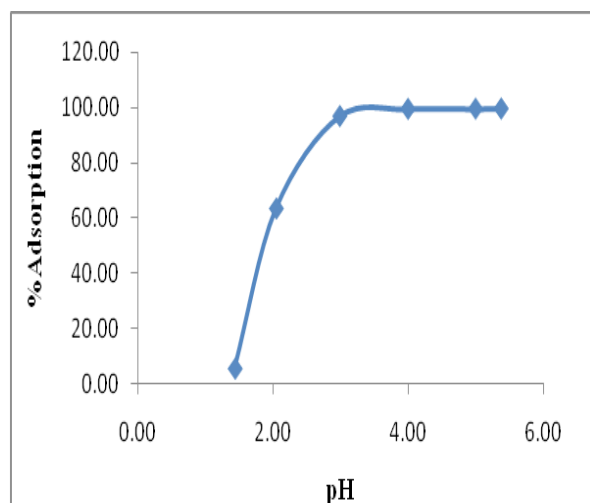


Fig.3: The effect of pH on the adsorption of Pb²⁺ by rice husk. 50cc volume equilibrium solution, Pb²⁺ concentration (250mgL⁻¹), Temperature 25°C, 0.2g adsorbent amount, contact time 60min.

3.3. The effect of pH values on Pb adsorption

FTIR spectrum showed that rice husk has -OH groups. So, it seems that the pH value can affect the adsorbent efficiency of rice husk. The effect of pH of the solution on the adsorption efficiency of rice husk has been shown in Fig. 3. Lower adsorption efficiency at acidic solution (pH < 3.0) is probably due to the presence of excess of H⁺ ions competing with the Pb²⁺ for adsorption sites. At higher pH values (3.0–5.0) the Pb²⁺ adsorption was almost constant with high adsorption efficiency. At higher pH values, however, the surface of rice husk particles may become negatively charged, which enhances the adsorption of positively charged Pb²⁺ cations through electrostatic forces of attraction. The result shows that the pH of Pb²⁺ solution plays an important role in the whole adsorption process. The adsorption profile as a function of solution pH can be explained based on surface charge density, having functional groups such as hydroxyl, carboxyl, amino and others. As the surface charge density decreases with an increase in the solution pH, the electrostatic repulsion between the positively charged metal ions and the interactions between the functional groups -COOH, OH, and -C-O-R in the carbohydrate backbone and metal ions

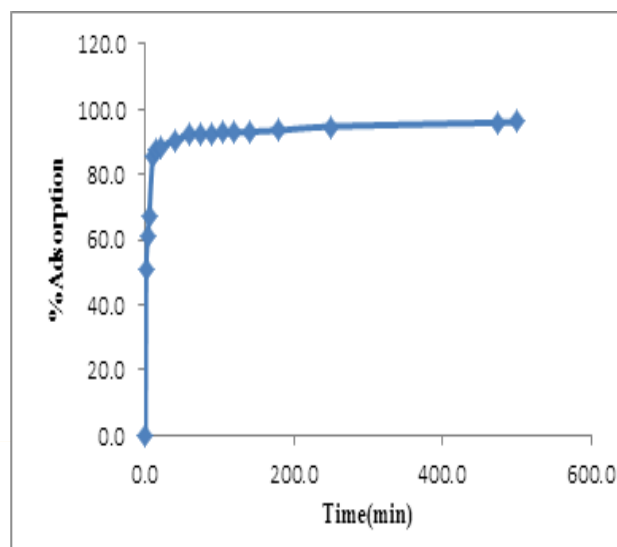


Fig.4: The effect of time on the adsorption of Pb²⁺ by rice husk. 180cc volume equilibrium solution, pH 5.0, Pb²⁺ concentration (250mgL⁻¹), Temperature 25°C, 0.5g adsorbent amount

have been confirmed by X-ray photoelectron spectroscopy and FT-IR. Also the presence of silanol groups on the surface of the rice husks, from the silica contained in the material, tends to form a surface presenting weakly acid characteristics ($K_a = 10^{-6}$ – 10^{-8}) (Dugger et al., 1964). At the higher pH 5.5 was observed lead precipitate. According to the results obtained, the initial pH for effluent treatment was fixed at 5. The effect of pH on the percent adsorption of Pb²⁺ by rice husk is shown in Fig. 3.

3.4. Adsorption kinetics

One of the most important parameters that can significantly describe the adsorbent characteristics is the sorption time. The main aim of the study of sorption kinetics is to determine the time required to reach the equilibrium sorption of adsorbent. It can be achieved by a plot of Pb²⁺ sorption versus contact time (Fig. 4). The plot clearly shows three distinct regions. At the initial 10 minutes, the adsorption of Pb²⁺ is very rapid and more than 85.5% of Pb²⁺ ions were adsorbed during this period. However, in the adsorption time from 10 to 60 minutes, sorption kinetics slows down and gradually tends to level off. At times greater than 60 minutes the sorption is at its maximum value and is independent of contact

time, illustrating that sorption equilibrium was achieved. The fast step of Pb^{2+} sorption may occur on the particle surface due to an immediate interaction between Pb^{2+} ions and the active $-SiOH$ groups on the surface of the rice husk. The equilibration was attained after 60 min. Thus to get the maximum Pb^{2+} adsorption, the contact time of 75min was selected as the optimum during the batch studies for confidence in establish equilibrium. The pseudo-first-order and pseudo second-order kinetic equations were chosen to fit the obtained sorption kinetics data and to estimate the rate constant of this phenomena. The pseudo-first-order rate equation is generally expressed as follows:

$$\begin{aligned} \log(q_e - q_t) &= \log q_e - k_1 t / 2.303 \\ \log(q_e - q_t) &= \log q_e - k_1 t / 2.303 \end{aligned} \quad (2)$$

Where q_e and q_t are the amount of species adsorbed per unit mass of adsorbent ($mg\ g^{-1}$) at equilibrium time and at any time t , respectively and k_1 is the rate constant of pseudo-first-order sorption (min^{-1}).

To interpret the specific rate constant of adsorption processes the following Ho–

Mckay pseudo-second-order rate expression was applied [9]:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (3)$$

Where k_2 is the rate constant of pseudo-second-order sorption ($g\ mg^{-1}\ min^{-1}$) and q_e and q_t are adsorption capacities at equilibrium and time t ($mg\ g^{-1}$), respectively.

The results of this study, are presented as plots of $\log(q_e - q_t)$ and t/q_t versus t for the contacting time from zero to 60 minutes. As it is shown in Fig. 5b and 5c, adsorption of Pb^{2+} on the rice husk particles is more appropriately described by a pseudo-second-order kinetic model since its correlation coefficient (0.999) is greater than the correlation coefficient of pseudo-first-order model (0.668).

3.5. Effect of initial Pb^{2+} concentration and sorption isotherms

To find the maximum capacity of the adsorbent which is very important in the design of adsorption systems, the equilibrium adsorption isotherms were constructed. The adsorption isotherm of Pb^{2+} by the rice husk particles is shown in Fig. 5a. Based on the

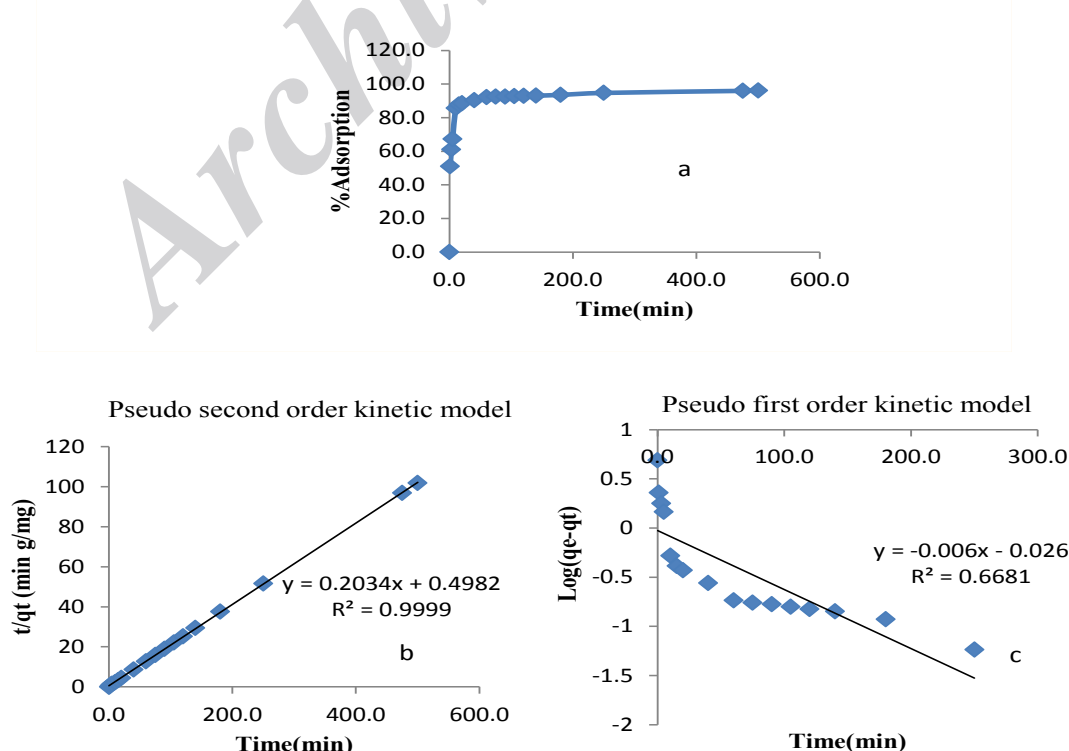


Fig. 5: Effect of time on sorption (a) and kinetic models (b,c)

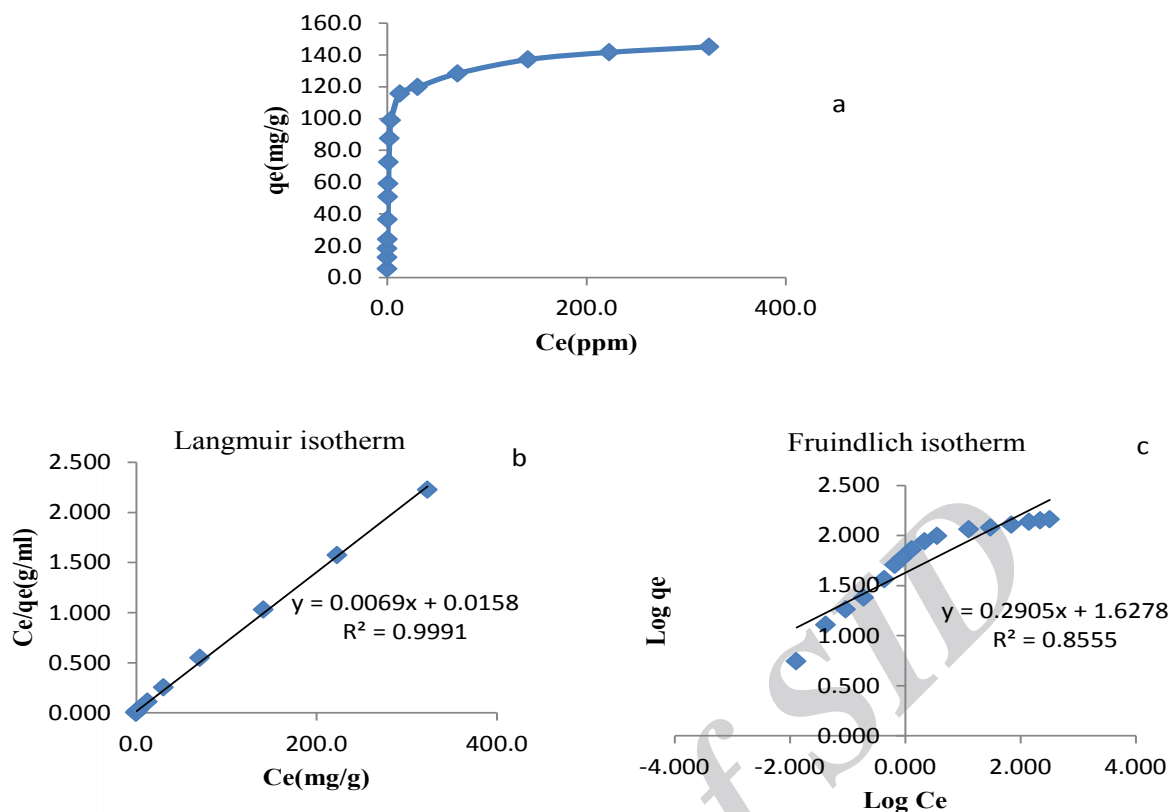


Fig. 6: effect of initial concentration of Pb ion (a), equilibrium models(b, c)

kinetics studies, 75 min was selected for the contact time to ensure that equilibrium was reached. The equilibrium data were analyzed in accordance with the linear representation of the Langmuir sorption isotherm [10] as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} C_e \quad (4)$$

Where q_e is the adsorption capacity (mg g^{-1}) based on the dry weight of adsorbent, C_e is the equilibrium concentration (mg L^{-1}) in solution, q_{\max} is the maximum adsorption capacity (mg g^{-1}) of metal that can be adsorbed in a monolayer, and K is the Langmuir adsorption equilibrium.

Langmuir model (Fig.6b.) has good agreement with the experimental data. This curve suggests that the Pb adsorbed on monolayer coverage on the adsorbent surface. The Freundlich model, which assumes that different sites with several adsorption energies are involved, was also tested to describe the sorption data. In this model the energy term, K_F , in the Freundlich equation varies as a function of the surface coverage. The

linear representation of the Freundlich [11] adsorption equation is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

The Freundlich plot is shown in Fig. 5c and its parameters.

The parameters and correlation coefficient show that the sorption behavior of Pb onto the adsorbent is best described by the Langmuir isotherm model because the Langmuir isotherm yields the highest correlation coefficient and smallest difference between theoretical q_{\max} (167 mg g^{-1}) and experimental q_e (147 mg g^{-1}).

4. Conclusions

In this work the adsorption of Pb^{2+} on rice husk as a cheap agricultural waste was studied. The best pH for sorption of Pb^{2+} on rice husk was 5.0. The best equilibrium model for sorption is Langmuir model and the maximum capacity for sorption was obtain 167 mg/g . the equilibrium time for sorption is 75 min. the best kinetic model for sorption is pseudo

second order kinetic model. This study shows that rice husk consider to capacity and other parameters can be used as an adsorbent for heavy metal removal.

Acknowledgments

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