

Equilibrium, Isotherm and Kinetics Studies for the Uptake of Lead Ions from Aqueous Solution Using Rice Husk

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Abstract: *Industrial and domestic effluents, as well as indiscriminate applications of various chemicals, pesticides etc. have contributed to the deterioration of environmental quality. Among these pollutants, heavy metals represent a special group because they are not chemically or biologically degraded in a natural manner. The adsorption process is being widely used by various researchers for the removal of heavy metals from waste streams and activated carbon has been frequently used as an adsorbent. Despite its extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon. The adsorption of Pb (II) metal ions on rice husk has been found to be pH, contact time, adsorbent dose and initial metal ion concentration dependent with the maximum removal efficiency of 80%. The adsorption parameters were determined using Langmuir and Freundlich isotherm models. Also, the adsorption kinetics was studied using pseudo first order and second order model showing that the adsorption process follows the second order kinetics.*

Keywords: Adsorption, Pb (II), Isotherm, Rice husk, Removal, Pollution, Kinetics, Adsorbent.

1. Introduction

Water pollution due to toxic heavy metals has been a major cause of concern with respect to the environment and human health. Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain. The main techniques that have been utilized to reduce the heavy metal ions from the effluents include lime precipitation, ion exchange, adsorption onto activated carbon, membrane process, and electrolytic methods. All these methods are generally expensive. Therefore, numerous approaches have been studied for the development of low-cost adsorbents. Several literature reviews describe the use of biosorbents to remove pollutants, mainly heavy metals, from wastewater. It is a promising technology for the treatment of pollutant streams. This process has several advantages such as low cost of materials, ease of operation, abundant availability etc. over the conventional methods. Lead is one such heavy metal which, if present in water, can cause many problems. In water, lead is released from lead treatment and recovery industries, especially from lead battery manufacturing units. Lead is toxic to living organisms and if released into the environment can both accumulate and enter the food chain. Lead is known to cause mental retardations, reduces haemoglobin production necessary for oxygen transport and it interferes with normal cellular metabolism [1]. Lead has damaging effects on body nervous system. Many researchers have done the research on using agricultural waste in adsorption of lead. The removal of poisonous Pb (II) from wastewater by different low-cost abundant adsorbents was investigated by Ghani et al. Rice husks, maize cobs and sawdust, were used at different adsorbent/metal ion ratios. Removal of the poisonous lead ions from solutions was possible using rice husk, maize cobs and sawdust as

adsorbents and rice husk was the most effective one [2]. Yasemin et al. studied the adsorption of lead, cadmium and nickel from aqueous solution by sawdust of walnut. The effect of contact time, initial metal ion concentration and temperature on metal ions removal had been studied. It was found that sawdust appears to be a promising adsorbent for removal of heavy metals from wastewater and this process is potentially more economical than any other current process technology [3]. Zuurro et al. studied to provide some information on the adsorption properties of tea waste and evaluated the removal efficiency of lead ions by spent leaves of green and black tea. The results from this study indicated that using spent tea leaves as an adsorbent may be an efficient and economical means for removing lead and, presumably, other heavy metal ions from aqueous solutions [4]. The ability of converting a waste product, rice husk, into an economically cheap adsorbents have been investigated for Pb(II) and NO³⁻ removal from aqueous solution through adsorption by Adediran et al. The results from this study showed that the chemically modified rice husk has considerable potentials for the removal of nitrate and Pb(II) ions from aqueous solutions over a wide range of experimental conditions through adsorption[5]. It was reported that the rice husk is a potentially useful material for the removal of lead from aqueous solutions. The rapid uptake, high proportion of cellulose (28-36%), and high adsorption capacity make it a very attractive alternative adsorption material (Khan et al., 2004) [6]. The purpose of the research is to study the adsorption of lead ions from aqueous solution using rice husk as an adsorbent.

2. Experimental

Sample preparation- Aqueous solutions were prepared by using analytical grade lead nitrate by using double distilled water. A 1M stock solution was prepared having a lead

concentration of 1000 mg/L. The solutions of various concentrations under study were made from stock solution by making appropriate dilutions.

Adsorbent Preparation- Rice husk was recovered from a local mill and repeatedly washed with distilled water in order to remove impurities. Then it was rinsed with distilled water and sun dried for 2 days. After that, it was crushed and sieved into a fine powder.

Method- The batch experiments were conducted in 250 mL conical flasks. The volume of the test solution was maintained as 100 mL. All the samples were mechanically agitated in low speed. The experiments were conducted at room temperature. The duration of the experiments was 150 minutes. The amount of Pb(II) adsorbed on the raw adsorbent was recorded titrimetrically by direct titration with EDTA as per the standard method given in Vogel (1978) [7]. The experiments were carried out to study the effect of pH (2-6), effect of adsorbent dose (0.4-1.2g/100 mL), effect of contact time (30-150 min) and effect of initial metal ion concentration (20-100 mg/L).

The amount of metal ion adsorbed was calculated as:

$$\% \text{ Adsorption} = \frac{(C_o - C_e)}{C_o} \times 100 \quad \text{--- (1)}$$

Where, C_o and C_e are the initial and final concentration of adsorbate, respectively.

The amount of metal adsorbed per Kilogram of the biomass was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \quad \text{--- (2)}$$

Where q_e is the adsorbed metal on the sorbent, m is the weight of sorbent, V is the volume of metal solution, C_o is the initial metal concentration, and C_e is the final metal concentration.

3. Results and Discussion

Effect of pH: Effect of pH on the adsorption characteristics of rice husk was determined in the pH range 2-6. As is apparent from fig.1, the system is pH dependent and shows maximum adsorption at pH 5. The sorption rate is lower in acidic ranges, because at low pH due to high positive charge density on the adsorbent surface, there is electrostatic repulsion resulting in lower rate of adsorption [8].

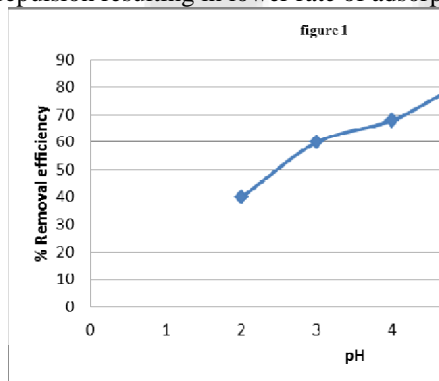


Figure 1: Effect of pH on adsorption

Effect of adsorbent dose: The results for adsorptive removal of Pb(II) with respect to adsorbent dose are shown in Fig. 2

over the range 0.4-1.2 g/L, at pH 5. It is observed that there was a slight increase in percentage removal of Pb (II) with increasing adsorbent dose due to the greater availability of the exchangeable sites or surface area.

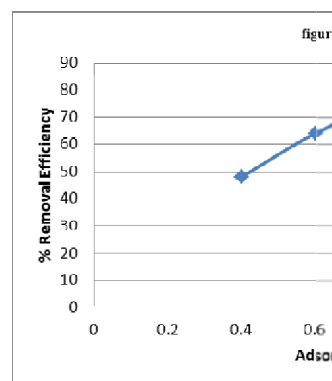


Figure 2: Effect of dose on adsorption

Effect of contact time: Contact time is also an important factor affecting removal. It is observed from fig. 3 that there is an almost linear increase in percentage removal with increasing contact time reaching 80% removal at 150 min, thereafter; no increase in removal efficiency was observed.

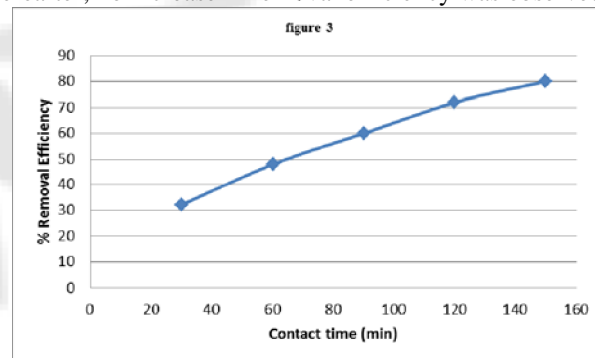


Figure 3: Effect of contact time on adsorption

Effect of Metal ion concentration: The amount of metal ion adsorbed increases with increase in metal ion concentration as observed in fig. 4. However, percentage removal decreases with increase in the concentration of Pb^{2+} ions. This can be explained by the fact that all the adsorbents have a limited number of active sites, which become saturated at a certain concentration [9]. The removal of Pb (II) was maximum of 88% for the lowest concentration of 20 ppm.

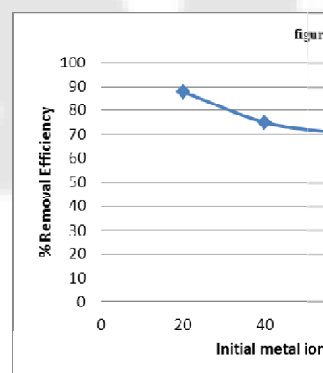


Figure 4: Effect of metal ion conc. on adsorption

Adsorption isotherm studies:

The data for the uptake of Pb (II) by rice husk has been analysed in the light of Freundlich and Langmuir isotherms of adsorption. The isotherm is represented in fig. 5 by

$$\frac{1}{q} = \frac{1}{q_e b} \left(\frac{1}{C} \right) + \left(\frac{1}{q_e} \right) \quad \text{--- (3)}$$

where q = adsorption capacity (mg/g), q_e = maximum adsorption capacity (mg/g), C = aqueous concentration of adsorbate (mg/L) and b = measure of affinity of adsorbate for adsorbent. Langmuir isotherm was expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which indicates whether adsorption is favourable or not, which is expressed by the following equation:

$$R_L = 1/1 + bC_0$$

Where C₀ is the initial concentration of adsorbate (mg/L) and b is the Langmuir adsorption equilibrium constant (mL/mg). Based on the effect of separation factor on isotherm shape, the R_L values in the range of 0 < R_L < 1 as per the criteria indicate favourable adsorption [10].

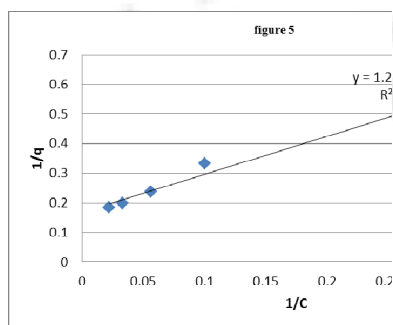


Figure 5: Langmuir Isotherm for adsorption

The Freundlich isotherm as shown in fig. 6 is introduced as an empirical model, where q_e represents the amount adsorbed per amount of adsorbent at the equilibrium (mg/g), C_e represents the equilibrium concentration (mg/L), and K_f and n are parameters that depend on the adsorbate and adsorbent. The linear equation used is:

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

where K_f and n are Freundlich constants which correspond to adsorption capacity and adsorption intensity, respectively [11]. The n value indicates the degree of nonlinearity between solution concentration and adsorption and the values of n > 1 represent favourable and good adsorption.

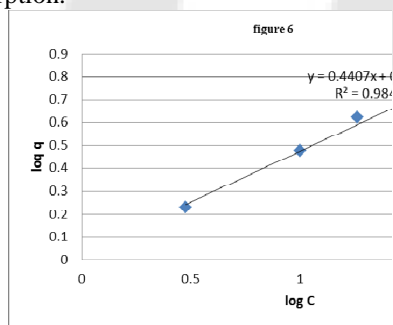


Figure 6: Freundlich Isotherm for adsorption

The n and R_L values are 2.269 and 0.232 respectively. The adsorption isotherm studies clearly indicated that the adsorptive behaviour of Pb (II) metal ions on rice husk fits to both Langmuir and the Freundlich model.

Adsorption kinetics

The kinetics of adsorption was determined by analysing adsorptive uptake of lead from the aqueous solution at different time intervals. The pseudo-first-order and pseudo-second-order model equations were fitted to model the kinetics of lead adsorption onto rice husk. The linearity of each model indicates the model suitability to describe the adsorption process [12]. The pseudo-first order equation used is expressed in fig. 7 as:

$$\log(q_e - q_0) = \log q_e - \frac{k_1}{2.303} t$$

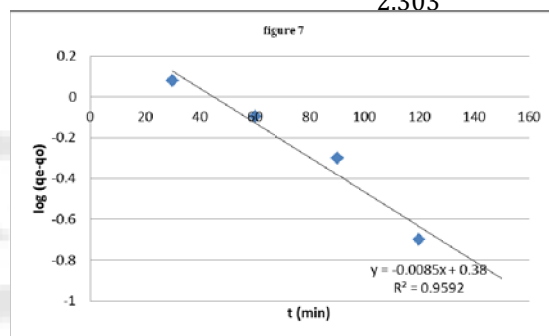


Figure 7: Pseudo first order kinetics for adsorption

The pseudo second order equation used is:

$$\frac{t}{q_0} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

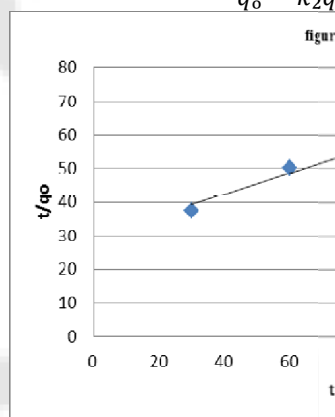


Figure 8: Pseudo second order kinetics for adsorption

The data is well represented by both the kinetic models. The results show that the kinetics show slightly better results for pseudo second order kinetics as compared to the first order. The values of q_{eobs} and q_{ecal} are 2.0 and 2.39 mg/g for pseudo first order and 2.0 and 3.27 for the second order respectively.

4. Conclusions

The potential of rice husk powder for the removal of Pb(II) ions from aqueous solutions was dependent on adsorption process such as solution pH, initial metal ions concentration, adsorbent dose, and contact time. Both the adsorption isotherms were demonstrated to provide the best correlation for the adsorption of Pb (II) ions onto rice husk. The kinetic results for the experimental data of adsorption of lead onto

rice husk were better followed by pseudo second-order equation. Rice husk is an easily, locally available, low-cost adsorbent and has a considerable high adsorption capacity. It can be chemically modified to enhance the adsorption efficiency. The future scope of the study involves using various other adsorbents for removal and chemical modification of the adsorbents to enhance the removal efficiency. However, a parallel comparison using naturally polluted water (e.g. effluent from dyeing and bleaching industries, textile industries, paint industries and battery manufacturing industries etc.) is desirable.

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