

Studies on the removal of Pb(II) from wastewater by activated carbon developed from *Apricot stone* activated with sulphuric acid

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Abstract

Studies on the utilization of low cost adsorbents for removal of heavy metals from wastewaters are gaining attention. Activated carbons were developed from Apricot stone, by chemically treating with sulfuric acid. Batch adsorption experiments were performed to find out the effective lead removal at different metal ion concentrations, adsorbent size and dosage. Operational parameters such as pH, agitation time and adsorbent concentration, initial ion concentration and particle size were also studied. Adsorption data fitted well with the Langmuir and Freundlich models. However, Freundlich isotherm displayed a better fitting model than Langmuir isotherm because of the higher correlation coefficient that the former exhibited. Apricot Adsorption kinetics data were modeled using the pseudo-first and pseudo-second-order models. The results indicate that the second-order model best describes adsorption kinetic data. The estimated maximum capacities of lead ions adsorbed by Apricot stone activated with sulphuric acid were 21.38 mg g⁻¹. In addition, the thermodynamic parameters, standard free energy (ΔG_0), standard enthalpy (ΔH_0), standard entropy (ΔS_0) of the adsorption process were calculated.

Keywords: *Lead; Adsorption; Isotherm; Activated carbon; wast water*

1 Introduction

The major sources containing lead are the wastewaters from process industries engaged in lead-acid batteries, paint, oil, metal, phosphate fertilizer, electronic, wood production and also combustion of fossil fuel, forest fires, mining activity, automobile emissions, sewage wastewater, sea spray, etc. There are two important advantages of chemical activation in comparison to physical activation. One is the lower temperature in which the process is accomplished. The other is that the global yield of the chemical activation tends to be greater since burn off char is not required. Among the numerous dehydrating agents, sulphuric acid in particular is the widely used chemical agent in the preparation of activated carbon.

The aim of this investigation was to determine the adsorption behavior of lead (II) on activated carbon developed from Apricot stone. The effects of the initial lead concentration, temperature and pH on adsorption were investigated systematically, and multilinear mathematical model representing the adsorption behavior of the lead (II) was proposed within the experimental conditions for the activated carbon samples. Most of the experiments in this study were performed by using distilled water containing different lead concentrations. The thermodynamic parameters such as ΔG , ΔH , and ΔS from the adsorption measurements in the present study are very useful in elucidating the nature of adsorption.

2 Method of experiment

Batch reactor tests were carried out to study the effect of various operating variables on the adsorption rate. Adsorption of Pb(II) on developed activated carbon was conducted containing different weighted amounts of each sample with 100 ml solution of 10, 30, 50, 80 and 100 mg/l of initial concentration. Analytical grades of $\text{Pb}(\text{NO}_3)_2$, HCl and NaOH were purchased from Merck (India) Lt. Lead ions were prepared by dissolving its corresponding nitrate salt in deionized water. The pH of solutions was adjusted with 0.1 N HCl and NaOH. All the experiments were conducted five times and the average values have been reported. Also, blank experiments were conducted to ensure that no adsorption was taking place on the walls of the apparatus used.

2.1 Adsorption experiments

Batch experiments included: the kinetic studies, pH effect and adsorption isotherms. Adsorption experiments for the kinetic study were conducted as follow: Batch adsorption experiments were carried out in a series of stoppered reagent bottles. A weighed amount (0.1 g) of adsorbent was introduced into reagent bottles (200 ml) containing various concentrations with 100 ml aqueous solutions of copper or cadmium. The solution pH was adjusted to the desired value by adding HCl or NaOH. Then, the bottles were shaken at room temperature (20 ± 2 °C) using a mechanical shaker for a prescribed time to attain the equilibrium. The solutions were filtered and the concentrations of metal ions were determined by AAS method. The effects of concentration (10–100 mg/l), contact time (2–180 min), solution pH (1.5–9) and adsorption dose (0.2–2 g) were studied. Blank solutions were treated similarly (without adsorbent) and the recorded concentration by the end of each operation was taken as the initial one.

3 Results and discussions

3.1 Characteristics of the adsorbent

The bulk density of the adsorbent was determined with a densitometer. The Pore volume (cm^3g^{-1}), bulk density, surface area and iodine number of ASAC were determined as 0.192 g/cm^3 , 0.81, 393.2 m^2/g and 154 mg/g, respectively. The zero point charge (pH_{ZPC}) was measured as 5.1. The FT-IR spectrum of the activated carbon ASAC before the adsorption process was recorded in the range 4000–400 cm^{-1} on a IRPrestige-21 spectrophotometer. Adsorption band at 3387 cm^{-1} indicates the presence of OH group, which was probably attributed to adsorbed water on the carbon. The bands appearing at 1315 and 1759 cm^{-1} are ascribed to the formation of oxygen functional groups like a highly conjugated C=O stretching in carboxylic groups, and caboxylate moieties. at 2482 cm^{-1} was corresponds to –N–H stretching.

3.2 Effect of agitation time and initial concentration on Pb (II) adsorption

Fig.1 shows the effect of agitation time and Pb(II) concentration on removal. This figure shows that the adsorption of Pb (II) increases with an increase in agitation time and attains equilibrium in 10 min for 10 mg l⁻¹ Pb(II) and 20 min for 30, 50, 80 and 100 mg l⁻¹ Pb(II). It is very clear from the results that the agitation time required for maximum uptake of metal ions by carbon was dependent on the initial Pb(II) concentration. This result is interesting because equilibrium time is one of the parameters for economical wastewater treatment plant applications. According to these results, the agitation time was fixed at 5 h for the rest of the batch experiments to make sure that equilibrium was reached. It also shows that increases in metal ion concentration increased the amount of metal ion uptake per unit weight of carbon (mg/g).

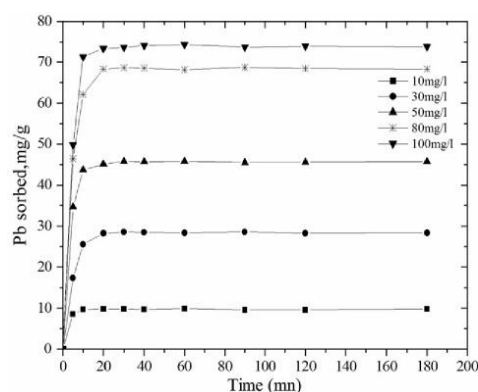


Figure 1. Effect of contact time for the adsorption of lead ions onto activated carbon from *Apricote stone* at T 20°C, pH 6, S/L 1g/1L.

3.3 Effect of adsorbent concentrations

Fig.2 shows the effect of adsorbent concentration on the % removed at equilibrium conditions. It was observed that the amount of lead adsorbed varied with varying adsorbent concentration. The amount of lead adsorbed increases with an increase in adsorbent concentration from 0.2 to 2g. The percentage of lead removed was increased from 86.51 to 98.13% for an increase in activated carbon concentration from 0.2 to 2g.

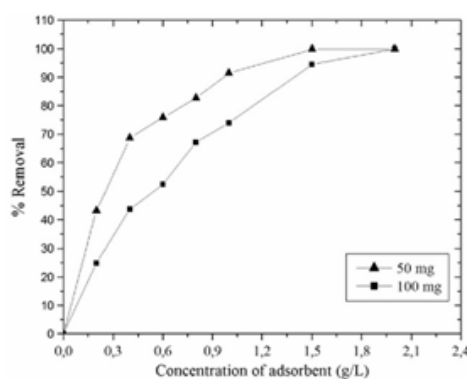


Figure.2 Effect of adsorbent concentration for the adsorption of lead ions onto activated carbon from *Apricote stone* at 20°C, C₀=50 mg/l and 100 mg/l, pH = 6.

This is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent. For the complete removal of Pb (II) from 1000 ml of 50 and 100 mg l⁻¹ a maximum carbon concentration of 1.5 and 2.0 g l⁻¹, respectively, is required

3.4 Effect of particle size on Pb (II) removal

The percent removal of Pb (II) decreased with increasing adsorbent particle size. The percent removal for particle size ranges of 750-500, 500-250 μm and 250 -125 μm were 76.47%, 81.65% and 86.74%, respectively. The adsorption of Pb (II) attains equilibrium in 120, 90 and 60 min for particle size ranges of 750-500, 500-250 μm , and 250 -125 μm with surface areas 212, 278 and 393 m^2g^{-1} , respectively. This is because adsorption is a surface phenomenon, so the smaller adsorbent particle size offers a comparatively larger and more accessible surface area and hence, higher adsorption occurs at equilibrium.

3.5 Effect of pH

The pH of the solution has a significant impact on the uptake of heavy metals, since it determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate. In order to establish the effect of pH on the biosorption of lead (II) ion, the batch equilibrium studies at different pH values were carried out in the range of 1.5–9 (Fig. 3). Fig.3 shows that heavy metal-removal capacity increased very sharply with an increase in pH from 4.5 to 7 and significantly decreased by reducing the pH values and slightly decreased at higher pH values. According to Low et al. [01], little sorption at lower pH could be ascribed to the hydrogen ions competing with metal ions for sorption sites. This means that at higher H^+ concentration, the biosorbent surface becomes more positively charged, thus, reducing the attraction between adsorbent and metal ions. In contrast as the pH increases, more negatively charged surface become available, thus, facilitating greater metal uptake [02]. At a higher pH, the lead ion precipitated as their hydroxides which decreased the rate of adsorption and subsequently the percent removal of metal ion.

3.6 Macro and micro-pore diffusion

The adsorption mechanism of a sorbate onto the adsorbent follows three steps viz. film diffusion, pore diffusion and intra-particle transport. The slowest of the three steps controls the overall rate of the process. Generally, pore diffusion and intra-particle diffusion are often rate-limiting in a batch reactor, which for a continuous flow system film diffusion is more likely the rate limiting step [03]. The adsorption rate parameter which controls the batch process for most of the contact time is the intra-particle diffusion. The possibility of intra-particle diffusion resistance affecting adsorption was explored by using the intra-particle diffusion model as:

$$q_t = K_{id} t^{1/2} + I$$

Where K_{id} is the intra-particle diffusion rate constant. A plot of q_t versus $t^{1/2}$ are presented for all adsorbents. The deviation of straight lines from the origin, as shown in the figure, may be because of the difference between the rate of mass transfer in the initial and final steps of adsorption.

3.7 Thermodynamic Parameters

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Gibb's free energy change, ΔG° , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative value. The thermodynamic parameters of ΔG° , enthalpy change, ΔH° , and entropy change, ΔS° , for the adsorption processes are calculated using the following equations [04]:

$$\Delta G^\circ = -RT \ln K \quad (01)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (02)$$

ΔH° and ΔS° values were obtained from the slope and intercept of this plot, respectively. ΔG° , ΔH° and ΔS° were obtained from the Eqs. (1) and (2) and are given in Table 1. Negative value of ΔG° indicate the feasibility of the process and spontaneous nature of the adsorption with a high preference of Pb (II) by . Positive value of ΔH° indicates the endothermic nature of the process, while positive value of ΔS° reflects the increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbents towards Pb(II) ions. The positive ΔS° value also corresponds to an increase in the degree of freedom of the adsorbed species [05].

Table. 1 Values of thermodynamic parameters for the adsorption of Pb (II) on ASC,

$T(K)$	$-\Delta G^{\circ} (kJ mol^{-1})$	$\Delta H^{\circ} (kJ mol^{-1})$	$\Delta S^{\circ} (J mol^{-1} K^{-1})$
293	13.978	17.324	107
313	13.721		
333	12.986		

4. Conclusion

The present study shows that activated carbon prepared from chemically treated apricot stone is an effective adsorbent for the removal of lead ion from aqueous solutions. The removal efficiency was controlled by solution pH, adsorbent concentration and agitation times, initial ion concentration and particle size. Adsorption data fitted well with the Langmuir and Freundlich models. However, Langmuir isotherm displayed a better fitting model than Freundlich isotherm because of the higher correlation coefficient that the former exhibited. The maximal adsorption capacity (q_{max}) of lead on *Apricot stone* was calculated as 21.38 mg g⁻¹. The adsorption process was found to be endothermic, spontaneous and can be explained with the pseudo-second-order type kinetic model. In addition to these results, it can be said that adsorption process is complex involves more than one mechanism. The results of this study suggest that activated carbon prepared from olive stone can be used as an adsorbent for removing of Cd(II) ions from water and wastewater.

References

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