Adsorption Studies of Pb (II) Ions by Using Modified Bengal Gram Husk (*Cicer Aritinum*): Thermodynamics And Kinetics

DEEPA PANHEKAR

Department of Chemistry, Dr. Ambedkar College, Deekshabhoomi, Nagpur, 440010, India
Corresponding author: deepa.panhekar@gmail.com

Abstract

Adsorption is a promising technology in the removal of toxic metal ions from waste waters. This work is aimed towards providing ecofriendly and cost effective waste management method by making use of natural resources. The study describes the use of bengal gram (husk) as potential raw material for the removal of Pb (II) from aqueous solutions. Adsorption capacity was tested by studying various factors such adsorbent dosage, initial concentration of Pb (II) and contact time. Adsorption kinetics and thermodynamic parameters such as enthalpy, entropy and free energy were determined.

Keywords: Adsorption

Introduction

The ground water contaminated by heavy metals from industrial effluents and their persistence in food chain has been of major concern as it is a serious threat to aquatic culture including fisheries. The ever increasing demand for water of high quality has caused considerable attention to be focused towards recovery and reuse of wastewater[1]. Awareness encouragement of pollutant toxicity has forced industries and municipal authorities to treat wastewater before discharging to the natural water bodies. Therefore, to remove toxic heavy metal from contaminated wastewater is one of the most important environmental and economic issues today.

Lead is one of the most toxic heavy metal that is attracting wide attention of environmentalists. The sources of lead release into the environment by waste streams are acid metal plating, fishing, ammunition, battery manufacturing, tetraethyl lead manufacturing, glass industries, printing, painting, dying and other industries. In human, lead poisoning causes problems to the kidney, nervous system, reproductive system, liver and brain. Severe exposure to lead leads to sterility, abortion, stillbirths and neo natal deaths2. Lead is known to cause mental retardations, it interferes with normal cellular metabolism and it reduces hemoglobin production which is necessary for oxygen transport3. There are number of various methods used to minimize for removal of metal ions from aqueous solutions, such as reduction, ion exchange, electro dialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, adsorption & electro flotation4 etc. Natural adsorbents are gaining importance due to their low cost and environment friendly nature.

This study was undertaken to explore the efficiency of bengal gram husk (Cicer arientinum) as adsorbent for the removal of lead from aqueous solutions. Batch experiment studies were carried out to investigate the effect of various parameters like weight of adsorbent, initial metal ion concentration & contact time. Equilibrium studies were performed by analyzing the Langmuir and Freundlich isotherms. The kinetics and thermodynamic parameters were evaluated.

Material and Methods

All the chemicals used were of analytical reagent grade. Filtrates were analyzed for lead concentrations on atomic absorption spectrophotometer.

Activation of adsorbent

250 ml H2SO4 and 62.5 ml of 39% HCHO was taken in a 500 ml beaker and 25g of finely ground powder of bengal gram husk was added to it. The solution was kept in a water bath at 600 for 6 hrs and the whole mixture was occasionally stirred. The mixture was filtered and the residue was washed with distilled water several times to remove traces of acid. The residue was then dried for 24 hrs at 500C in a vacuum oven and used as adsorbent for the removal of metal ions.

Batch Adsorption Studies

To study the effect of weight of bengal gram husk on the Pb2+ ions adsorption, different amounts of adsorbent (0.05, 0.2, 0.3g) were added into a 250 ml conical flask containing a definite volume (50 ml) of fixed initial concentration (100 ppm) of Pb2+ions solution . The pH of the solution was 4.5. The mixtures were agitated at 100 rpm for 5 hr. and then filtered. The filtrate containing the residual concentration of lead was determined spectrophotometrically5.

Effect of initial concentration was studied by carrying out batch experiments on 50 ml of different concentration of Pb2+ ion solution (100, 250, 500 ppm) in a 250ml conical flask containing 0.3 g of bengal gram husk adsorbent. The mixtures were agitated at 100 rpm for 5 hr.

Adsorption experiments were performed at different temperatures of 300C & 400C for the initial lead concentrations with previous reaction conditions to know the effect of temperature. Effect of contact time was studied by agitating 50 ml of 100 ppm lead solution and 0.3 g of adsorbent for different time intervals. Studies on adsorption isotherm (Langmuir and Freundlich), thermodynamic and kinetic parameters were conducted as per literature6-9.

Results and Discussion

Effect of amount of adsorbent, initial concentration and contact time

The results showed that as the adsorbent dosage increased, the percentage of adsorbed Pb (II) also increased. The removal of Pb(II) ion is found to increase with decrease in initial concentration. Experiments on effect of contact time showed that the rate of percent lead removal is higher at the beginning. This is probably due to larger surface area of the bengal gram husk being available at the

beginning for the adsorption of Pb2+ ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles.

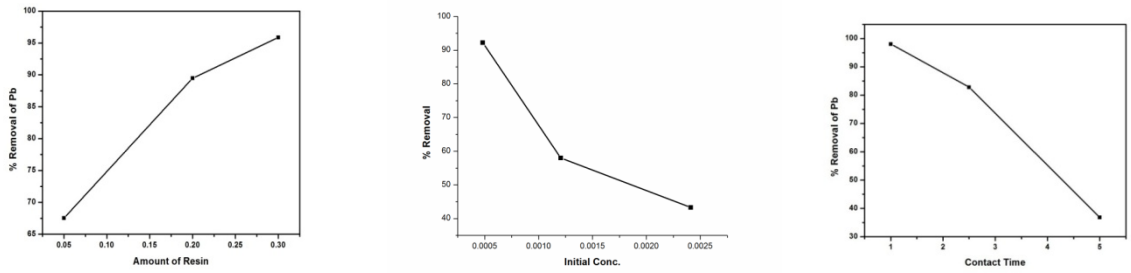

Fig 1, 2 & 3: Effect of amount of adsorbent, initial conc. and contact time on lead at 300 min.

The Langmuir isotherm

The Langmuir adsorption equilibrium isotherm of lead onto activated bengal gram husk at 300C is presented in Fig. 4. Regression analysis reveals that the Langmuir model fits the Experimental data well with correlation factor higher than 0.98. A plot of 1/□□ versus 1/□ □ was found to be a straight line with 1/□ m, KL as intercept and slope, and hence KL can be calculated. Langmuir constants KL, and the correlation coefficient □ 2 are given in Table 1.

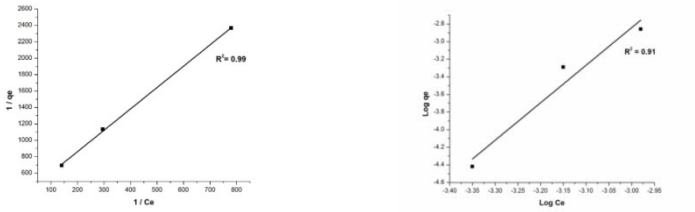

Fig 4 & 5: Langmuir and Freundlich adsorption isotherm for lead on bengal gram husk at 300C.

The Freundlich isotherm:

The Freundlich adsorption equilibrium isotherm of lead onto activated bengal gram husk at 300C (Fig: 5) is studied. Plot of Log qe versus Log Ce is found to be a straight line. The magnitudes of Kf and n show easy separation of lead ions from the aqueous solution and indicate favourable adsorption. The intercept Kf value is an indication of the adsorption capacity of the adsorbent; the slope 1/n indicates the effect of concentration on the adsorption capacity and represents adsorption intensity. Both the Langmuir and Freundlich isotherm parameters for the adsorption of lead onto activated bengal gram husk and the correlation coefficients are shown in Table 1. The correlation coefficients of the Freundlich model were higher than that of Langmuir model suggesting towards monolayer adsorption process.

Table 1. Constants for Adsorption isotherm

Langmuir Isotherm		Freundlich Isotherm		Temperature
KL	R2	Kf	R2	
-0.1102	0.99	-7.345	0.91	3030K

Since the value of R2 is nearer to 1 which indicates that the respective equation better fits the Experimental data. The observations confirm the capacity of bengal gram husk to adsorb lead.

Adsorption Kinetics:

The kinetic studies of Pb (II) adsorption on activated bengal gram husk was carried out using the pseudo-first order and pseudo-second-order models on Experimental data. The effect of initial lead concentrations was investigated to find the best fit kinetic model. The kinetic constants and correlation coefficients of pseudo first-order kinetic model fail to give straight line. Therefore, pseudo second-order kinetic model is preferred.

The pseudo-second-order kinetic model was applied by plotting t/qt versus t, and this model gave high values of regression correlation coefficient as seen in Figure 6. This implies that the mechanism of adsorption of Pb(II) ion on the activated bengal gram husk follows the pseudo second-order kinetics.

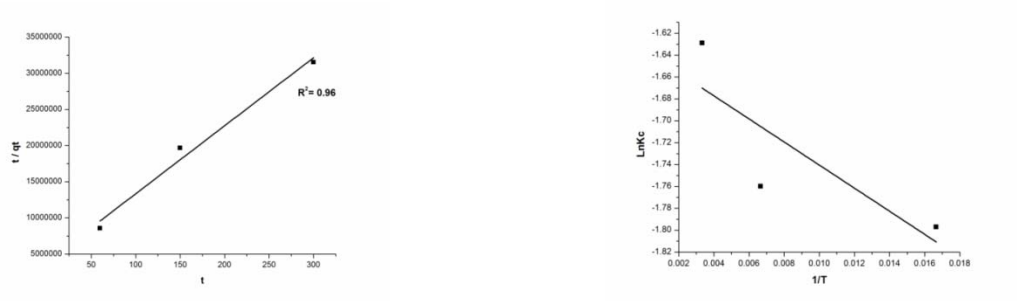

Fig 6 & 7: Pseudo-second order kinetics and Thermodynamic parameter for adsorption of Pb(II)

This is compared with the kinetic studies of Ni (II) adsorption of coconut husk conducted by Kehind10 where regression coefficients showed high values for the pseudo-second-order kinetic model (R2 = 0.96) indicating its applicability to adsorption. Both factors indicate that the adsorption of metal ions followed the second-order kinetic model, indicating that the rate-limiting step was a chemical adsorption process between the metal ion and activated bengal gram husk11. It was observed that the adsorption rate follows pseudo second-order kinetics.

Thermodynamic Studies:

A plot of lnKc versus 1/T was found to be linear (Fig 7), ΔH and ΔS were determined from the slope and intercept of the plot, respectively (Table 2). Positive ΔG indicates that the adsorption process of lead ions by activated bengal gram husk can be enhanced at elevated temperature. The negative values of change in

enthalpy (ΔH) suggest the exothermic nature of adsorption and the negative values of change in entropy (ΔS) can be used to describe the randomness at the solid solution interface during the adsorption of Pb(II) ion on bengal gram husk .

Table 2: Thermodynamic parameters for the adsorption of Pb(II) ions onto activated bengal gram husk.

Initial Pb(II) conc.(mg/L)	ΔG(kJ/mo	ΔH(kJ/mo	ΔS(kJ/mol	Temp.(k
0.00120656	499.65	-10.54	-1.63	303

Conclusion

Equilibrium, kinetic and thermodynamic studies were conducted for the adsorption of Pb2+ ions from aqueous solution onto activated bengal gram husk. The equilibrium data have been analyzed using Langmuir, Freundlich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Freundlich isotherm was demonstrated to provide the best correlation for the sorption of Pb2+ ions onto activated adsorbent. The suitability of the second-order equations kinetic model for the sorption of Pb2+ions onto activated bengal gram husk is also discussed. The pseudo second-order kinetic mode agrees very well with the dynamical behavior for the adsorption of Pb2+ ions onto adsorbent for different initial Pb2+ ions concentrations over the whole range studied. It may be concluded that activated bengal gram husk may be used as a low-cost, natural and abundant source for the removal of Pb2+ ions from the wastewater.

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