

Isotherm Studies for Heavy Metal Adsorption on Rice Husk

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Abstract: A number of methods for heavy metal removal from waste water have been used, but most have several disadvantages, such as continuous input of chemicals, high cost, toxic sludge generation or incomplete metal removal. The use of rice husk not only provides a less costly sorbent to activated carbon or synthetic ion-exchanger as it is cheap, but also available in abundant quantity. Various modifications on rice husk have been reported in order to enhance sorption capacities for metal ions and other pollutants. The study reported in this paper deals with the adsorption of heavy metals such as lead (Pb), copper (Cu), zinc (Zn) and manganese (Mn) on the low cost adsorbents such as Rice Husk (RH) and Phosphate treated Rice Husk (PRH) from the synthetic solutions. Batch studies were conducted to find out the optimum dose of adsorbent, optimal pH and contact time for individual metal solution, both with RH and PRH. It was found that the equilibrium was attained after 30 min for Pb, 40 min for Cu and 50 min both for Zn and Mn and the maximum removal efficiency was attained at a pH of 6 for Pb, pH of 7 for Zn, Cu and Mn for the single metal solutions. The adsorption data could be fitted with Freundlich, Langmuir isotherm equation to find the characteristic parameters. It was found that linear form of Freundlich isotherm seems to produce a better model than linear form of Langmuir equation.

Key words: Heavy metal removal, adsorption study, batch experiments, isotherm.

Introduction

Heavy metals are nowadays among the most important pollutants in source and treated water, and are becoming a severe public health problem, can be toxic to aquatic life and cause natural waters to be unsuitable as potable water sources (Bayat, 2002). Heavy metal contamination can also be found in landfills, from which metals can leach for very long periods of time (Chen, 1996; Ringqvist et al., 2002). Usually these heavy metals are found at moderate concentration levels in municipal landfill leachate (Abu-Rukah and Al-Kofahi, 2001). Due to migration of leachates, soils have been contaminated with heavy metals such as lead, copper, zinc, manganese, chromium and cadmium. The presence of heavy metals in soils leads to serious problems because they cannot be biodegraded (Hong et al., 2002). Leaching of these heavy

metals during initial degradation of organic solid waste can influence the groundwater quality and may enter the food chain causing adverse health effects. Heavy metals are toxic because they are present as ions in an aqueous system and can be readily absorbed into the human body. Even a very small amount can cause severe physiological or neurological damage (Wong et al., 2003).

Conventional technologies for the removal and recovery of heavy metals from wastewater include chemical precipitation, ion exchange, membrane separation, adsorption into activated carbon and electrolytic methods. However, all these techniques have their inherent advantages and limitations in application. Most of these methods suffer from some drawbacks such as high capital or high operational cost or disposal of resulting sludge. In the last few years, adsorption has been shown to be an alternative method for removing

dissolved metal ions from liquid wastes (Bayat, 2002). In recent years interest has been directed to the investigation of low cost materials such as agricultural by-products, waste materials (Namasivayam and Yamuna, 1995), biosorbents, industrial wastes like slag (Ćurković et al., 2001) and clay materials as sorbents for the removal of heavy metal. These materials, including peanut shells, rice husk, wheat straw, apple residues, sawdust, fungal biomass and seaweed have the advantage of being inexpensive and readily available. Applications of these materials could result in tremendous cost saving and waste minimization (Wong et al., 2003).

Rice husk contains lots of silica and organic compounds such as cellulose, hemicellulose and lignin. It was reported to be good sorbent for a variety of metallic cations and basic dyes (Low and Lee, 1997). In recent years, attention has been focussed on the utilization of unmodified or modified rice husk as a sorbent for the removal of pollutants. Unmodified rice husk has been evaluated for their ability to bind metal ions. Various modifications on rice husk have been reported in order to enhance sorption capacities for metal ions and other pollutants (Low and Lee, 1997).

In this study, an effort has been made to study the effect of adsorption of heavy metals by low cost adsorbent and its effectiveness was evaluated for the removal of different heavy metals (lead, copper, zinc and manganese). Removal efficiency of individual metals (prepared synthetically) was studied by using rice husk with and without treatment through laboratory experiments.

Materials and Methods

Reagents

All chemicals used were of analytical grade. Stock solutions of 10 mg/l was prepared for Pb (II), Cu (II), Zn (II) and Mn (II) using lead nitrate ($\text{Pb}(\text{NO}_3)_2$), copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), zinc chloride (ZnCl_2) and manganese sulphate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) respectively.

Preparation of Adsorbent

Rice husk was obtained from local rice mill and sieved through 1 mm sieve. Before pretreatment, it was washed with distilled water for several times to remove the impurities.

Phosphate Treated Rice Husk

After complete washing with distilled water, it was dried at 60°C for 2 h and preserved at room temperature. 45 g

of dried husk was treated with 900 ml of 1.0 M K_2HPO_4 for 24 h. The mixture was filtered and washed several times with distilled water to remove the excess phosphate from the treated husk. The resultant adsorbent was finally dried at 70°C for 2 h and preserved at room temperature.

Batch Sorption Studies

Batch studies were conducted at room temperature with two adsorbents such as rice husk (RH) and phosphate treated rice husk (PRH). A total quantity of 20 ml of the synthetic single metal solution was used each time for the batch studies. Kinetic study was conducted with a 2 g/l of dose of adsorbent and the samples were shaken at an agitation rate of 150 rpm. The samples were taken out at 5, 10, 20, 30, 40, 50, 60, 120, 180 and 240 minutes. The sorbent solution mixtures were then centrifuged at 3000 rpm for five minutes and the supernatant was analyzed for the metal concentration in the AAS. The removal efficiencies with respect to the time were calculated. For determining the optimum dose of adsorbent, the quantity of RH and PRH were varied from 1 to 25 g/l and 0.5 to 12 g/l respectively for 20 ml of the synthetic single metal solution taken into conical flasks and the samples were shaken at an agitation rate of 150 rpm for 1 hr at room temperature. For determining the optimum pH corresponding to the maximum removal efficiency, the pH of the synthetic single metal solution was adjusted to 2-10 using 0.01N and 1N HCl and NaOH after adding the optimized dose of adsorbent for the 20 ml of sample taken into the conical flasks.

Adsorption Isotherm

Experimental isotherm are useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application, for selection of the most appropriate adsorbent, and for preliminary determination of adsorbent dosage requirements. Moreover, the isotherm plays an important role in the predictive modelling procedures for analysis and design of sorption systems. The Langmuir and Freundlich isotherms are most frequently used to represent the data of sorption from solution.

Langmuir Isotherm

The simplest proposed model for characterizing adsorption is the Langmuir isotherm. The Langmuir isotherm assumes that each unit of surface area consists of "n" sites, which can adsorb one molecule, and all of the sites are energetically equivalent. Surface contains

uniform energies of adsorption. Maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface. This model is an adequate approximation for uniform surfaces. However, it is inaccurate for inorganic solids commonly used in catalytic materials. In addition, the model does not account for the interaction of adsorbed species and multilayer adsorbate growth.

The Langmuir isotherm is developed by assuming that a fixed number of adsorption sites are available, and that the adsorption is reversible. The Langmuir isotherm may be used when the adsorbent surface is homogeneous. The Langmuir isotherm is expressed as Eq. (1)

$$q_e = \frac{X}{M} = \frac{abC}{1 + aC} \quad (1)$$

where a = constant that increases with increasing molecular size and b = the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent).

The above equation can be recast in a linear form as Eq. (2)

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{ab} \frac{1}{C} \quad (2)$$

Freundlich Isotherm (Van Bemmelen Equation)

The Freundlich isotherm is more accurate by considering an exponential distribution of enthalpies for low coverage of adsorbed species. The Freundlich isotherm is an improvement over the Langmuir isotherm by including physical adsorption of species. This equation is a special case for heterogeneous surface energies. The Freundlich equation is an empirical equation that is very useful as it accurately describes much adsorption data. The Freundlich isotherm is expressed as Eq. (3).

$$q_e = \frac{X}{M} = kC^{1/n} \quad (3)$$

where X = weight of substance adsorbed in mg, M = weight of adsorbent in g, C = concentration remaining in solution mg/l, and k, n = constants depending on temperature, the adsorbent, and the substance to be adsorbed.

The above equation can be recast in a linear form as Eq. (4).

$$\log q_e = \log k + \frac{1}{n} \times \log C \quad (4)$$

The coefficients k and n can be estimated from slopes and by substituting values from a line fitted to a graph of $\log (X/M)$ versus $\log C$. Each of these isotherms has two constants in their general forms (Rao and Bhole, 2001). It includes

- Adsorption capacity: b of Langmuir equation and k of Freundlich equation
- Energy of adsorption: a of Langmuir equation
- Intensity of adsorption: $(1/n)$ of Freundlich equation

The constants a and k are used to estimate the enthalpy of adsorption. A smaller value of $(1/n)$ indicates a stronger bond between adsorbate and adsorbent, while a higher value for k indicates that rate of adsorbate removal is high. Hence it should be noted that the isotherm constants are important in understanding the adsorption mechanism and their subsequent application for prediction of some important design parameters. The adsorption data from the batch experimental studies are fitted to Langmuir and Freundlich isotherms.

Results and Discussion

From the experiments conducted in the laboratory for all the individual synthetic heavy metal ion solutions, the variations of removal efficiencies with respect to time, dose of adsorbent and pH were plotted and are discussed below.

Kinetic Study

Kinetic study was conducted for each individual metal solution. The results from the analysis are shown in Figure 1.

From Figure 1, similar trend of the variation can be observed, with the RH as well as with PRH. It can also be observed that the removal of metal ions was increasing with increase in contact time. The equilibrium time obtained is 30 min for Pb, 40 min for Cu and 50 min both for Zn and Mn.

Optimization of Adsorbent Dosage

The dose of RH was varied from 0.2 to 2 g/l for Pb, 2 to 10 g/l for Cu, 1 to 10 g/l for Zn and 2 to 22 g/l for Mn and the dose of PRH was varied from 0.2 to 2 g/l for Pb, 2 to 11 g/l for Cu, 1 to 10 g/l for Zn and 1 to 12 g/l for Mn for the determination of optimized dose and the removal efficiencies with respect to the adsorbent doses are shown in Figure 2.

From Figure 2(a), it can be seen that the variation of percentage removal of heavy metal was almost same for both RH and PRH. Also the optimum dose for Pb as

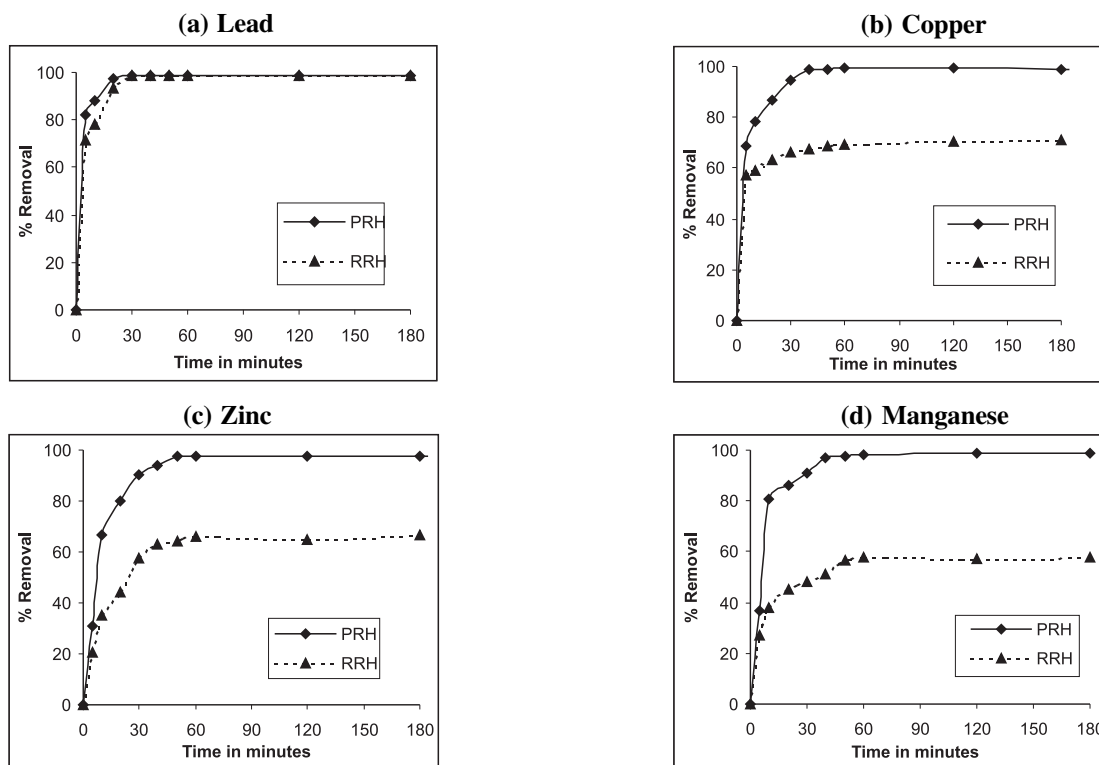


Figure 1: Results of equilibrium study for all metal ions.

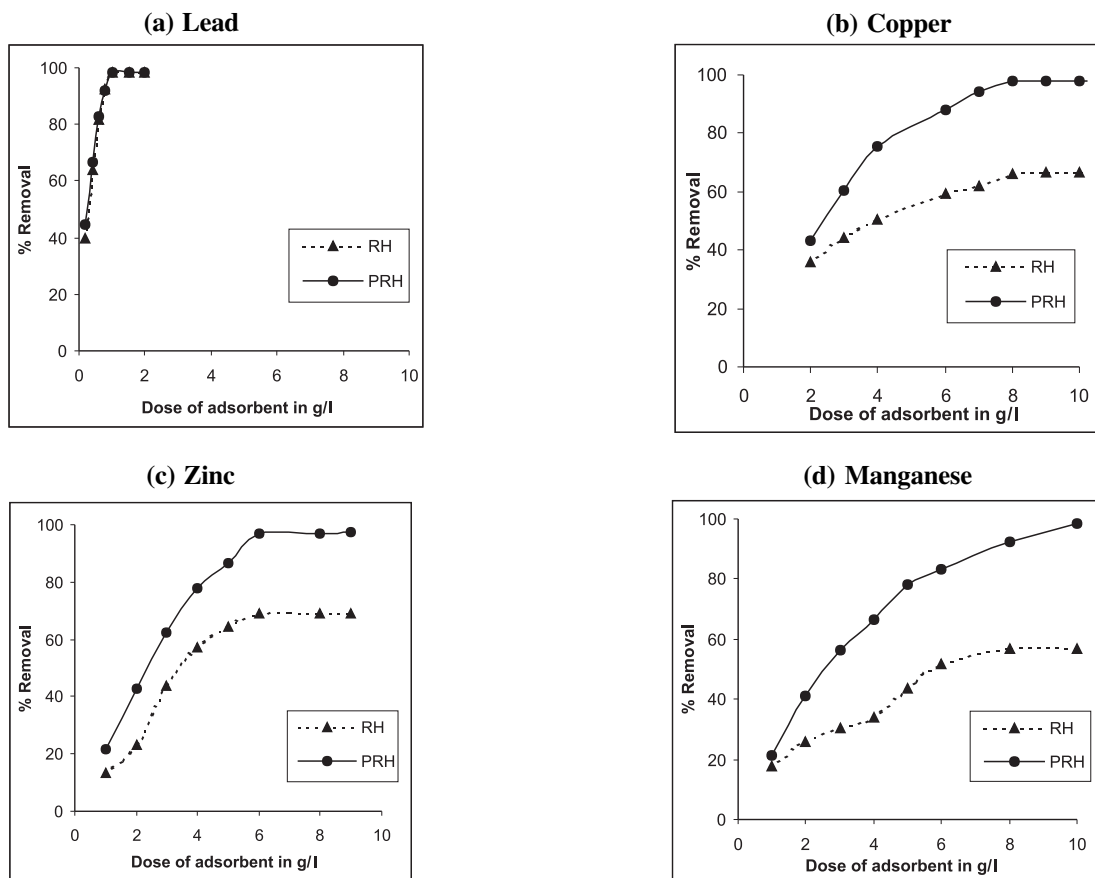


Figure 2: Variation of percentage removal with different dosage of adsorbent.

1 g/l for RH and PRH corresponding to the maximum removal efficiency of 98%. It can be observed that there is no change in the removal efficiency with treated rice husk. This is mainly due to high ionic radius of lead when compared to heavy metals such as Zn, Cu and Mn. From Figure 2 (b), it can be observed that the optimum dose for Cu removal is 8 g/l with an efficiency of 66.9% with RH and 98.6% with PRH. From Figure 2(c), the optimum doses are observed to be 8 and 6 g/l with 69 and 97% removal efficiencies. Similarly from Figure 2(d) for the manganese 15 g/l was observed as the optimum dose of RH but it is reduced to 10 g/l with PRH with the increase in the efficiency from 56 to 98%. The removal efficiency is increasing initially with the increase in dose of the adsorbent and then it remains constant. This is due to the saturation of the adsorbent sites by the adsorption of the metal ions. Optimum dosage for heavy metals such as Pb, Cu, Zn and Mn with PRH is comparatively less than that of RH.

Optimization of pH

Optimum pH for the maximum removal efficiency was carried out with the optimized dose of RH and PRH. The results of the analysis are shown in Figure 3.

From Figure 3, it can be observed that the uptake of metals is increasing with increasing pH. The optimum pH was found to be 6 for Pb and 7 for Cu, Zn and Mn. The minimum adsorption at low pH may be due to high concentration and high mobility of H^+ ions, and due to this reason the hydrogen ions are preferentially adsorbed compared to heavy metal ions.

Isotherms

The Langmuir equation is applicable to homogenous sorption where the sorption of each molecule has equal sorption activation energy (Allen et al., 2003). The adsorption isotherms such as Langmuir and Freundlich for individual heavy metals with RH and PRH are plotted from the results obtained from the experimental data and are shown in Figures 4 and 5.

From Figures 4 and 5, it can be found that there is a linear variation that indicates that the adsorption of all the metal ions can be fitted to the Freundlich isotherm, instead of the Langmuir isotherm using both RH and PRH. The sorption parameters are estimated by linear regression analysis from the experimental adsorption data for the individual heavy metals. The values of sorption parameters for all heavy metals with both the adsorbents were summarized in Table 2.

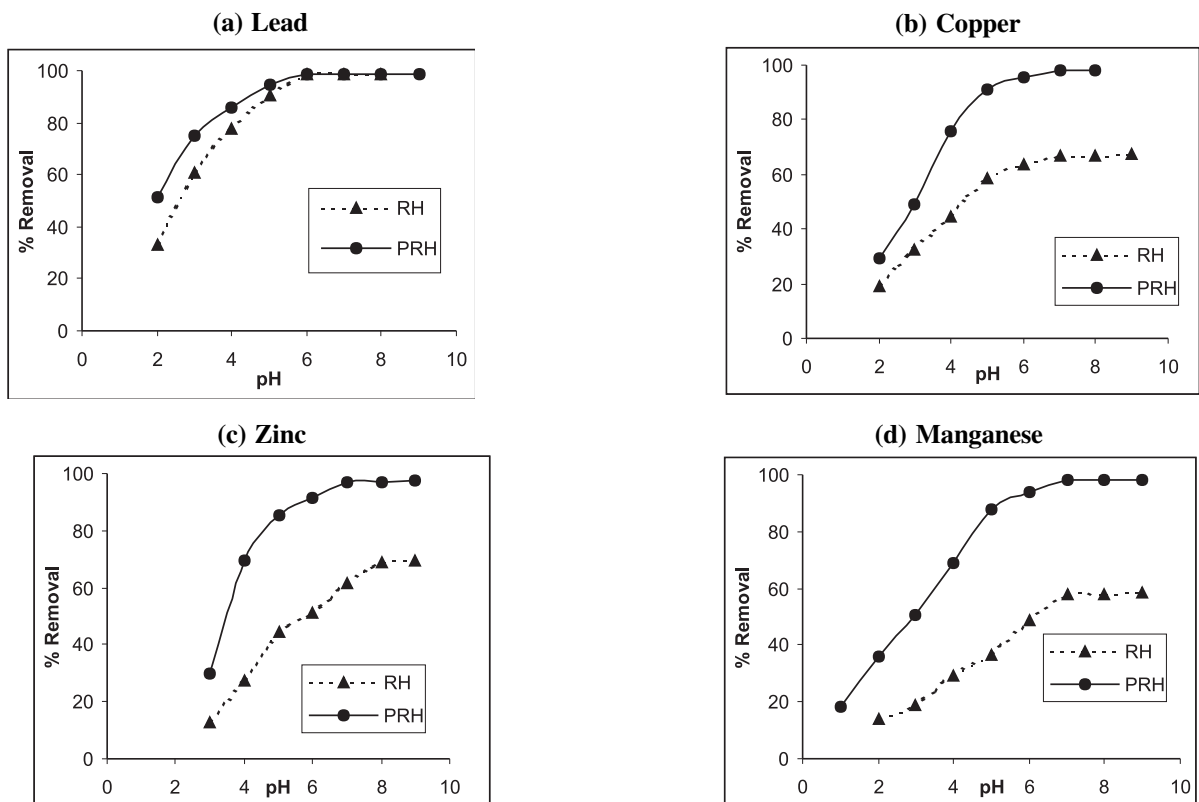
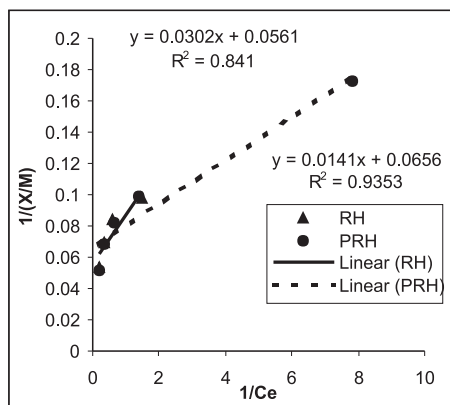
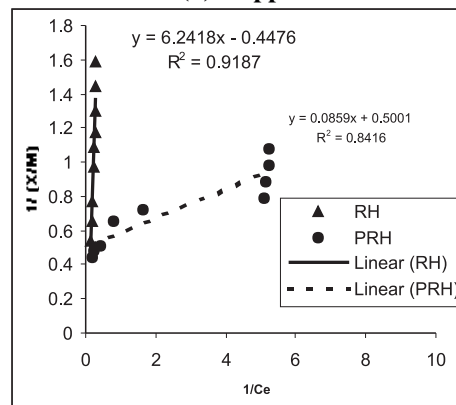


Figure 3: Results of optimization of pH for all metal ions.

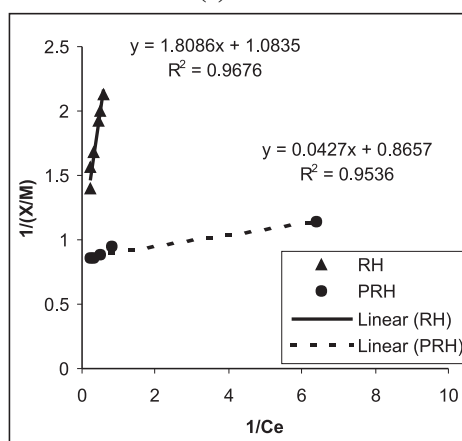
(a) Lead



(b) Copper



(c) Zinc



(d) Manganese

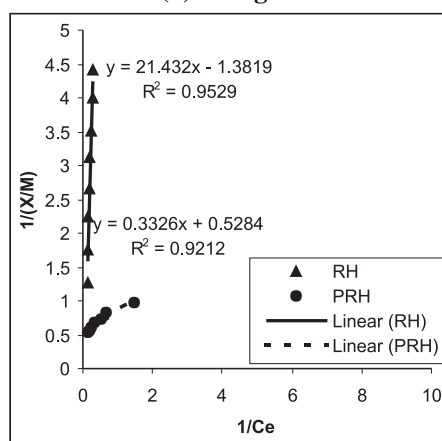
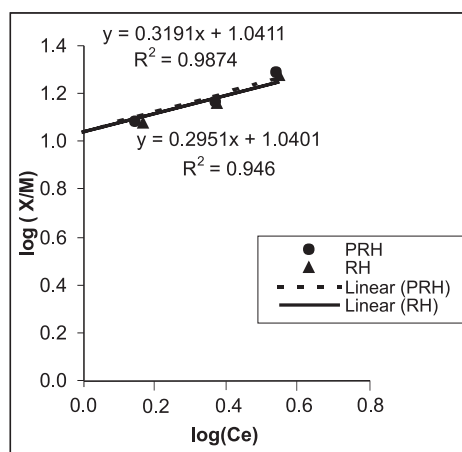
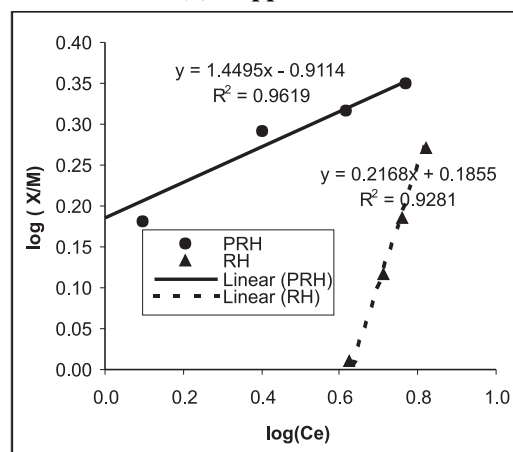


Figure 4: Langmuir isotherms for different heavy metal adsorption.

(a) Lead



(b) Copper



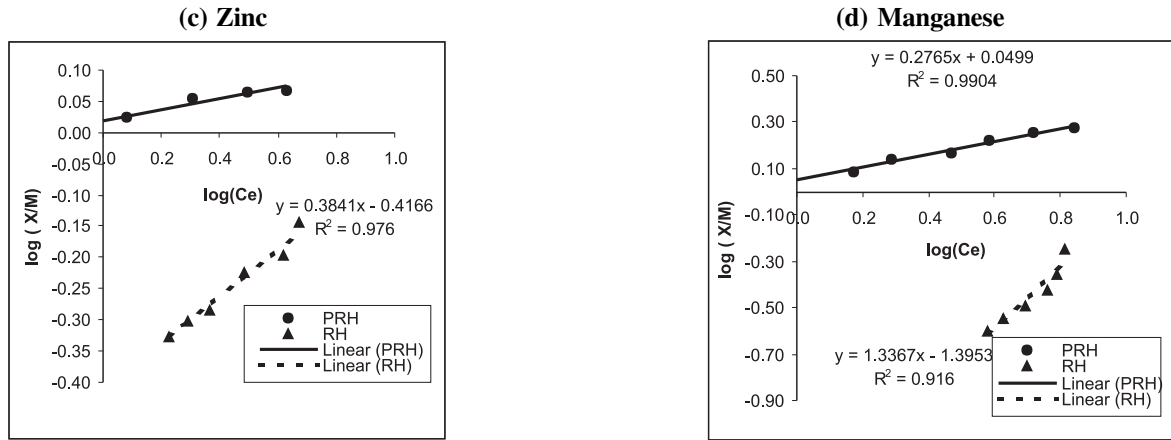


Figure 5: Freundlich isotherms for different heavy metal adsorption.

Table 2: Langmuir and Freundlich isotherm constants

Adsorbent	Heavy metal	Langmuir isotherm			Freundlich isotherm		
		<i>a</i>	<i>b</i>	<i>R</i> ²	<i>n</i>	<i>K</i>	<i>R</i> ²
RH	Pb	1.86	17.83	0.84	3.389	10.967	0.946
	Cu	0.07	2.23	0.92	0.690	0.123	0.9619
	Zn	0.6	0.92	0.97	2.603	0.383	0.976
	Mn	0.06	0.72	0.95	0.616	0.026	0.9214
PRH	Pb	4.65	18.25	0.94	3.134	10.993	0.9874
	Cu	5.82	2.72	0.84	4.613	1.533	0.9281
	Zn	20.27	1.16	0.95	11.236	1.043	0.9849
	Mn	1.59	1.89	0.92	3.617	1.122	0.9904

From Table 2, it can be found that the Freundlich adsorption isotherm gave a better fit than the Langmuir based on the correlation coefficients (R^2) value. It was observed that the R^2 value for RH is less compared to that of the PRH. This is due to the rice husk's surface modification with the phosphate treatment, and was conformed to the fractional value of $1/n$ of 0.2951 ($0 < 1/n < 1$) (Low et al., 1995). The values of ' a ' calculated from the Langmuir equations were more for the PRH when compared to RH. From the values of ' b ', the adsorption capacity of the treated rice husk was found to be more when compared to the RH for all metals. The K values estimated for the PRH samples are significantly higher than those of the untreated materials for all the heavy metals, indicating an increased adsorption capacity of the former one. The Freundlich model, which is an empirical model used to describe adsorption in aqueous systems, applies to adsorption on heterogeneous surfaces with interaction between absorbed molecules. The adequate applicability of the Freundlich equation to our data showed that the adsorbents' surface was heterogeneous. The adsorption capacity obtained for RH are lower compared to PRH except for lead. For the

remaining heavy metals the adsorption capacity is increased with treatment showing better results.

Conclusions

1. The percentage adsorption of metal ions increases with the increase in shaking time. From the kinetic study, the equilibrium time obtained is 30 min for Pb, 40 min for Cu and 50 min both for Zn and Mn.
2. From the optimization of adsorbent dosage study, it can be concluded that the percentage removal of Pb, Cu, Zn and Mn are increased with increase in the adsorbent. The optimum dose of adsorbent required for maximum efficiency with PRH is 1 g/l for Pb, 8 g/l for Cu and Zinc and 10 g/l for Mn, which is comparatively less than with RH.
3. For RH and PRH, the removal efficiency of heavy metals increases with increase in pH. The maximum removal efficiency is attained at a pH of 6 for lead and 7 for other metal ions. For further increase in pH, the metal starts precipitating out.
4. The linear variation of isotherm plots indicates that adsorption of all the metal ions fitted to the Freundlich

isotherm compared to the Langmuir isotherm with higher R^2 value.

5. Better adsorption with PRH when compared to RH, and was conformed with the high K values and the values of Freundlich exponent n were greater than one for all four heavy metals confirming the adsorption of these metals onto RH. Hence the hypothesis of adsorption of heavy metals using phosphate treated rice husk as a significant mechanism of removal is confirmed by the batch adsorption test results.

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