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A Comparative Study on the Sorption Characteristics of Pb(II) and Hg(II) onto Activated Carbon

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Abstract: Biosorption equilibrium and kinetics of Pb(II) and Hg(II) on coconut shell carbon (CSC) were investigated by batch equilibration method. The effects of pH, adsorbent dosage, contact time, temperature and initial concentration of Pb(II) and Hg(II) on the activated carbon of coconut shell wastes were studied. Maximum adsorption of Pb(II) occurred at pH 4.5 and Hg(II) at pH 6. The sorptive mechanism followed the pseudo second order kinetics. The equilibrium data were analysed by Langmuir, Freundlich and Dubinin- Radushkevich isotherm models. The equilibration data fitted well with both Langmuir and Freundlich isotherm model. The Langmuir adsorption capacity for Pb(II) was greater than Hg(II). The mean free energy of adsorption calculated from Dubinin-Radushkevich (D-R) isotherm model indicated that the adsorption of metal ions was found to be by chemical ion exchange. Thermodynamic parameter showed that the sorption process of Pb(II) onto SDC was feasible, spontaneous and endothermic under studied conditions. A comparison was evaluated for the two metals.

Keywords: Hg(II) ions, Pb(II) ions, CSC, Isotherms, Kinetics.

Introduction

The presence of heavy metals in water is of great concern because of their toxicity to life forms even in small concentration. Mercury and lead are two important toxic elements found in industrial effluents causing water pollution. Pollution by mercury usually comes from industries such as chloroalkali, paint, pharmaceutical, pulp and paper[1]. Lead pollution is caused by storage batteries, lead smelting and plating industries[2].

The presence of lead in drinking water above the permissible limit of 0.05 mg/L[3] can delay the physical and mental development of children and develop high blood pressure in adults[4] whereas the presence of mercury in water in above quantity will cause damage to the central nervous system and chromosomes and will cause chest pain[5]. Because of increased environmental awareness, the development of cost effective methods for the removal of lead and mercury from aqueous solutions has gained momentum.

Adsorption by activated carbon from cheap and readily available sources like ricehusk ash[1], Ceiba pentandra hulls[6], Polymerised sawdust[7], Carica papaya[8], tea waste[9] and hazelnut husks[10] have been reported for the removal of lead and mercury from aqueous solution. The current investigation discusses the characterization of a low cost adsorbent for the removal of lead and mercury.

Coconut shell, a hard and thick bony endocarp material, is an abundantly available agricultural waste from the local coconut industry. Conversion of coconut shell into activated carbon, which can be used as an adsorbent for water purification, would add its economic value, help reduce the cost of waste disposal, and most importantly, provide a potentially inexpensive alternative to the existing commercial activated carbon.

The present study aims at investigating the feasibility of Pb(II) and Hg(II) removal from aqueous solutions by an indigenous, economically viable, coconut shell carbon as adsorbent under varied conditions.

Experimental

Coconut shells were crushed, washed with deionised water and sun dried. The activation was done by treating with concentrated sulphuric acid and held in an oven at 150 ^{0}C for 24 h. The obtained acid carbonized coconut shell was washed several times with deionised water and 5% sodium bicarbonate solution followed by deionised water again. The adsorbent was dried at 90 ^{0}C for 10 hours, powdered and then sieved into different sizes and a particle size of 90 µm was used in this study.

Stock solutions of 1000 mg/L Pb(II) and Hg(II) were prepared by dissolving lead nitrate and mercuric chloride salts (AR grade) in double distilled water. All aliquots of varying concentrations were prepared from the stock solution. 50 mL of the metal solutions of different concentrations were taken in iodine flasks of 100 mL capacity. Known amounts of the adsorbent were added into the flasks and the solutions were agitated in a mechanical shaker at preset time intervals and at desired pH environments. The spent CSC materials were separated by centrifugation and the supernatant adsorbate solutions were analyzed for the residual Pb(II) and Hg(II) concentrations spectrophotometrically by using UV Visible spectrophotometer. (Genesus 2 Thermospectronic make) employing PAR reagent (2, 4-Pyridyl azo resorcinol) and Rhodamine 6G as a complexing agent respectively.

Specifications of various studies

Isothermal, pH and kinetic studies were carried out at different initial concentrations of metal ions from 10 to 50 mg/L while maintaining the adsorbent dosage at 0.8 g/L. Temperature effect was studied with a concentration of 50 mg/L of the adsorbate at temperatures 20^0, 30^o, 40^o and 50 ^{o}C.

Results and Discussion

Effect of pH

Knowledge of the optimum pH is very important since pH affects not only the surface charge of adsorbent, but also the degree of ionization and speciation of adsorbate during reaction. The binding of metal ions to the adsorbent as a function of pH is represented in Figures 1 and 2. It is clear that the metal binding is strongly pH dependent and maximum adsorption occurs at pH 5 for lead and pH 6 for mercury. The increase in metal removal with increase in pH is due to a decrease in competition between proton and metal ions for the surface sites and by the decrease in positive surface charge. The decrease in metal removal at low pH values is due to increasing competition of protons for the same binding sites that metal can use.

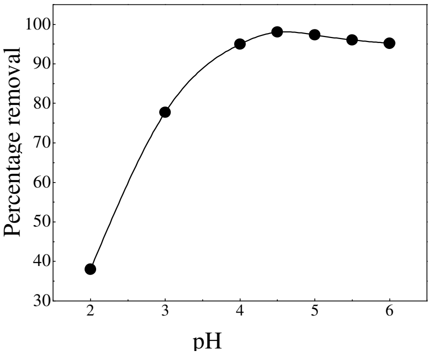

Figure 1. Effect of pH on the removal of Pb(II) ions by CSC (Initial Concentration-10 mg L^{-1}).

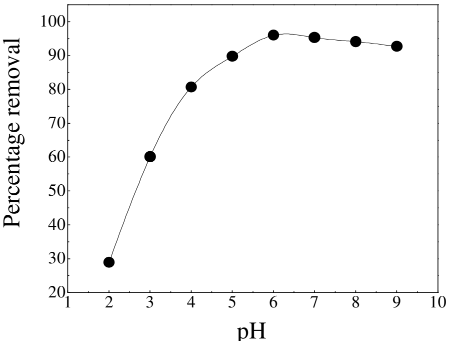

Figure 2. Effect of pH on the removal of Hg(II) ions on CSC (Initial Concentration-10 mg L^{-1}).

The Pb(II) and Hg(II) speciation diagram indicates that in the highest sorption range, the dominant species of adsorption are Pb^{2+}, $Pb(OH)^+$, Hg^{2+}, $Hg(OH)^+$[7,11]. The exchange /sorption properties of coconut shell are due to the presence of some functional groups, such as carboxylic, hydroxyl and lactone, which have high affinity for metal ions[12]. The ion exchange mechanism between H^+ ions at the CSC surface and metal ion may be illustrated as follows[13].

$$2S\text{-}COH + M^{2+} \leftrightarrow (R\text{-}CO)_2M + 2H^+$$
$$S\text{-}COH + MOH^+ \leftrightarrow RCOMOH + H^+$$

Where S is the CSC surface.

A slight decrease in adsorption was observed above pH 4.5 for lead and at pH 6, Pb(II) started precipitating as $Pb(OH)_2$. Hence pH experiments at alkaline ranges were restricted. Hg(II) adsorption at higher pH is due to electrostatic attraction between $Hg(OH)^+$ ions and the negatively charged adsorbent surface[14].

Effect of agitation time and initial concentration of metal ions on adsorption

Effect of agitation time and initial metal concentration on the removal of metal by CSC is represented in Figure 3. The uptake of metal (mg/g) increased with time and high amount of metal ions was adsorbed in the first 15-30 minutes. The attainment of equilibrium was observed at 120 minutes for Pb(II) and 90 minutes for Hg(II). The removal curves are single, smooth and continuous leading to saturation suggesting the possible monolayer coverage of metal ions on the surface of the adsorbent. The rate of metal removal is higher in the beginning due to a larger surface of the adsorbent being available for the adsorption of metals. The percent metal removal decreased from 99.08 to 62.76 for Pb(II) and 96 to53.64 as the metal concentration was increased from 10 to 50 mg/L. This trend can be attributed to the progressive increase in electrostatic interactions relative to covalent interactions, of the sites with lower affinity for metal ions with an increase in the initial concentrations[15].

Effect of adsorbent dose on adsorption

Figure 4 is indicative of the removal of metal as a function of different adsorbent dosages for an initial concentration of 10 mg/L solution. It is obvious from the Figure 4 that, the increase in the dose of adsorbent, decreases the adsorption per unit mass of adsorbent. At an initial concentration of 10 mg/L metal ions, the unit adsorption decreased from 62.41 mg/g to 12.383 mg/g for Pb(II) and 59 mg /g to 12 mg/g at an adsorbent concentration of 0.1 mg/L to 0.8 g/L. This may be due to the aggregation/agglomeration of sorbent particles at higher sorbent concentrations, which would lead to a decrease in the total surface area of the adsorbent particles available to the metal ions. As a result the adsorption capacity of the adsorbent is not fully utilized[16].

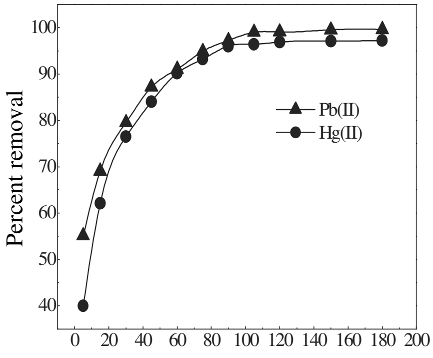

Figure 3. Effect of contact time on the removal of Pb(II) and Hg(II) ions on CSC (Initial Concentration- 10 mg L^{-1})

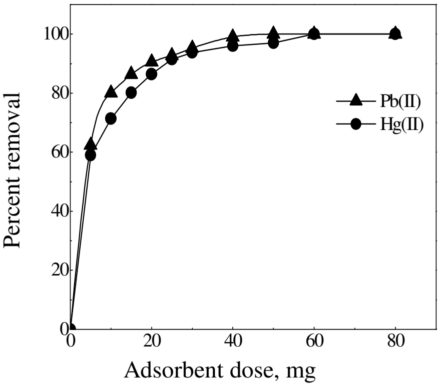

Figure 4. Effect of adsorbent dose on the removal of Pb(II) and Hg(II) ions on CSC (Initial Concentration- 10 mg L^{-1}).

Adsorption kinetics

Pseudo-second order kinetic model

The linearised form of pseudo second order equation can be written as[17]

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

where, k_2 is the rate constant of second order adsorption (g/mg/min). k_2 and q_e can be obtained from the intercept and slope of plotting t/q_t *vs.* t (Figure 5). The correlation coefficient was found to be 0.9995 for all the concentrations studied and the calculated q_e values showed that pseudo second order model describes the adsorption kinetics of both the metals. The k_2 values are shown in Table 1.

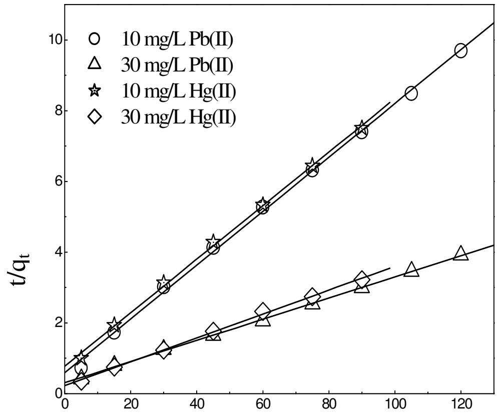

Figure 5. Pseudo second order kinetic plots for the removal of Pb(II) and Hg(II) ions on CSC.

Table 1. Pseudo second-order rate constants and thermodynamic parameters for Pb(II) and Hg(II).

	Pb(II)	Hg(II)		Pb(II)		Hg(II)	
Initial Concentration, mg /L	k_2 x10^{-3} g/mg/min	k_2 x10^{-3} g /mg/min	Temperature K	k_2 x10^{-3} g/mg/min	- ΔG kJ mol^{-1}	k_2 x10^{-3} g/mg/min	- ΔG kJ mol^{-1}
10	9.84	7.43	293	1.11	0.19	3.66	0.10
20	4.12	5.21	303	1.33	1.32	3.95	0.37
30	2.89	5.09	313	1.65	2.29	4.05	1.26
40	1.78	4.99	323	2.16	4.03	4.26	2.15
50	1.33	3.95					

Adsorption Isotherms

Langmuir isotherm

The Langmuir equation assumes that the solid surface presents a finite number of identical sites which are energetically uniform and a monolayer is formed when the solid surface reaches saturation. Langmuir equation can be described by the linearised form[18]

$$C_e / q_e \quad = 1 / Q_0 b + Ce / Q_0 \qquad (2)$$

Where C_e is the equilibrium concentration of adsorbate (mg/L), q_e is the amount adsorbed at equilibrium (mg /g), Q_o and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The linear plot of C_e/q_e versus C_e showed that the adsorption obeys Langmuir isotherm. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L which is defined by

$$R_{L\,=} = \quad 1/1{+}b\ C_0$$

Where, C_o is the initial concentration of adsorbate. R_L values between 0.02 to 0.09 for Pb(II), 0.03 to 0.133 for Hg(II) indicate favourable adsorption of metals on CSC at the concentration studied[19].

Freundlich isotherm

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface suggesting that binding sites are not equivalent and/or independent. The linearised logarithmic form of Freundlich equation is[18]:

$$qe \ = \log K_F + 1/n \log \ C_e \qquad (3\ )$$

Where K_F and n are Freundlich constants related to the sorption capacity and sorption intensity of the sorbent respectively. Linear plots of log q_e *versus* log C_e showed that the adsorption obeys Freundlich isotherm. The regression values indicate that the adsorption data for metal removal fitted well within the Langmuir and the Freundlich isothermal plots for the concentration studied.

Dubinin- Radushkevich (D-R) isotherm model

The equilibrium data were also applied to the D-R isotherm model to determine the nature of adsorption processes as physical or chemical The linearized form of the the D-R isotherm equation[20] is:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \qquad (4)$$

where q_e is the amount of metal ions adsorbed on per unit weight of adsorbent (mol/g), q_m the theoretical saturation sorption capacity (mol/g) , β is a constant related to mean free energy of sorption per mole of the sorbate (mol^2/J^2),and ε is the Polanyi Potential, which is equal to RT ln $(1+1/C_e)$,where R is the gas constant (J mol^{-1} K^{-1}) and T(K) is the absolute temperature. A plot of ln q_e *versus* ε^2 should give straight line (Figure 9 and 10).

The constant β gives an idea about the mean free energy E (kJ/mol) of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship.

$$E = 1/(2\beta)^{1/2} \quad (5)$$

This parameter gives information about sorption mechanism as chemical ion exchange or physical sorption. The magnitude of E is between 8 and 16 kJ/mol, the sorption process follows chemical ion exchange, while for the values of E < 8 kJ/mol, the sorption process is of a physical nature[21]. In the present study, the mean free energy of sorption was found to be 12.23 and 10.19 kJ/mol for Pb(II) and Hg(II), indicating support to chemical ion exchange mechanism or chemisorption.

The values supportive of Langmuir, Freundlich and D-R parameters for the adsorption of Pb(II) onto CSC are listed in Table 2.

Table 2. Isotherm constants for the metal ions.

Metal ion	Langmuir Constants			Freundlich Constants			D-R isotherm constants		
	Q_0 mg/g	b L/g	R^2	K_F mg/g	n	R^2	q_e mg/g	E kJ/mol	R^2
Pb(II)	40.49	1.01	0.9969	20.99	4.52	0.9993	42.27	12.29	0.9896
Hg(II)	35.09	0.652	0.9982	15.65	3.89	0.9947	38.60	10.19	0.9980

Effect of temperature on adsorption rate

It was observed that Pb(II) and Hg(II) biosorption followed pseudo second order kinetics at different temperatures. Linear plots of t/q_t *versus* t corresponding to the pseudo second order kinetic model were obtained. The values of kinetic parameters obtained are presented in Table 1. The rise in temperature increased the values of q_e and k_2.

In the present investigation, it was observed that the adsorption of Pb(II) and Hg(II) increase with rise in temperature. The ratio of increase in the rate constant was 1.2 for Pb(II) and 1.05 for Hg(II) for every 10 ^{o}C rise in temperature.

The enhancement of adsorption capacity at higher temperature may be attributed to the enlargement of pore size and/or activation of adsorbent surface[22].

Adsorption dynamics

The thermodynamic equilibrium constant K_c for the adsorption was determined by using the equation $K_c = C_A/C_e$, where C_A is the amount of Pb(II) adsorbed on the adsorbent of the solution at equilibrium (mol /L) and C_e is the equilibrium concentration of Pb(II) in the solution (mol/L).The change in standard free energy, enthalpy and entropy of adsorption were calculated using the following equation:

$$\Delta G^\circ = -RT \ln K_c \quad (6)$$

where R is the gas constant and T the temperature (K).

According to Vant Hoff's equation:

$$\ln K_c = \Delta S^\circ/R - \Delta H^\circ/RT \quad (7)$$

where ΔS° and ΔH° , the changes in entropy and enthalpy of adsorption respectively.

A plot of ln K_c *versus* 1 / T was found to be linear. The values of ΔH° and ΔS° were evaluated from the slope and intercept of Vant Hoff's plot .The positive value of ΔH° 38.45 kJ mol^{-1} for Pb(II) and 23.82 kJ mol^{-1} for Hg(II) confirms the endothermic nature of adsorption. When the temperature was increased from 20°C to 50°C, the magnitude of free energy change shifted to a high negative value suggesting that the adsorption was rapid and spontaneous (Table1). The positive value of ΔS° 131.1 and 80.3 J $mol^{-1}K^{-1}$ for Pb(II)and Hg(II) suggested an increase in randomness at the solid – solution interface during the adsorption of Pb(II) on SDC[23]..

Comparative study

The experimental results showed that the adsorption capacity (Q_o) and the adsorption intensity (K_F) obtained from the Langmuir and Freundlich model is greater for Pb(II) compared to Hg(II). The Q_0 and q_m obtained from Langmuir and D-R isotherm model are almost in the same order. For ions of same valence, the sorbent prefers the metal with higher atomic number. Moreover, the observed order was the same as that of their increasing ionic radii or their decreasing hydrated ionic radii. Smaller the hydrated ionic radius, the greater is its efficiency to activate groups of the adsorbent. This suggests that the energy required in the dehydration of metal ions, in order that they could occupy a site in the adsorbent, plays an important role in determining the selectivity series for the metal ions[24].

The higher binding capacity of Pb(II) ions over Hg(II) ions on the CSC could be explained by comparing the covalent index of Pb(II) (7.18) with Hg(II) (6.75) ions[15]. The covalent index of metal ions can be calculated by Eq. (8), taking into accounts of electro negativity (X) and ionic radius (r) of the metal ions. The value 0.85 in Eq. (8) represents an appropriate constant assumed to reflect the radius of oxygen and nitrogen donor atoms. The high value of the covalent index shows the high degree of binding capacity of metal ions to the functional groups of the adsorbent.

$$X_m^2(r+0.85) \qquad (8)$$

Working with crop milling waste as an adsorbent Asma Saeed *et al*[25] concluded that higher is the value of b and n, the higher is the affinity of adsorbent towards the metal being adsorbed. It is evident from the values of b and n for Pb(II) and Hg(II), that the affinity of CSC to adsorb is highest for Pb(II). Increase in temperature stimulates more adsorption for both the metals especially for lead. The thermodynamic parameters ΔH° and ΔS° are greater for Pb(II) compared to Hg(II).

Conclusion

The study indicated that activated carbon prepared from coconut shell carbon can be used as an effective adsorbent material for the treatment of lead and mercury bearing aqueous wastewaters. The adsorption of lead and mercury on activated carbon is found to be time, concentration, pH and dose dependent. The Langmuir and Freundlich equation agrees very well with the equilibrium isotherm for the entire concentration range studied. The pseudo second order kinetic model agrees very well with the dynamical behaviour for the adsorption of lead and mercury on CSC under different initial metal ion concentrations. This suggests that the rate limiting step may be chemical sorption rather than diffusion. The thermodynamic calculations indicated the feasibility, endothermic and spontaneous nature of the adsorption of Pb(II) and Hg(II) onto CSC. The present study enlighten that Pb(II) is preferentially adsorbed on the surface of the coconut shell carbon than Hg(II). Hence, acid activated coconut shell carbon is an effective and alternative adsorbent for the removal of lead and mercury from wastewater in terms of its high sorption capacity, abundant availability and inexpensive nature.

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