Bimetal Adsorption by Cottonseed Carbon: Equilibrium and Kinetic Studies

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Abstract: The simultaneous adsorption of Pb(II) and Hg(II) on cottonseed carbon (CSC) was employed for the removal of these metals from wastewater. The influence of various factors such as agitation time, pH and carbon dosage on the adsorption capacity has been studied. Langmuir and Freundlich equation could be used to interpret adsorption data. Sorption kinetics has indicated that reversible first order kinetics model could be applied with film diffusion as the controlling mechanism.

Keywords: Cottonseed Carbon, Lead(II) adsorption, Mercury(II) adsorption, Langmuir isotherm, Freundlich isotherm.

Introduction

Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Significant quantities of Pb(II) containing wastewater are introduced into water bodies from the effluents of storage batteries, pigments, protection of television picture tubes. The concentration of lead in water below the WHO standard (5.0 mg/L) cannot be considered as serious sources of lead intake¹. Higher concentration of lead causes severe destruction of reproductive system, liver, brain and central nervous system.

Significant quantities of Hg(II) containing wastewater are introduced into water bodies from the effluent of industries which produce electrical equipments, paints, pesticides, pulp and paper, domestic thermometers, insecticides, fungicides, batteries and chlor-alkali plants. Mercury causes damage to the central nervous system and chromosomes, impairment of pulmonary function and kidney, chest pain and dyspnoea^{2,3}. Higher dose may damage the liver⁴. These harmful effects of Pb(II) and Hg(II) necessitate its removal from wastewaters before release into streams.

Many reports are available on the development of activated carbon from cheaper and readily available materials such as rice husk, coconut shell *etc*⁵⁻⁷. In this connection it was proposed to make use of carbon from cottonseed, a waste agricultural byproduct, utilized for the simultaneous removal of Pb(II) and Hg(II) from water and wastewater.

Experimental

50 g of dried cottonseeds treated with 200 g of sulphuric acid and then kept in an air oven maintained at 140-160 °C for a period of 24 hours. The product was washed with water to remove sulphuric acid and dried at 110 °C followed by soaking in 5% NaHCO₃ for a period 24 hours to eliminate any free acid as well as to convert any ion exchange sites on the carbon into sodium loaded sites. After soaking period, the material was washed with distilled water and then dried at 110 °C. This material was sieved to particle sizes in the range (20-50) Mesh and used for simultaneous removal of Pb(II) and Hg(II). The carbon characteristics were found out using ISI-877 procedures and given in Table 1. It could be seen that this carbon contains sufficient bulk density, phenol number, surface area and ion exchange capacity so that it can be used for adsorption purposes.

Table 1. Carbon characteristics (CSC).

S. No.	Description	Results
1	Bulk density, g/cc	0.54
2	Moisture content, %	12.32
3	Ash, %	8.00
4	Matter soluble in water, %	2.37
5	Matter soluble in acid, %	5.27
6	Decolorizing power, mg/g	0.15
7	Phenol numbers	15
8	Ion exchange capacity milli equivalent / g	0.294
9	Surface area sq.m/g	545.6
10	Iron contents, %	1.15
11	pH	6.50

Batch mode studies

A stock solution of 100 mg/L of Pb(II) and 100 mg/L of Hg(II) was prepared by using analar grade lead nitrate and mercuric chloride. Batch experiments have been conducted for the simultaneous determination of lead and mercury. Experiments have been conducted with 100 mL of 10 mg/L of lead and 10 mg/L of mercury taken together in 300 mL stopper bottles. Solutions were equilibrated in mechanical shaker. At the end of equilibration period the solutions were filtered using a G3 crucible if necessary and the concentration of Pb(II) and Hg(II) ions were established simultaneously by Atomic Absorption spectrophotometer.(Elico Model 60).

Results and Discussion

Effect of agitation time

Figure 1 shows the effect of agitation time on the simultaneous removal of lead and mercury by CSC. The extent of removal increases with time and attains equilibrium in 3 hours for both metals, for an initial concentration of 10 mg/L of Pb(II) and Hg(II) and for a carbon dosage 100 mg/100 mL. It could be seen that 90-92% of Pb(II) and Hg(II) was removed on CSC. It could be seen that Hg(II) removal was more when compared with Pb(II).

Figure 1. Effect of equilibration time.

Effect of pH

Figure 2 presents the effect of initial pH on the simultaneous removal of lead and mercury by CSC. It is evident that maximum removal of lead occurred at pH 4 to 6 and for mercury occurred at pH 4 to 5.

The influence of pH on Pb(II) and Hg(II) removal may be explained as follows. A pure carbon surface is considered to be non-porous but in actual practice some carbon-oxygen complexes such as CxO , COx , and CxO_2 are usually present which render the surface slightly polar⁸. Based upon the work of frumkin⁹ the surface oxide groups available on the surface of a carbon can undergo hydrolytic reaction with the result proton exchangeable sites such as $CxOH_2^{2+}$, $CxOH^+$ may be formed. Since CSC was prepared upon treatment with sulphuric acid groups such as $CxOH^+$, $CxOH_2^{2+}$ and $CxSO_3H$ may also be present. Hence it is expected that H^+ in the group got exchanged with Pb^{2+} and Hg^{2+} and soluble complexes of Pb(II) and Hg(II) as follows.

Effect of carbon dosage

Figures 3-6 show the simultaneous removal of Pb(II) and Hg(II) as a function of carbon dosage by CSC. It is evident that 99% removal of both metals could be achieved for an initial concentration of 10 mg/L of Pb(II) and Hg(II) ions in 100 mL, with a carbon dosage of 100mg. Higher levels of removal capacity may be due to larger surface area and moderate ion exchange capacity.

In order to find out whether the increase in the concentration of Hg(II) affects lead adsorption solutions containing Pb(II) and Hg(II) were prepared in the ratio 1:2, 1:3, 1:4. It could be seen that quantitative removal was maintained in the case of Pb(II) whereas Hg(II) removal came down from 99 to 95%

Figure 2. Effect of pH.

Figure 3. Effect of carbon dosage.

Figure 4. Effect of carbon dosage (1:2) for Pb:Hg solution.

Figure 5. Effect of carbon dosage (1:3) for Pb:Hg solution.

Figure 6. Effect of carbon dosage (1:4) for Pb:Hg solution.

Adsorption isotherms

The Langmuir equation was applied for adsorption equilibrium for both Pb(II) and Hg(II).

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \quad (5)$$

where, C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/L) and Q_0 and b are Langmuir constant related to adsorption capacity and energy of adsorption respectively. The linear plots C_e/q_e vs. C_e shows that the adsorption obeys the Langmuir model for both Pb(II) and Hg(II) and it is shown in Figures 7& 8. Q_0 and b were determined from the Langmuir plots and found to be 48.31 mg/g and 4.31 mg/L respectively for Pb(II) in distilled water and 33.00 mg/g and 0.168 mg/L respectively for Pb(II) in tap water. In the case of Hg(II), 7.246 mg/g and 6.899 mg/L were found out respectively for Hg(II) in distilled water and 36.00 mg/g and 3.613 mg/L respectively for Hg(II) in tap water. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (or) equilibrium parameter, R_L which is shown as $R_L = 1/(1+bC_0)$ where, b is Langmuir constant and C_0 be the initial concentrations of Pb(II) and Hg(II). R_L values are shown in Table 2. The values of $1 < n < 10$ show favorable adsorption of Pb(II) and Hg(II) on CSC⁸.

Figure 7. Langmuir adsorption isotherm for Pb(II).

Figure 8. Langmuir adsorption isotherm for Hg(II).

Table 2. R_L values for Pb(II) and Hg(II).

S.No.	Concentration in mg/L	R_L values, Distilled water		R_L values (Tap water)	
		Pb(II)	Hg(II)	Pb(II)	Hg(II)
1	10	0.01882	0.01266	0.08562	0.02167
2	20	0.00941	0.00633	0.04281	0.01084
3	30	0.00627	0.00422	0.02854	0.00723
4	40	0.00471	0.00316	0.02140	0.05419
5	50	0.00376	0.00253	0.01712	0.00434

The Freundlich isotherm is represented by the equation⁸

$$\log x/m = \log K + 1/n (\log C_e) \quad (6)$$

Where C_e is the equilibrium concentration (mg/L) and x/m is the amount adsorbed per unit weight of CSC (mg/g). Plots of $\log x/m$ vs. $\log C_e$ are linear for both metal ions. Figures 9&10 show the Freundlich adsorption isotherm for Pb(II) and Hg(II) metal ions in tap water

and distilled water. The processes followed were of Freundlich adsorption type. The 'K' and 'n' values for both metal ions were calculated from the intercepts and slopes, respectively and shown in Table 3. It could be seen that Pb(II) and Hg(II) removal was found to be more in distilled water when compared with tap water. The decrease in removal may be due to competition of common ions available in water for the sites of lead and mercury.

Table 3. K and n values of Freundlich adsorption isotherm.

S. No.	Metal ions	Distilled water		Tap water	
		K	n	K	n
1	Pb (II)	54.95	0.60	33.11	0.22
2	Hg (II)	41.68	0.23	27.54	0.311

Figure 9. Freundlich adsorption isotherm in distilled water.

Figure 10. Freundlich adsorption isotherm in tap water.

Adsorption kinetics

The kinetics of bimetal adsorption follows the first order rate expression. The kinetic fits for both metal ions are shown in Figures 11&12. The detailed mathematical derivations for calculating the reversible first order kinetics and the values of film and pore diffusion coefficient are described elsewhere⁹. The kinetic data are furnished in Table 4. Since the forward rate constants are much higher than the backward rate constants for the heavy metals under consideration, it could be concluded that adsorption is a well favored process. According to Michelsen *et al.*, if the film diffusion is the governing process of adsorption on carbon, then the coefficient (D_f) value should be between 10^{-6} - 10^{-8} cm^2 / sec . If pore diffusion D_p were to be rate determining, its values should be in the range 10^{-11} - 10^{-13} cm^2 / sec . Using kinetic data, the values for film and pore diffusion constants were calculated and shown in Table 5. It is evident that the removal of Pb(II) and Hg(II) follow film diffusion process as outlined by Michelsen since the co-efficient values are very close to the range of 10^{-8} cm^2 / sec .

Figure 11. Kinetic fits of lead.

Figure 12. Kinetic fits of mercury.

Table 4. Rate constants for the removal of lead and mercury (CSC).

Concentration of metal ions, mg/L	K, overall rate constant		K ₁ , forward rate constant		K ₂ , backward rate constant	
	Pb(II)	Hg(II)	Pb(II)	Hg(II)	Pb(II)	Hg(II)
10	9.20	2.50	8.92	2.39	0.27	0.10
7	5.60	2.89	5.52	2.84	0.08	0.04
5	3.60	3.75	2.80	3.67	0.79	0.07
3	8.00	5.31	7.46	5.14	0.53	0.17

Table 5. Diffusion co-efficient for the simultaneous removal of lead(II) and mercury(II) by CSC.

Concentration of metal ions, mg/L	Film diffusion $\times 10^{-10}$, cm ² /s		Pore diffusion $\times 10^{-8}$, cm ² /s	
	Pb(II)	Hg(II)	Pb(II)	Hg(II)
10	7.3179	2.6505	9.1474	2.4849
7	2.1196	1.0942	5.5638	2.8724
5	2.0992	1.9879	3.5782	3.7273
3	1.4140	4.6989	7.9538	5.2863

Conclusion

The results have clearly demonstrated that cottonseed carbon could be employed successfully for the simultaneous removal of mercury and lead. The carbon has moderate hardness and surface area so that it can be applied for wastewater treatment containing heavy metals such as lead and mercury.

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