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Removal of Lead from Aqueous Solution Using Black Liquor – A Pulp Mill Waste

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Abstract: ***Adsorption appears to offer the best prospects for overall treatment of waste water as the process is useful for a broad range of substances and is normally excepted to be reversible so that regeneration of the adsorbent with resultant economy of operation may be possible. Lignin, an adsorbent obtained by precipitating it with concentrated hydrochloric acid from black liquor, a byproduct formed after digestion of mixed wood during pulping which was managed from a pulp mill in northern India. Lignin is inexpensive, mostly non-toxic, and also available in large quantities so it was investigated as a replacement for the current expensive methods of removing lead, a toxic and hazardous metal. The toxicity symptoms are mild anemia, brain damage, vomiting, loss of appetite, convulsions, uncoordinated body movements and stupor, eventually producing coma and death when lead accumulation is greater than 500 mg. Adsorption studies on lignin have been performed to remove lead from water as a function of equilibrium time, temperatures, pH, concentration and particle size of lignin. The data fits very well into Langmuir model. The Langmuir constants have been evaluated. Low desorption results are observed with a number of desorbing solutions. Adsorption kinetics has also studied by batch method and kinetic data suggests that the rate determining step is diffusion through the particle. Kinetic parameters like diffusion coefficient, activation of energy and entropy of activation have also evaluated. Studies proved that bio adsorbent lignin has good potential as an adsorbent for removing lead metal ions from water and waste water. It acts as a good scavenger of lead metal and the capacity of this adsorbent is quite significant.***

Keywords: Lignin, adsorbent, isotherm, pH, diffusion

1. Introduction

Of the known pollutants, heavy metals are the most frequently occurring substances which are widely spread in water and create problems in wastes and receiving water. Lead is such a poisonous heavy metal which accumulates in living bodies. The toxicity symptoms are mild anemia, brain damage, vomiting, loss of appetite, convulsions, uncoordinated body movements and stupor, eventually producing coma and death when lead accumulation is greater than 500 mg. Many treatment methods (1-11) have been reported in literature yet adsorption appears to offer the best prospects for overall treatment of waste water as the process is useful for a broad range of substances and is normally excepted to be reversible so that regeneration of the adsorbent with resultant economy of operation may be possible. In most of the studies activated carbon (12-15) has been used as adsorbent. Intensive Studies have been carried out to develop more effective and inexpensive adsorbents which was comparable to that of activated carbon. Thus, the search for good alternatives of activated carbon (16) is still on. suitable low cost (17) alternative adsorbents are either natural material such as wood, peat, coal, lignite, clays, sand, microorganisms, plant etc. or industrial waste/ bye products such as slug, fly ash, baggasse, red mud etc. These are generally available free of cost or at very low cost as compared to activated carbon. The utilization of industrial wastes as adsorbents (18-23) meets to a small extent and beneficial for management of waste disposal problem. Lignin, a bye product from pulp mill, is a material known to exhibit adsorption properties. Therefore, in the present work, adsorption of most toxic lead metal ion on to lignin as an adsorbent has been investigated.

2. Experimental

Materials

Lead nitrate, dihydrogen ethylene diamine tetra acetate (EDTA) obtained from Qualigens chemicals, Mumbai, India was of AR grade and used as such for estimation of lead ions.

Lignin was isolated from black liquor from mixed wood pulping which was obtained from a pulp mill in northern India. It was malodorous, deep black and its original pH was 11.2. Its specific gravity is 1.10 g/l and total solid content is 21%.

The black liquor was acidified with diluted HCl until precipitation was complete. The resulting precipitate was centrifuged, washed repeatedly with a distilled water to remove chloride ions and dried at room temperature. Lignin was further purified by dissolving in dioxane (10% w/w solution) followed by re precipitation into magnetically stirred anhydrous ether. The precipitate was then washed with ether and then benzene. Finally, the precipitate was washed with low boiling ether and dried over anhydrous calcium chloride under vacuum at room temperature. The sample of pure lignin was ground and passed through different sieves and the fraction 100 to 200 B.S. mesh size (.0075 to 0.0037 cm) were collected. It was finally dried to remove moisture content by placing it in an oven at 90^0C for about 12 hours.

Measurements of pH were made by using Systronic pH meter model 335 and pH of adsorbate solution samples was adjusted by adding 1N HCl and 1N NaOH solutions.

Equilibration time of adsorption was decided by performing adsorption experiments in which 50 ml of lead nitrate solution contained fixed concentration ($5x10^{-4}$ M) and 0.1 g of lignin was taken into a number of conical flasks and conical flasks were removed one after another at certain time period. After centrifugation quantity of Pb^{2+} ion upto equilibrium was determined until the values were constant. The major part of the removal seems to be complete in 28 hours. As such all adsorption determination have been made after equilibrating the solution with adsorbent for 36 hours.

Estmation of lead nitrate solution after equilibration carried out by EDTA method using Xylenol orange as indicator.

Adsorption studies were carried out by Batch method (finite bath method). A series of conical flasks fitted with stop cork were used for adsorption studies. 50 ml of aqueous solution of varying concentration of Pb^{2+} at a fixed pH (3. 0 and 5.0) was added to flask, maintained at the desired temperature. Equal amount of lignin (0.1g) in each flask was added. The flasks were shaken for five minutes and equilibrated for pre-decided time (36 hours) with intermittent shaking. The supernatant liquid was centrifuged and analyzed for Pb^{2+} ion concentration. The concentration of unabsorbed lead was estimated by EDTA method as described above. A range of adsorbate concentration has been chosen for running of adsorbate isotherms was 10^{-4}M to 10^{-3}M.
Adsorption studies were performed at two pH 3.0 and 5.0. Lignin is soluble in alkaline solution (pH > 7) so adsorption studies were performed in acidic media.

To investigate the thermodynamics of sorption process, experiments were performed at different temperature (20, 30 and 40 $\pm$ 0.1^0C)

To investigate effect of metal ion concentration varying volume of stock solution of lead nitrate were added and made up to 50 ml, equilibrated and then estimated as mentioned above. The concentration range studied was 1 x 10^{-4} M to 7 x 10^{-4} M for Pb^{2+} ions.

In order to understand the effect of particle size of lignin on the adsorption of lead, lignin samples of different sizes (<100, 100-200, >200 B.S.S. Mesh size) were taken by removing the adhering fine particles suspended in water. Keeping in view the most conventional removal of metal 100-200 mesh size of lignin particles have been used throughout the investigations.

The effect of varying concentration of NaCl in the solution on uptake of Pb^{2+} ions on lignin has also been studied. Experiments were set by taking fixed concentration of Pb^{2+} ion (5 x 10^{-4} M) containing varying concentration of NaCl in conical flask at 30^0C. After equilibration the concentration of Pb^{2+} ion was determined as mentioned before.

3. Results and Discussion

The adsorption isotherms at pH 3.0 and pH 5.0 and are shown in Fig. 1 and 2 respectively. The results (Fig. 1 and 2) show a positive adsorption in all adsorption isotherms. These are regular and concave to equilibrium concentration axis. Although the extent of adsorption increases with increasing concentrations of adsorbate, the percent removal is quite high at low adsorbate concentration. The nature of isotherms also reveals a relatively rapid initial rate of adsorption at low adsorbate concentrations which markedly decreases at high adsorbate concentration with a slow approach to saturation. At low lead concentration (10^{-4} M) about 70-96% of the metal ion gets removed showing that lignin is quite suitable for removal of trace quantities of Pb^{2+} ions.

From the adsorption isotherms (Fig. 1 and 2) it is observed that adsorption increases with temperature. With the help of these figures heat of adsorption for the process have been calculated.

The heat of adsorption is calculated by the equation:

$$Q = R \frac{T_1 T_2}{T_1 - T_2} \log \frac{C_1}{C_2}$$

Where, for the same amount of adsorption:
C_1= equilibrium concentration of the solute at temperature T_1.
C_2= equilibrium concentration of the solute at temperature T_2. R= Universal gas constant.
Heats of adsorption given in table 1showsthat the process is exothermic in nature.

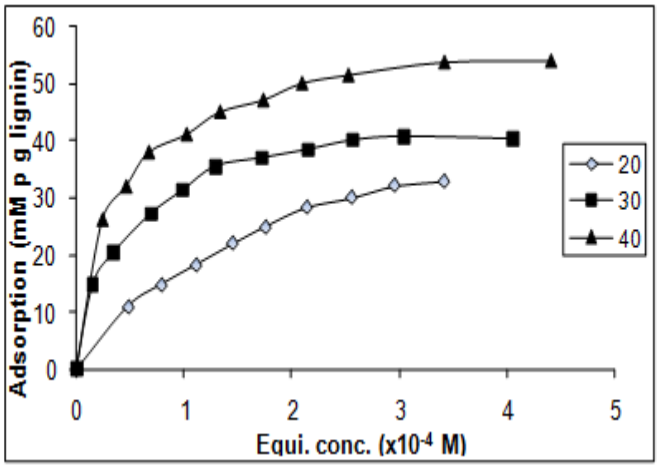

Figure 1: Adsorption isotherms at different temperatures and pH 3.0

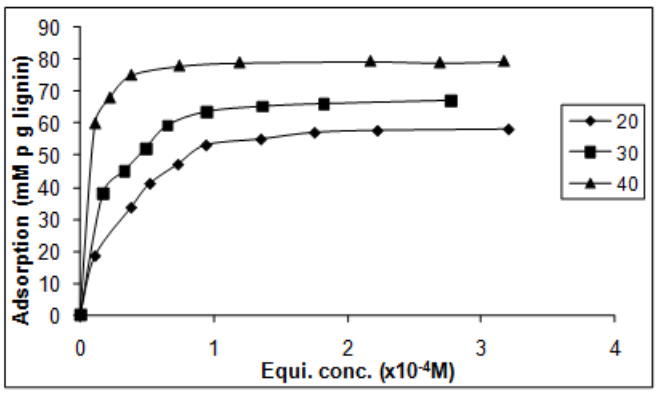

Figure 2: Adsorption isotherms at different temperatures and pH 5.0

Figure 1 clearly indicates that removal of metal at pH 3.0 is quite low than the removal of metal at pH 5.0 (Figure 2). It concludes that the removal of Pb^{2+} ions increases with the solution pH. Singh and Mishra (24) observed an increase in adsorption of Cu^{2+} and Cd^{2+} ions from solution by hydrolytic lignin due to dissociation of phenolic –OH and carboxylic groups. Similarly, Dinesh Mohan et al. (25) also reported same behavior for the adsorption of copper and cadmium metal ions on kraft lignin. Lignin carries a negative charge on its surface. The negative charge on the surface of lignin arises from the dissociation of phenolic –OH groups. At low pH, the dissociation of –OH group is suppressed and this results in a negative charge on the lignin surface. The negatively charged points, balanced by counter ions of opposite charge on lignin surface, provide the adsorption sites. As the number of adsorption sites increases with increasing pH of the surfactant solution, the uptake of solute also increases.

Table 1: Values of heat of adsorption

p^H	*S. No.*	*Adsorption mM.g^{-1} lignin*	Heat of adsorption K.Cal.M^{-1}
3.0	1.	16	- 1.83
	2.	18	- 2.92
	3.	20	- 5.67
5.0	1.	20	- 6.64
	2.	30	- 7.36
	3.	40	- 9.17

Langmuir Adsorption Models

The entire adsorption data fits Langmuir model and found linear. The values of Q^o and b as obtained from Langmuir model are listed in Table 2. The values of Q^o, represents the amount of adsorbate adsorbed for forming a complete monolayer on the lignin surface. The value of b is the reciprocal of the concentration at which half saturation of the adsorbate is obtained. It can be seen from that the value of Q^o and b are higher at pH 5.0, indicating a greater tendency towards adsorption at higher pH 5.0 then at pH 3.0. The value of Q^o also increases with increasing the temperature of adsorbate solution. This is in an accordance with the concept discussed above.

Table 2: Values of Langmuir constants

pH	Temperature (°C)	b (1/mM)	Q (mM/g)
3.0	20	0.55	51.02
	30	1.18	53.51
	40	2.64	58.76
5.0	20	3.81	63.94
	30	6.58	71.17
	40	10.17	80.26

Adsorption results given in Table 3 show that the adsorption capacity of lignin for Pb^{2+} ions increases as the particle size of adsorbent decreases. This indicates that the surface area associated with the pores inside the particles is being freed at least partially and that the effective adsorption regime is confined to the external surface and a narrow layer just below the surface.

Table 3: Effect of particle size of lignin on the removal of lead at temperature 30°C

Initial concentration = 5 X10^{-5} M
Quantity of lignin added = 0.1 g
Total volume = 50 ml

S. No.	*Particle Size (Mesh)*	*Adorption mM g^{-1} lignin*	
		pH 3.0	*pH 5.0*
1.	> 200	40.61	65.89
2.	100 - 200	31.86	52.35
3.	< 100	19.32	36.62

Many times dissolved salt are also present in waste water. Hence, effect of salt (NaCl) concentrations on the sorption of fixed concentration (5 x 10^{-4} M) of Pb^{2+} ions has also been studied. This indicated that adsorption of Pb^{2+} ion decrease with increasing NaCl concentration. Studies showed that % removal for 5 x 10^{-4} M Pb^{2+} solution decreased from 39% to 22.8% at pH 3.0 and from 63.6% to 42.8% at pH 5.0 when NaCl concentration increased from 10^{-4} M to 10^{-3} M. Decrease in adsorption is due to the fact that not only Pb^{2+} ion but also Na^+ ion compete for adsorption and adsorbs on some of the adsorption sited on the lignin.

Desorption studies has been made with desorbing solutions. Very low desorption results are observed with a number of desorbing solutions. Since thermal regeneration of adsorbent is likely to cause air pollution problems and chemical regeneration will lead to increased water pollution, it is not desirable to regenerate lignin in view of its low-cost and ease of availability, provided its disposal after use is easy and safe. The spent carbonaceous adsorbent can be disposed of simply by burning one option can be fired in a steam boiler.

4. Conclusion

The present study demonstrates that black liquor directly obtained from paper mill gives lignin by a simple and inexpensive method and also serves as a value added adsorbent (over its fuel value) for the removal of Pb^{2+} ions from water and waste water. Its metal binding capacity is appreciably high under suitable experimental conditions with comparable efficiency.

Results show that lignin can act as a good adsorbent for the removal of Pb^{2+} ions. It is possible to remove 96% of 3.0X10^{-4} M solution and 55% of 7.0X10^{-4} M solution of Pb^{2+} ions at pH 5.0 and temperature 30°c using 2g/l of lignin. Adsorption of metal ions increase with increase in temperature and pH and decrease in particle size of lignin. The adsorption data fits into the Langmuir model at various temperature and pH. The adsorption data also fits into B.E.T. model at various temperature and pH but only at low concentrations. Desorption of the metal with different electrolytes is very low (below 4%). Thus, regeneration of the adsorbent is not feasible.

Present study will contribute to the development of research in this area and will be extended by similar experiments for other metal ions and also for other pollutants/contaminants

from aqueous solution that would make a significant impact on the potential commercial application of lignin to industrial system.

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