Nature Environment and Pollution Technology © Technoscience Publications	Vol. 7	No. 1	pp. 117-122	2008

ADSORPTION OF ZINC METAL FROM PAPER MILLS WASTEWATER BY ACTIVATED CARBON PREPARED FROM *SHOREA ROBUSTA* LEAF LITTER

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ABSTRACT

In this paper, a study of removal efficiency of zinc from a simulated Paper Mills Effluent by adsorption on a non-convectional material, activated carbon from *Shorea robusta* leaf litter, is presented. AS the adsorption potential of activated carbon varies as a function of contact time, initial metal concentration in the aqueous solution, temperature of solution, particle size of the adsorbent used, pH of solution, flow rate and the chemical and physical characteristics of the activated carbon and the wastewater, the chemical and physical properties of the activated carbon have been carried out.

The controlling efficiency of the adsorption of zinc is affected by aqueous solution pH, contact time, adsorbent dose and initial metal ion concentration, which are investigated for the batch process. Results of the investigation were used for the kinetic studies to understand the mechanism of the adsorption process. The adsorption equilibrium is well correlated by Langmuir and Freundlich isotherms. From the experimental results it was found that the optimum activated carbon dose is 2.8 g/L. At this optimum carbon dose, by varying the contact time, it was found that the equilibrium occurs at one hour of operation and maximum adsorption (83.23%) at high values of solution pH (9.0) and high initial metal ion concentration.

INTRODUCTION

Pollution of water with toxic heavy metals is considered dangerous because of the potential toxic effects on aquatic life as well as to other animals and plants and humans. Industrial wastes containing heavy metals are one of the major sources of water pollution. Zinc in particular has received a great deal of attention as it is one of the heavy metals which can cause considerable damage to human and aquatic life even at trace levels. Zinc is a prime metal, which is used in manufacturing of galvanizing, brass making, sheets for roofing and guttering, dye casting, alloys, chemicals and pigments and comes out in the wastewaters (Lotfi & Nafaa 2002, Recordet et al. 2001, Gupta & Ali 2002, Cheung et al. 2000).

There are several methods to remove zinc from aqueous solutions, such as chemical precipitation, ion exchange, electrolysis and carbon adsorption. Most of these methods require high capital cost, skilled supervision, post treatment, and produces toxic byproducts. Much has been exhibited lately in the use of adsorption technique for removal of zinc from wastewaters. A number of sorbents used so far include insoluble starch, xanthates, modified cotton and wood, tree leaves, agricultural products, etc. The intensity of adsorption is very less in most of these studies. Activated carbon, with its high surface area and porosity is a versatile adsorbent used for the water treatment. The so far used commercial activated carbon uses precursors like wood, bamboo, low rank Turkish coal (Cheung et al. 2000), coconut shell (Lotfi & Nafaa 2002), saw dust and rice husk etc. Most of these have high operating costs, and are limited in supply. Hence, withered leaf litter of *Shorea robusta*, with limited use as fodder, is used as a precursor in the present paper for preparation of activated carbon. This leaf litter activated carbon was used as a sorbent for removal of zinc from low concentration solution.

MATERIALS AND METHODS

The withered leaf litter was dried at 50°C in an oven after sorting the twigs and foreign material etc. The sample was then ground in a ball mill. The resulting powder was sieved to sizes 80-90 mesh and washed with diluted acids, followed by distilled water to remove the foreign materials adhering to these particles and dried at 100°C for 4 hours. This was impregnated with $ZnCl_2$ solution (2N) after soaking for 6 hours. It was dried before carbonizing at 400°C for 1 hour in an inert atmosphere. The resulting material was washed with 0.1 N HCl and subsequently with distilled water to remove the unreacted $ZnCl_2$ and ash.

Adsorption Experiments: Batch sorption experiments were carried out at room temperature using prepared zinc solution with distilled water. A certain amount of adsorbent was transferred into bottles containing 100 mL of Zn^{2+} solution (in the form of $ZnSO_4$) to make the final sorbent concentration 5.12 ppm. Zinc concentrations were in the range of 3-9 ppm. A shaker was used to agitate the mixture. Samples were taken at certain intervals for the purpose of studying the dynamics of the sorption process. Equilibrium was allowed to occur and then the bottles were removed from the shaker for analysis. The sorbent was separated from the samples by centrifugation and the upper layer was analysed for zinc using spectrophotometer following the standard procedure. Each experiment was carried out in duplicate and the average results are presented in this paper.

RESULTS AND DISCUSSION

Effect of carbon dose: The effect of adsorbent (activated carbon) dose on the removal of zinc was studied by varying the dose of adsorbent from 0 to 5 g/L at fixed amount of pH, temperature and adsorbate concentration. The uptake of zinc metal is shown in Fig. 1. The adsorption of zinc increases from 0% to 78% as the adsorbent dose increases from 0 to 3 g/L and then remains constant. This is due to the increased availability of active adsorption sites arising due to the increase in effective surface area resulting from the increases in dose of adsorbent or due to conglomeration of the adsorbent. So by optimizing the adsorbent dose it was found that the optimum uptake of zinc would occur at 2.8 g/L. It indicates that the optimum carbon dose for adsorption of zinc by this low cost activated carbon is 2.8 g/L.

Effect of contact time: Fig. 2 depicts the effect of contact time on the rate of uptake of zinc. It is found that the rate of removal of zinc ions increases with increase in contact time to some extent. Further increase in contact time does not increase the uptake due to deposition of metal ions on the available adsorption sites on the adsorbent material. Taking the optimum adsorbent dose of 2.8 g/L and varying the contact time, it is found that up to 1 hour the uptake of zinc increases and remains constant after that. The removal is around 78.03%. Therefore, the optimum contact time for the removal of zinc from the wastewater will be 1 hour. For further optimization of other parameters, the contact time was considered as the equilibrium time corresponding to the adsorbent and adsorbate.

Effect of initial zinc concentration: For a strictly adsorptive reaction in the optimized period of contact, the rate of adsorption varies directly with concentration of the adsorbate. The activity of any adsorbent material falls sharply with an increase in initial concentration of the metal. It is well known fact that the rate of adsorption is controlled by diffusion through a hydrostatic boundary layer called film diffusion control or through the pores of the resin matrix called particle diffusion on control. The rate of adsorption is mainly controlled by film diffusion under the conditions of small resin particle, dilute solution and mild stirring and vice versa in case of pore or particle diffusion. The three distinct steps involved in the adsorption of an organic or inorganic compound onto the pores of the adsorbent materials are:

1. The adsorbed molecule must be transferred from the bulk phase of the solution to the external surface of the adsorbent particle, called film diffusion.
2 Transfer of adsorbed molecule to an adsorption site on the inside of the adsorbent particle, known as pore or particle diffusion.
3 The adsorbent particle must become attached to the interior surface of the adsorbent particle, that is adsorbed.

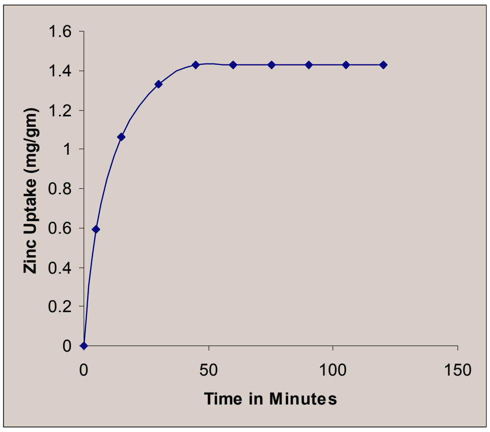

Fig. 1: Effect of carbon dose on zinc uptake.

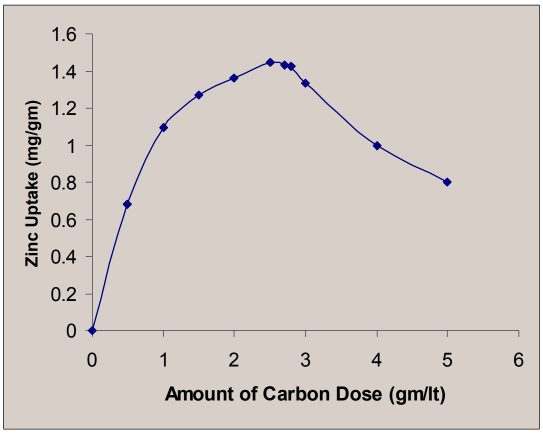

Fig. 2: Effect of contact time on zinc uptake.

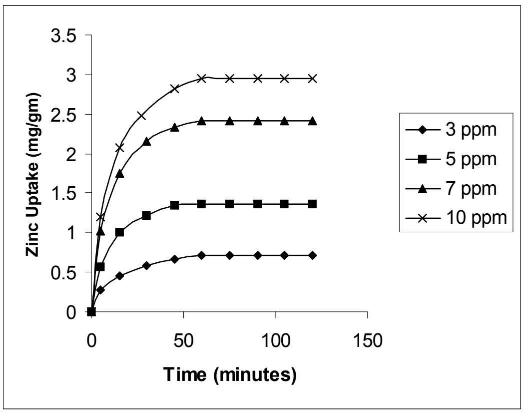

Fig. 3: Effect of initial zinc concentration on zinc uptake.

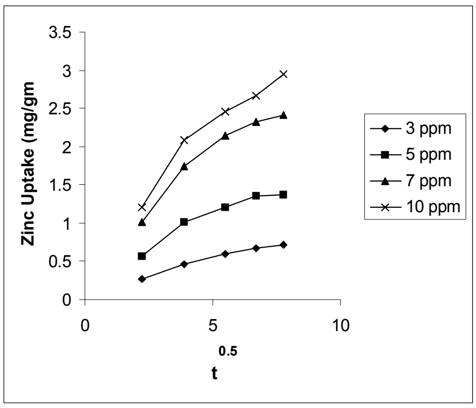

Fig. 4: Effect of initial zinc concentration for intrapore diffusion.

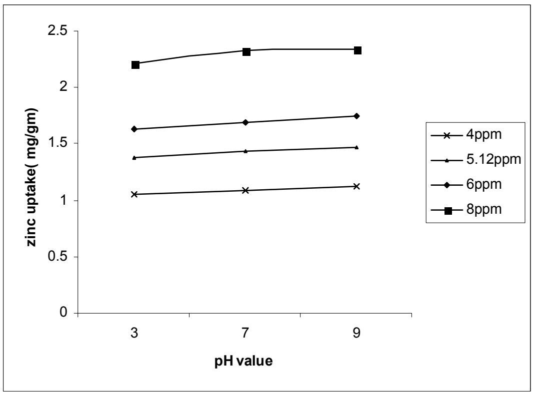

Fig. 5: Effect of pH on zinc uptake.

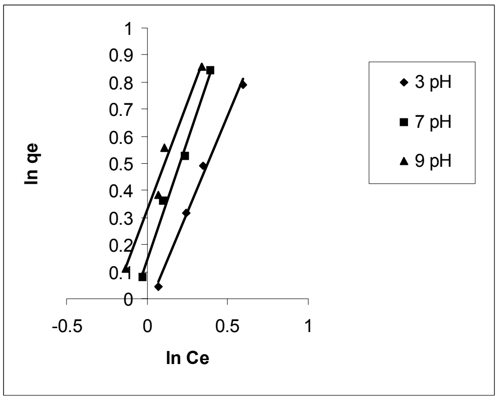

Fig. 6: Freundlich isotherms.

In case of particle diffusion external transport is greater than internal transportation, and in film diffusion external transport is less than internal transportation. If external transport is similar to the internal transportation, the transport of ions to the boundary may not be possible at significant rate.

From the experiment, the rate of adsorption of zinc increased from 65.9% to 82.84% as the concentration increases from 3 to 10 g/L (Fig 3). Hence, it is clear that as the initial zinc metal concentration increases, the adsorption rate also increases. To demonstrate the participation of intrapore diffusion in this adsorption process, the uptake of zinc was plotted against the square root of the time. These plots are shown in Fig. 4 for different zinc concentrations. It is seen that most of the data can be represented by straight lines, but these data do not pass through the origin. According to Weber and Morris, these linear correlations indicate that intrapore diffusion was involved in this adsorption process, but it is not the controlling step, because the lines do not pass through the origin.

Effects of pH: The pH of the wastewater or the aqueous solution is an important controlling factor in the adsorption process and, thus, the role of hydrogen ion concentration was examined from the solution at different pH. It was observed that with the increase in pH of the solution, the removal of zinc also increases. The extent of removal was investigated at solution ion concentrations of 4 mg/L to 8 mg/L from pH 3 to 9, whose results are shown in Fig. 5. By changing the pH from 3 to 9, it was observed that the percentage of removal increases from 73.25% to 82.34%. This happens as the pH increases the activated carbon surface changes. The electrostatic repulsion between cations and positively charged surface of activated carbon took place at low pH values, while with an increase in pH, metal ions replaced hydrogen ions from the carbon and, therefore, the adsorption increases. With further increase in pH, the adsorption of zinc decreases because it was indicated that generally the sorption of metals would increases up to some extent and then decreases, which was not done in this work. Adjustment of pH was accurately made in adsorbate solutions of various concentrations, otherwise a very slight change in final equilibrium pH disturbs the uptake process.

Adsorption isotherms: In order to determine the adsorption potential of the prepared activated carbon, the study of sorption isotherm is essential in selecting the adsorbent for the removal of zinc. Two important physicochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and the kinetics. An equilibrium study gives the capacity of the adsorbent. The equilibrium relationships between adsorbent and adsorbate are de-

Table 1: Freundlich isotherm constants.

pH of solution	1/n	K_f	R^2
3	1.4138	0.0316	0.9695
7	1.7511	0.1147	0.9921
9	1.5979	0.3226	0.9782

scribed by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. There are two types of adsorption isotherms: Langmuir adsorption isotherms and Freundlich isotherms. But here the adsorption process satisfies the Freundlich isotherm.

Freundlich isotherm: Hebert Max Finley Freundlich, a German physical chemist, presented an empirical adsorption isotherm for non-ideal systems in 1906. The Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as:

$$q_e = K_f C_e^{1/n} \qquad ...(1)$$

Where,

q_e = x/m, the amount adsorbed (mg/g)

C_e = the equilibrium concentration of the adsorbate (mg/L)

K_f = the Freundlich constant related to the adsorption capacity

1/n = the Freundlich constant related to the adsorption intensity

The above equation is conveniently used in the linear form by taking the logarithm of both the sides as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad ...(2)$$

When ln q_e was plotted against ln C_e, straight lines with slopes 1/n were obtained (Fig. 6), which shows that the adsorption of zinc follows the Freundlich isotherm. The Freundlich constants 'K_f' and '1/n' are calculated from Fig. 6 and the values at different pH are tabulated in Table 1. From the results it was concluded that K_f values increase with increase of pH, which means that the adsorption capacity of zinc increases with increase in the initial pH of solution; and the intensity of adsorption initially increases and then decreases.

CONCLUSION

The adsorption of zinc by the activated carbon, prepared from *Shorea robusta* leaf litter, increases by increasing the amount of carbon dose, and equilibrium occurs at 2.8 mg/L. The adsorption of zinc also increases with increase of contact time and maximum sorption reaches after one hour of treatment. The sorption capacity increases with increase in the initial zinc metal concentration in the aqueous solution. The adsorption of zinc increased with increase in pH of the aqueous solution and maximum reaches at the pH of 9.0 in the experiment. Adsorption of zinc on to the activated carbon surface satisfied the Freundlich isotherm. Intrapore diffusion was involved in this adsorption process, but it is not the controlling step. Due to this activated carbon prepared from the leaf litter effectively removed the low metal concentration in the aqueous solution, but it can also be high in case of higher metal ion concentration of wastewater.

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