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Adsorbent from Pongamia Pinnata Tree Bark for Zinc Adsorption

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Abstract—In the recent years, *Pongamia pinnata* trees are widely grown at farms for its seeds utilised for biofuel activities. Due to the easy availability of this tree bark, it is used as a viable adsorbent for removing some heavy metals from aqueous and waste water. In this context, the adsorption of Zinc on prepared adsorbent is very effective. In this study, investigations were made for the adsorption of zinc ions from aqueous and waste water. Batch adsorption studies to determine the optimum conditions of zinc ion removal were conducted to know the influence of experimental conditions such as pH of the solution, metal ion concentration, amount of adsorbent and contact time at room temperature. The results obtained show that the optimum pH range for the zinc removal is 5 – 5.4 and adsorption percent is higher than 95 %. Kinetic study was also made to determine rate constants.

Keywords—Adsorbent, Adsorption Isotherms, Effluent, Kinetics, *Pongamia pinnata*, Zinc.

I. INTRODUCTION

Increase in the population and present day life conditions have proven demanding needs of various types of materials. This in turn has led to growth of a number of industries. Alarming increase in the number of industrial and domestic activities has caused environmental degradation due to accumulation of pollutants into the surroundings. In this regard, effects of heavy and toxic metal ions because of their non-biodegradability are a major issue of the present day. Assimilation of high levels of zinc through food and water can result in metal fume fever, stomach cramps, skin irritations, anaemia, damage pancreas, disturb protein metabolism, arteriosclerosis and respiratory disorders etc., Zinc can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms. The breakdown of organic matter may seriously slow down because of this. [1]

Zinc is widely used in various industries such as automobile industry, rubber, paints, pigments and iron and steels, plastics, cosmetics, photocopier paper, wall paper, printing inks, pharmaceuticals and metal industries. [2] As a consequence, industrial effluents are contamined with zinc. Hence, removal to permissible levels of zinc is essential. [3]

Conventional methods for treating effluents, such as precipitation, redox, membrane technologies, electrolysis etc., are both costly and have problem of secondary waste such as sludge.[4] The safe disposal of sludge is another issue for the industry. In this context, adsorption has proven to be a better option with large varieties of adsorbents available that overcomes the problem of sludge formation and disposal as many of these adsorbents are biodegradable. [5] Thus adsorbents such as fly ash [6], zeolites [7], biosorbents [8], polymers [9], cassava [10], Agricultural waste [11], aquatic macrophytes [12], bagasse and rice husk [13] etc., are reported in literature for zinc removal from effluents.

The present study was carried out to assess the potential of adsorbing zinc from aqueous and waste waters onto adsorbent prepared by using *Pongamia pinnata* tree bark. Adsorption isotherm and kinetics parameters have been studied.

II. MATERIALS AND METHODS

A. *Preparation of Adsorbent*

Pongamia pinnata bark was collected in the study area, Davangere, Karnataka, India. The raw bark was Sun dried for 3 days, oven dried at 80^0 C for six hours in hot air oven. Dried bark was powdered in pulverizer and washed several times with double distilled water to remove solubles, again dried in hot air oven at 60^0 C for 8 hours. The powdered bark was sieved (Indian Standard Sieve) and various fractions of adsorbent was separately stored in air tight containers.

B. Aqueous Solution

Zinc Nitrate (AR) was used to prepare stock solution. Double distilled water was used to prepare stock solution. Solutions of required concentrations were prepared using stock solution. 0.1 N HCl and 0.1N NaOH solutions were used to adjust the pH of the solutions.

C. Batch Adsorption Studies

The adsorption of zinc ions on *Pongamia pinnata* were studied in batch conditions. Adsorbent of 2 to 10 g/L was used for 2 hours with 100 mL of each aqueous solution in the range of 10 to 100 ppm. The pH was maintained from 2 to 8 and agitation of 200 rpm at room temperature. The mixture was then filtered and analyzed for the cation content. The zinc concentrations in solutions were determined using atomic absorption spectrophotometer. The amount of metal ions adsorbed onto adsorbent was calculated from the difference between the initial and final concentrations of the solutions. The spectral analysis of the bark shows the presence of 8 compounds which are degraded by microorganisms. [14]

III. RESULTS AND DISCUSSIONS

A. Adsorption Characterization

The SEM photograph as shown in Fig 1 shows progressive changes in the surface of the adsorbent. The number of active sites available for adsorption increases as the surface area increases.

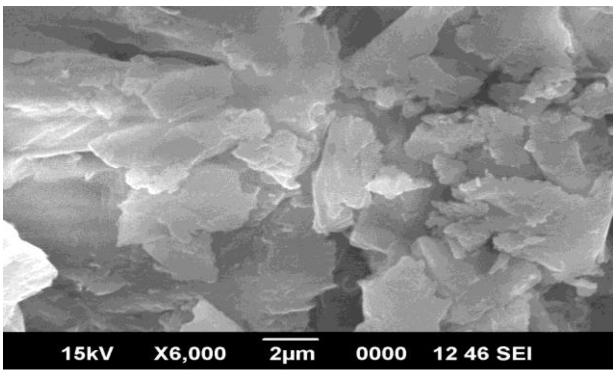

Fig.1. SEM Photograph of *Pongamia pinnata* tree bark

B. Effect of pH

The present study was investigated with solutions of 25 ppm initial concentration to 100 ppm solution. This estimation was most reliable at pH values when no hydroxide precipitation occurred. Hence, the zinc adsorption on prepared adsorbent was studied in the range of pH 2– 8.The effect of initial pH on adsorption of zinc ions is shown in Fig. 1.

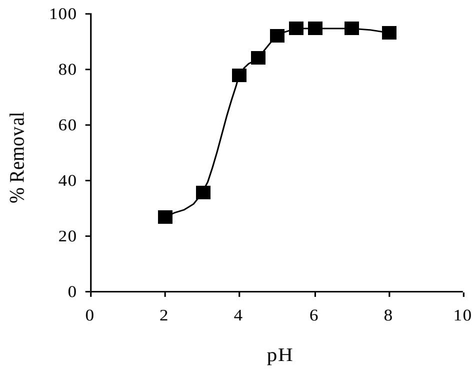

Fig. 2 Effect of pH on zinc adsorption

As shown in Fig. 2, the smallest percentage of zinc removal was found at pH 2. The retention percentage then slowly increased until to 80% in the initial pH range 2-4. At pH higher than 5, the increase of adsorption attained 95%. This behaviour was due to variation of the charge of the adsorbent as function of pH. The metal ion uptake with increase in pH was due to the negative charges at the active sites on the surface. These results are in good agreement with other literature [6] that showed the competitive adsorption with H^+ as predominant mechanism of heavy metal ions removal.

C. Effect of Zinc Concentration in Initial Solution

The amount of zinc adsorbed on adsorbent increased with decreasing initial metal ion concentrations in solutions as shown in Fig.3. Lower initial concentrations might be closely associated with number of available binding sites, thus resulting in an enhancement of the metal uptake. As the total active sites on the adsorbent decreases the access of heavy metal ions consequently decreased the adsorption percentage.

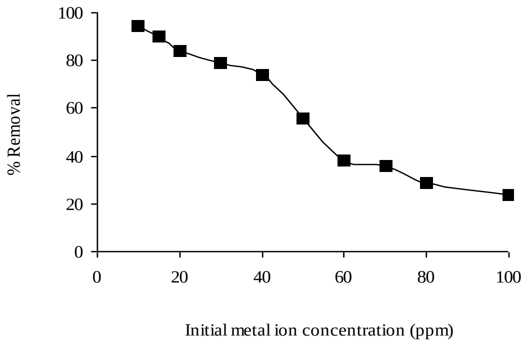

Fig. 3 Effect of initial metal ion concentration in solution

D. Effect of Amount of Adsorbent

As the amount of adsorbent increased from 2.5 to 10 g/L, the amount of zinc adsorbed also increased as shown in Fig. 4. The surface area available for adsorption increases to a large extent for the metal ion to adsorb into the active sites. As the amount of adsorbent increased, the time taken for adsorption is also less as the metal ions come in contact with the active sites without any competition. Zinc ions having the ionic radius of 0.074 nm very easily adsorb onto the adsorbent in this case.

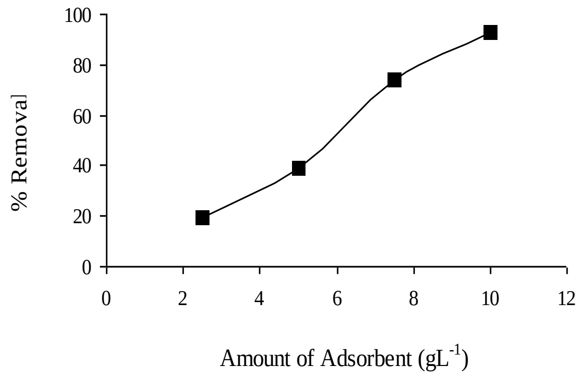

Fig. 4 Effect of amount of adsorbent

E. Effect of Contact Time

The effect of contact time on the amount of zinc ions on adsorbent surface is as shown in Fig.5. Equilibrium conditions have established at 50 minutes. The vacant sites are saturated within 40 min and further there was no change in adsorption level.

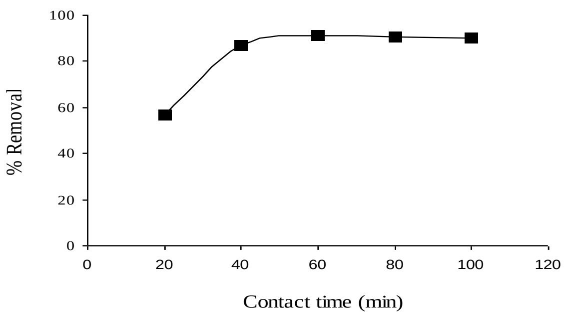

Fig. 5 Effect of contact time

F. Adsorption in Waste Water

Raw effluent was collected from a local industry, filtered and analysed for various heavy metals in it. The water consisted of Zinc, Iron, Copper and Nickel. When this water was treated with *Pongamia pinnata* adsorbent, interference of the metal ion on one another was observed. Zinc removal up to 70% was observed when 100mL sample at pH 5 was treated with 5g/L of adsorbent within 30 min at agitation of 200 rpm. When compared to aqueous solution the adsorption percentage was less showing the interference of other metal ion present in the effluent. The interference can be avoided by treating the waste water at the source of individual metal ion generation itself so as to increase the adsorption levels.

G. Adsorption Isotherms

The experimental data obtained in this study were analyzed using the Langmuir isotherm model. The Langmuir isotherm is expressed as shown in equation (1). The validity of the Langmuir equation assumes a monolayer sorption of zinc on a surface containing a finite number of vacant sites.

$$q_e = \frac{q_m C_e}{K_d + C_e} \quad (1)$$

On rearrangement of (1) to linear form as (2)

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{K_d}{q_m} \quad (2)$$

Where C_e (mg/L) is the equilibrium concentration of zinc ions in solution, q_e (mg/g) the adsorption capacity at equilibrium, q_m (mg/g) the maximum adsorption capacity and K_d is the effective dissociation constant. The values of q_m, K_d and correlation coefficient estimated for adsorption of zinc are as shown in Table I. The values shown in Table I allow the conclusion that the adsorption of zinc ions on *Pongamia pinnata* is very well described by means of Langmuir adsorption isotherm (R^2 >0.99).

TABLE I
LANGMUIR ADSORPTION ISOTHERM VALUES

q_m (mg/g)	K_d	R^2
41.7	8.5	0.9996

H. Adsorption Kinetics

The adsorption kinetics involved in the adsorption of zinc ions onto Pongamia pinnata were applied on two models namely, the pseudo first order and pseudo second order model. For the adsorption of zinc ions from liquid solutions, pseudo first order model is used as in equation (3).

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (3)$$

Where q_e is the mass of metal ion adsorbed at equilibrium (mg/g), q_t is the mass of metal adsorbed at time t (mg/g), K_1 is the first order reaction rate constant (min^{-1}).

Pseudo second order model is as shown in the equation (4)

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where K_2 is the second order reaction rate constant (g/mg. min). The Parameters of both the kinetic models are as shown in Table II.

TABLE II
PARAMETERS OF KINETIC MODELS

Metal ion	First order		Second order	
	R^2	K_1	R^2	K_2
Zinc	0.9965	0.048	0.9887	1.25

The values of R^2 show that pseudo first order model suits the adsorption of zinc when compared to pseudo second order indicating the feasibility of *Pongamia pinnata* as a viable adsorbent in waste water treatment.

IV. CONCLUSIONS

Pongamia pinnata used in this study is easily available and preparation does not involve activation of the bark. The only added costs are for size reduction and drying. The problem of sludge disposal was minimal as a number of microorganisms are proven to degrade the components of *Pongamia pinnata* bark after adsorption. The study reveals that the adsorbent has high affinity toward the zinc ions.

The optimum pH value of the initial solutions is in the range from 5 to 5.4. The amount of zinc adsorbed increases with decreasing initial concentrations of solutions. The adsorption rate, expressed as time variation of the retained ions is high, especially in the initial stage of the process. The equilibrium distribution of zinc between the adsorbent and solution was described by using the Langmuir model showing mono layer adsorption.

The results indicate that this adsorbent also fits for pseudo first order kinetics, but when waste water from industry was considered interference played a major role in the binding of metal ions. The order of metal ion uptake depended on type of metal ion competing with zinc ions.

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