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Equilibrium and Kinetic Studies of Zinc (II) Ion Adsorption from Aqueous Solution by Modified Soybean Hulls

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Abstract:- Water used in industries creates a wastewater that has potential hazards for our environment, because of introducing various contaminates such as heavy metals in to soil and water resources. In this study, a modification method was adopted to enhance metal ion adsorption on soybean hulls using NaOH and citric acid. The batch experiments were carried out to optimize parameters like pH, adsorbent dose, initial concentration and contact time. Equilibrium data were best represented by Freundlich isotherms. The adsorption kinetic data were adequately fitted to the pseudo-second order kinetic model. At optimum conditions of the parameters investigated, 99% removal of Zn (II) was achieved. On the basis of experimental results MSH was found to be an excellent adsorbent for the Zn (II) removal from wastewater.
Keywords: - Adsorption, Citric acid, Modified Soybean hulls, Sodium Hydroxide, Zinc Ion Solution

I. INTRODUCTION

Population explosion, haphazard and rapid urbanization, industrial and technology expansion, energy utilization, waste generation from domestic and industrial sources have rendered many waters unwholesome and hazardous to man and other living resources. There is no strict implementation of laws and guide lines of environment pollution in India. Hence many industries discharge untreated and inadequately treated wastewater in to water ways. Toxic metals are often discharged by a number of industrial processes and this can lead in turn to the contamination of fresh water and marine environment (1). Heavy metals are major pollutants in marine ground, industrial and even treated wastewater (2). Industrial waste constitutes the major source of various kinds of metal pollution ion natural water. The important toxic metals zinc, cadmium, nickel and lead find their way to the water bodies through wastewater (3). The release of large quantities of heavy metals into the natural environment e.g. irrigation of agricultural field by using sewage has resulted in a number of environmental problems (4,5) and due to their non-biodegradability and persistence can accumulate in the environment elements such as the food chain, and thus may pose a significant danger to human health. Many methods have been proposed such as precipitation, sedimentation, membrane processes, biological processes, ion exchange, electrodespostion, chemical reduction and adsorption. All these methods have their merits and limitations in application but adsorption is an effective purification and separation technique used in industry especially in water and wastewater treatment (6). The effective adsorbents reported for the removal of heavy metal ions are tea leaves carbon (7) saw dust (8), fly ash (9), peat (10), linseed flax straw (11), wheat rice (12), rice husk (13) and activated carbon prepared from agro waste (14). One promising option is the use of easily available soybean hulls that may serve as potential adsorbents for removal of heavy metals ions.

II. MATERIALS AND METHOD

2.1 Method to Modify Soybean Hulls

The soybean hulls were collected locally from Ujjain (M.P.). The Malwa region of M.P. has ample source of soybean hulls.In this study soybean hulls has been washed, rinsed with distilled water and then dried. After drying hulls was ground and screened (20 mesh). Powder soybean hulls are now treated with 0.5 M NaOH. The slurry was stirred at 100 rpm for 60 min and rinsed with distilled water. The moist hulls were added to 200 ml of distilled water and stirred at 100 rpm for 30 min to remove the excess NaOH. This procedure was repeated three times to ensure removal of NaOH. The soybean hulls were blended with 0.1M citric acid in a proportion of 1.0 g of soybean hulls to 7.0 ml citric acid. The citric acid/ soybean hulls slurry was dried overnight at 50˚C. The acid-modified soybean hulls were then cleaned by washing with distilled water and filtered. Finally, the modified hulls were dried overnight at 50˚C.

2.2 Reagents and Equipments

Certified Atomic Absorption Spectrophotometer standard stock solutions of Zn (II) were prepared by dissolving reagent AR grade $ZnSO_4.7H_2O$ (500 mg/l) respectively. Standards for the establishment of calibration curves for AAS were prepared as follows:

Make up 20, 40, 60, 80 and 100 mg/l standard of Zn (II) by diluting 4, 8, 12, 16 and 20 ml of the 500 mg/l standard solution to 100 ml (using a 100 ml volumetric flask).

Table 1: Operating conditions for the AAS

Metal	Lamp Current (mA)	Wavelength (nm)	Flame Gases	Slit Width (nm)
Zinc (II)	15	213.9	Air-acetylene	0.7

2.3 Batch Adsorption Experimentation

Batch experimentation were carried out at room temperature (25±1)˚C to study the effects of important parameters such as pH, contact time, initial concentration and amount of adsorbent. Batch mode was selected due to its simplicity and reliability (15). Prior to each experiment, a predetermined amount of adsorbent was added to each flask. The stirring was kept constant (100 rpm) for each run throughout the experiment to ensure equal mixing. The pH of synthetic wastewater solution was adjusted by 0.1 M NaOH and 0.1 M HCl. Each flask was filled with 100 ml of sample having desired pH before commencing stirring. The flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered through Whatman filter paper 42 and then the supernatant solution in each flask was analyzed by Atomic Absorption Spectrophotometer (AA-6300 SHIMADZU) for residual metal content. Langmuir and Freundlich isotherm models were tested to the adsorption data and their constants were evaluated. The experiments were carried out under different experimental conditions are shown in Table 2.

Table 2 : Ranges of system parameters studies for batch experiments for the removal of Zn (II).

Sr.No.	Parameters	Units	Ranges Undertaken
1	Initial Adsorbate Concentration	mg/l	20-100
2	Adsorbent Dose	g/l	01-10
3	pH	-	2.0 -9.0
4	Contact Time	Minutes	10 – 140

III. RESULT AND DISCUSSION

3.1 Effect of pH

The effect of pH on adsorption of Zn (II) ion is shown in Fig. 3.1. The highest removal for Zn (II) adsorption with MSH was obtained at pH 5.0. At lower pH values, the adsorption efficiency was decreased due to presence of H^+ ions competing with zinc cation for adsorption sites. At higher pH zinc hydroxyl species may participate in the adsorption and precipitate onto MSH and attribute reduction in percentage removal.

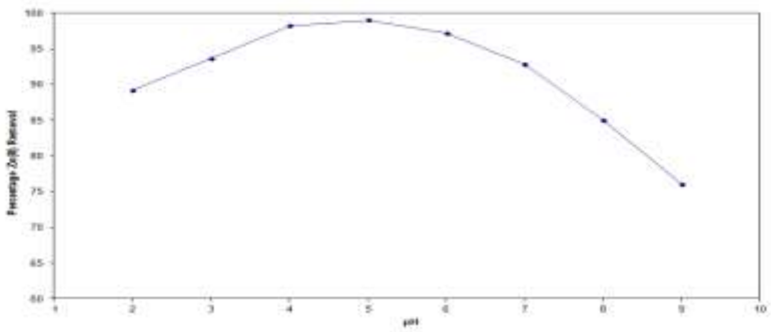

Fig.3.1 : Effect of pH on Adsorption of Zn (II) onto MSH Concentration of Zn (II) 20 mg/l Contact Time 120 Minutes Dose 8 g/l at Room Temperature (25±1)°C

3.2 Effect of Adsorbent Dose

Adsorbent dose is representing of important parameter due to its strong effect on the capacity of an adsorbent at given initial concentration of adsorbate. Effect of adsorbent dose on removal of Zn (II) ion was monitored by varying adsorbent dose from 1.0 g/l to 10.0 g/l. The adsorption of Zn (II) ion increased with the adsorbent dose upto 7.0 g/l. After 7.0 g/l, very slight increase in adsorption was observed and system reached to equilibrium after 8.0 g/l of adsorbent (Fig. 3.2). As one was expected, the percentage of Zn (II) ion removal increased with increasing amount of MSH, however the ratio of Zn (II) ion adsorbed to MSH (mg/g) decreased with increasing amount of adsorbent MSH.

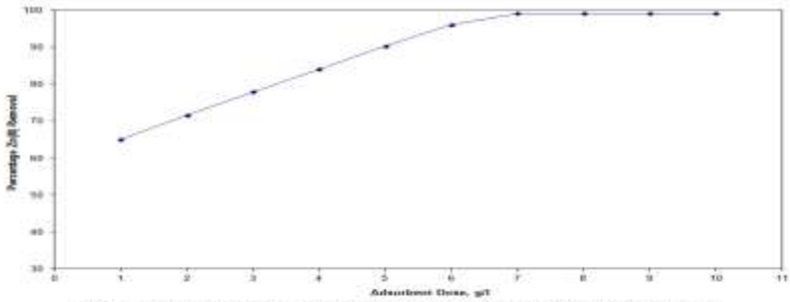

Fig.3.2 : Effect of Adsorbent Dose on Removal of Zn(II) for Concentration 20 mg/l and 120 Minutes Contact Time at pH 5.0

3.3 Effect of Initial Concentration and Contact Time:

The effect of contact time and initial concentration (20 to 100 mg/l) of Zn (II) ion adsorption on to MSH is presented in Fig.3.3. A rapid removal is observed at the initial stages and it then proceeds slowly until reached equilibrium. This may be due to the availability of number of vacant adsorption sites at initial stage. The equilibrium adsorption capacity of MSH is increased from 2.50 mg/g to 9.67 mg/g as increasing concentration from 20 to 100 mg/l. It was significant different with percentage removal that decreased from 99.0% to 77.4% as initial concentration increased. At lower metal ion concentration, the available adsorption sites are relatively high and consequently the dye species can find easily the accessible adsorption sites. However, at higher concentrations the available site of adsorption become fewer and consequently the metal ions take more time in order to reach the last available sites. Furthermore, the adsorption dynamic profile shows that equilibrium has been reached in 120 minutes.

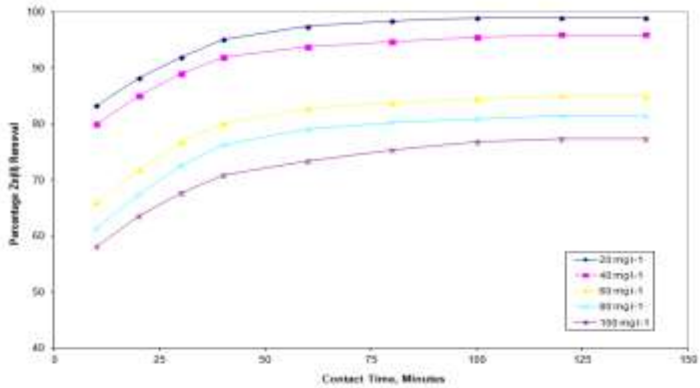

Fig 3.3 : Effect of Contact Time and Initial Zn (II) Concentration on Percentage Removal of Zn (II) onto MSH

3.4 Isotherm Modeling

The adsorption isotherm represents the relationship between the amount adsorbed by a unit weight of solid adsorbent and the amount of adsorbate remained in the solution at equilibrium time (16). Langmuir and Freundlich isotherms were used to describe the equilibrium adsorption. Langmuir isotherm (17) refers to homogeneous monolayer adsorption where as the linear form of the Freundlich isotherm (18) model is derived by assuming a heterogeneous surface of adsorption capacity and adsorption intensity with a non uniform distribution of heat of adsorption. The equation for these models are given as Langmuir isotherm

$$C_e / q_e = 1/q_{max}K_L + (1/q_{max})\, C_e \qquad \text{……… 3.1}$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration (mg/l) and q_{max} and K_L are the Langmuir isotherm constants related to free energy. The above equation can be linearized to get the maximum capacity, q_{max} by plotting a graph of C_e/q_e Vs C_e . Freundlich isotherm

$$q_e = K_f\, C_e^{\ 1/2} \qquad \text{………. 3.2}$$

On rearranging this equation we get

$$\log q_e = \log K_f + 1/n \log C_e \qquad \text{………..3.3}$$

where K_f and 1/n are Freundlich isotherm constants related to adsorption capacity and adsorption intensity respectively. A plot of log q_e vs log C_e yields a straight line with a slop of 1/n and intercept log K_f. The Langmuir and Freundlich adsorption isotherms of Zn (II) ion on MSH are shown in Figs. 3.4 and 3.5. Table 3 gives the values of parameters and correlation coefficient of the Langmuir and Freundlich equations.

Table 3: Langmuir and Freundlich isotherms parameters associated with adsorption of Zn (II) onto MSH

Langmuir Equation			**Freundlich Equation**		
q_{max}	K_L	r^2	K_f	1/n	r^2
9.80	0.46	0.9593	3.92	0.271	0.9812

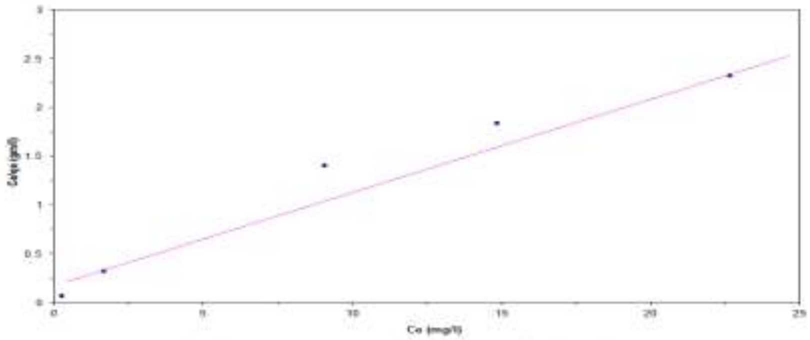

Fig.3.4 : Langmuir Isotherm for Adsorption of Zn (II) on MSH

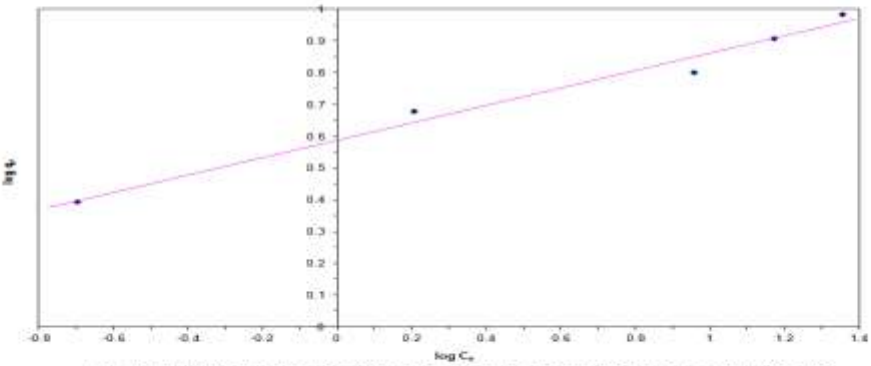

Fig.3.5 : Freundlich Isotherm for Adsorption of Zn(II) on MSH at Room Temperature (25±1)°C

3.5 Adsorption Kinetics

The pseudo-second order adsorption kinetic rate equation as expressed by (19) is :

$$t/q_t = 1/h_o + 1 / q_e (t) \quad ..………3.4$$

Thus, from Equation (3.4) plots of (t/q) vs. t were made and the values of q_e and K_2 determined from the slopes and intercepts respectively. The sorption data obtained when the type of metal ion and its initial concentration was varied as shown in Fig. 3.6. The constants in Equation 3.4 are derived. These constants are summarized in Table 4 and Fig. 3.6. The experimental points are shown together with theoretical generated graphs. The agreement between the sets of data reflects extremely high correlation coefficients. These trends show typical sorption kinetics of metal ions onto chemical modified soybean hulls (MSH)). In other words, the data showed good compliance with proposed pseudo-second order equation. The data also showed that the initial metal ion concentration influenced the contact time necessary to reach equilibrium. The adsorption capacity increased for the higher initial metal ion concentrations. The values of the initial sorption rates, h_o, were determined by using the values of the intercept of the straight lines plotted in Fig. 3.6. The values of rate constant, K_2, were found to increase for a decrease in initial metal ions concentration. The kinetic studies showed that the adsorption rates could be described well by a pseudo-second expression. These results are on similar lines to previous works (20, 21, 22).

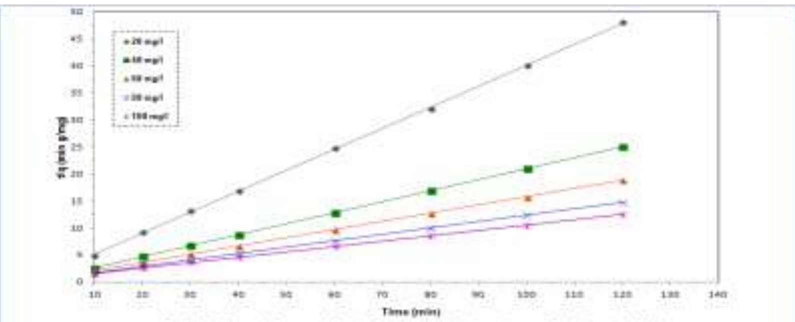

Fig.3.6 : Pseudo-Second Order Plot for the Adsorption of Zn (II) onto MSH

Table 4 : Adsorption of rate constants and coefficients of correlation associated with the pseudo-second order kinetic model using MSH

Metal	C_o (mg/l)	q_e (mg/g)	K_2	h_o (mg/g. min)	r^2
Zinc (II)	20	2.05	0.083	0.351	0.9991
	40	3.84	0.036	0.545	0.9998
	60	5.14	0.024	0.638	0.9994
	80	6.25	0.018	0.715	0.9990
	100	7.00	0.016	0.815	0.9996

IV. CONCLUSION

Citric acid modified soybean hulls can be used successfully for the removal of Zn (II) ion from aqueous solution. The optimum pH was found to be 5.0. This is due to the increase in carboxyl group implanted on to the hulls by reaction with citric acid. Citric acid treatment greatly increased total negative charge. The Zn (II) efficiency was found to be 99% and the concentration of Zn (II) was reduced below the industrial standard. Soybean Hulls are easily available in the Malwa region of Madhya Pradesh in plenty thus can be successfully used to develop inexpensive adsorbent. Data reported here should be useful for the design of batch or stirred tank flow reactors which can be used in small scale industries for treatment of heavy metal laden effluent.

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