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Adsorption Studies of Zn (II) Ions from wastewater using Calotropis procera as an adsorbent

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Abstract - Zinc is an essential mineral of "exceptional biologic and public health importance"2. Zinc is an essential trace element, necessary for plants, animals, and microorganisms. Zinc deficiency affects about two billion people in the developing world and is associated with many diseases4.In children it causes growth retardation, delayed sexual maturation, infection susceptibility, and diarrhea1. Treatment of zinc from polluted water and wastewater has received a great deal of attention. Adsorption technique is one of the most technologies for the treatment of polluted water from zinc 3, but seeking for the low-cost adsorbent is the target of this study. Removal of zinc was studied using adsorbent prepared from Calotropis procera leaves. Batch adsorption experiments were performed by varying adsorbate dose, pH of the metal ion solution and contact time. Adsorption of Zn (II) is highly pH-dependent and the results indicate that the maximum removal (75.2%) took place in the pH range of 6 and initial concentration of 60 ppm. Kinetic experiments revealed that the dilute Zinc (II) solutions reached equilibrium within 105 min. The adsorbent capacity was also studied. The zinc adsorption followed both the Langmuir6and Freundlich's equation isotherms5. Comprehensive characterization of parameters indicates Calotropis procera to be an excellent material for adsorption of Zn (II) ions to treat wastewaters containing low concentration of the metal.

Key words: Wastewaters, Zinc, Adsorption, Adsorption isotherms, Calotropis procera

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Introduction:

Removal of heavy metals from industrial wastewater is of primary importance. This is because contamination of wastewater by heavy metals is a very serious environmental problem. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders[2]. Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies and are also toxic to many life forms[4]. According to the World Health Organization (WHO)[7], the metals of most immediate concern are Aluminum, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc, Cadmium, Mercury and Lead. These heavy metals have harmful effect on human physiology and other biological systems when they exceed the tolerance levels. Zinc is an element commonly found in the Earth's crust. It is released to the environment from both natural and anthropogenic sources; however, releases from anthropogenic sources are greater than those from natural sources. Zn has many commercial and industrial uses[11]. The primary industrial use of Zn is as a corrosion resistant coating for Fe and steel. Zinc is most often found in plating, galvanizing and roller coating operation. In plating shops, the Zn is often complexes with cyanide and the cyanide must be treated to free the Zn before precipitation can occur. Exposure of Zn in large amounts is extremely toxic to living organisms. In humans, it can cause a range of serious ailments including anemia, damage to pancreas, lungs, metal fume fever, decreased immune functions, ranging from impaired neuropsychological functions, growth retardation and stunting, impaired reproduction, immune disorders, dermatitis, impaired wound healing, lethargy, loss of appetite and loss of hair[10].

The aim of this research is to develop an inexpensive and effective metal ion adsorbent from plentiful natural waste sources, such as Calotropis leaves, and to explain the adsorption mechanism taking place.

MATERIALS AND METHODS

Preparation of Activated Charcoal from Calotropis Procera (AC-CP):

The naturally dried leaves of the plant Caltrops procera were obtained locally. It was cut into small pieces. The leaves were treated with concentrated sulphuric acid (five times its volume) and kept in oven at 150°C for 24 hours. It was filtered and washed with distilled water repeatedly to remove sulphuric acid (washings tested with two drops of Barium chloride solution) and finally dried. This material was used as adsorbent for removing metals.

Physical Characteristics of adsorbent (Table:-1)

Particle Size	40-60 mesh size
Solubility in water	Nil
Solubility in 1N HCl	Nil
Bulk Density	0.431

Zinc sulphate solution: A stock solution of aqueous solution of Zinc (II) was obtained by dissolving 0.4404 g of AR grade Zinc Sulphate in 1000ml of double distilled water to give 100 ppm solution

Batch adsorption studies-

Known isotherm models like Freundlich[5] and Langmuir[6] isotherm fit the adsorption equilibrium data of metals used on various low cost adsorbents.

Langmuir isotherms

Irving Langmuir, an American chemist who was awarded the Nobel Prize for chemistry in 1932 for "his discoveries and researches in the realm of surface chemistry", developed a relationship between the amount of gas adsorbed on surface and the pressure of that gas. Such equations are now referred to as Langmuir adsorption isotherms, theoretical adsorption isotherms in the ideal case. The Langmuir adsorption isotherm is often used for adsorption of a solute from a liquid solution. The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and is often expressed as:

$Q= Q_obCe/(1+bCe)$ (Casey, 1997)[15]

Where:

Q is the adsorption density at the equilibrium solute concentration Ce (mg of adsorbate per g of adsorbent)

Ce is the concentration of adsorbate in solution (mg/l)

Q_o is the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent)

b is the Langmuir constant related to energy of adsorption (l of adsorbent per mg of adsorbate)

The above equation can be rearranged to the following linear form:

$Ce/Q= 1/Q_ob + Ce/Q_0$

The linear form can be used for linearization of experimental data by plotting Ce/Q against Ce. The Langmuir constants Q_0 and b can be evaluated from the slope and intercept of linear equation. Separation factor or equilibrium parameter R_L that defined as (Waber and Chakrobroty, 1974):

$R_L= 1/(1+b\ C_0)$

Values of dimensionless equilibrium parameter R_L (0.99614) show the adsorption to be favorable ($0< R_L<1$). More ever the higher correlation cofficent value (R^2=0.997) confirmed the suitability of the modal.

Freundlich Adsorption Isotherm:

Herbert Max Finley Freundlich, a German physical chemist, presented an empirical adsorption isotherm for nonideal systems in 1906. The Freundlich equation is used for heterogeneous surface energies in which the energy term, Q_o in the Langmuir equation varies as a function of the surface coverage, q_e strictly due to variations in the heat of adsorption.

$$q_e = K_f\ (Ce)^{1/n}$$

The linear form of the equation or the log form is

$$\text{Log } q_e = \log K_f + 1/n \log C_e$$

K_f and n are Freundlich constants; n gives an indication of the favorability and k_f the capacity of the adsorbent. . The values of 1/n, less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentrations and vice verse. The higher the K_F value, the greater the adsorption intensity. The value of 1/n, less than unity was obtained mostly for the AC-CP. Also the K_f value, the greater the adsorption intensity. Present study verifies value of 1/n (0.6380) & value of K_f (2.46332) from table (1).

The equilibrium concentration was calculated using following formula

$$C_e = C_0 – (\%\text{ adsorption x } C_0 / 100)$$

The amount of metals adsorbed per unit weight of an adsorbent 'q' was calculated using following formula

$$q = (C_0 – C_e) \text{ x } V /m$$

Where C_e is the equilibrium concentration (mg/l) and q_e the amount adsorbed (mg/g) at equilibrium time; C_0 is the concentration (mg/l), m is the mass of the adsorbent (gm) and V is the volume of the solution (L)..

The correlation coefficient (R) for Freundlich and Langmuir isotherms are merely equal. The correlation coefficient (R^2) for Freundlich (0.990) & Langmuir (0.997) were obtained from Table (2). Therefore for the present adsorption study it can be stated that Freundlich and Langmuir adsorption equations are found to be better fitted. ($R^2 \approx 0.999$)

Experimental conditions;

Effect of contact time:-

In adsorption system, the contact time play a vital role irrespective of the other experimental parameters, affecting the adsorption kinetics. Figure 1 depicts that there was an appreciable increase in percent removal of Zinc up to 105 min. thereafter further increase in contact time the increase in removal was very small. The amount of metal adsorbed at various intervals of time indicates that the removal of metal initially increases with time but attains equilibrium within 105 minutes. The adsorption process was found to be very rapid initially, though it was observed that adsorption of metal increased in metal concentration in the solution. But as a whole the % remove decreases with increase in metal concentration as observed in the plot. Thus the effective contact time (equilibrium time) is taken as 105 min. and it is independent of initial concentration. (60ppm)

Effect of pH:

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It affects both the surface charge of adsorbent and the degree of ionization of the heavy metal in solution. The role of Hydrogen ion concentration was observed at different pH 3-8. The influence pH of solution on the extent of adsorption of adsorbent material used is shown in figure-2 .The removal of metal ions from solution by adsorption is highly dependent on the pH of the solution. The adsorption of Zn (II) at conc. Of 60 ppm is minimum at lower pH 3(32.9%), it increases with increase in pH up to 6 (75.2%). After pH 6 it decreases pH 7=63.8%, pH 8=52.9% up to alkaline pH. Thus the optimum adsorption pH for Zn (II) removal was found to be 6.

Effect of adsorbent dose:

The effect of adsorbent dose on percent removal of Zinc is shown in Figure 3. Adsorbent dose was varied (3, 6, 9, 12, 15,18gm/l) and performing the adsorption studies at pH 6. The present study indicated that the amount of Zn (II) adsorbed on ACCP increase with increase in the ACCP dose up to 15gm/l and thereafter further increase in dose the increase in removal was very small. Thus the effective dose is taken as 15gm/l.

Conclusion: Pollution of the aquatic environment with toxic valuable metals is widespread. Consideration of the modes of purifying these contaminations must be given to strategies that are designed to high thorough put methods while keeping cost at minimum. Adsorption readily provides an efficient alternative to traditional physiochemical means for removing toxic metals[13]. In conclusion, AC-CP could be used as potential adsorbent for the removal of Zn (II) from aqueous solutions. The optimium data were found from this adsorption studies is given below in **Table-2**

Sr No.	Particular	Optimium data (AC-CP)

1	Time (min.)	105 min
2	pH	6
3	Dose (gm/l)	15 gm/l
4	Max. % removal of Metal (Zn)	75.2%

Table 3

Langmuir and Freundlich constants for adsorption of Zinc (II)

Dose (gm/l)	Freundlich isotherm (linear equation)	Langmuir isotherm (linear equation)	R^2 Freundlich	R^2 Langmuir
15	y=0.638 x-0.259	y=0.078x+3.732	0.990	0.997

Table -4

Dose (gm/l)	Freundlich constants			Langmuir constants		
	K_f	n	1/n	Q (mg/g)	b (l/mg)	R_L
15	2.46332	1.567398	0.6380	12.82056	0.0209	0.92764

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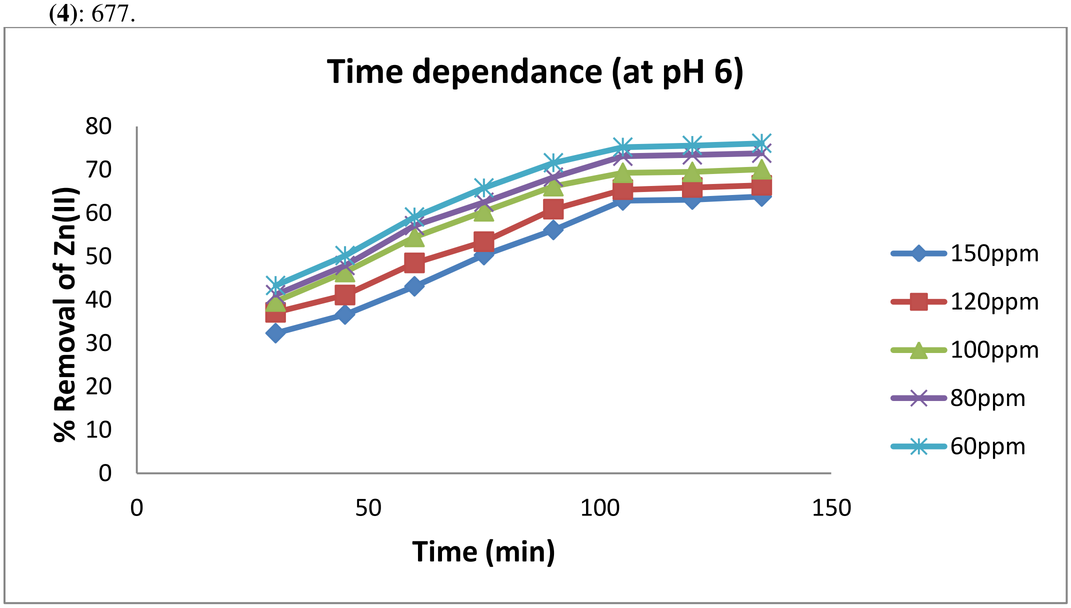

Figure 1: Effect of contact time on removal of Zn (II) at different concentration by ACCP at pH 6

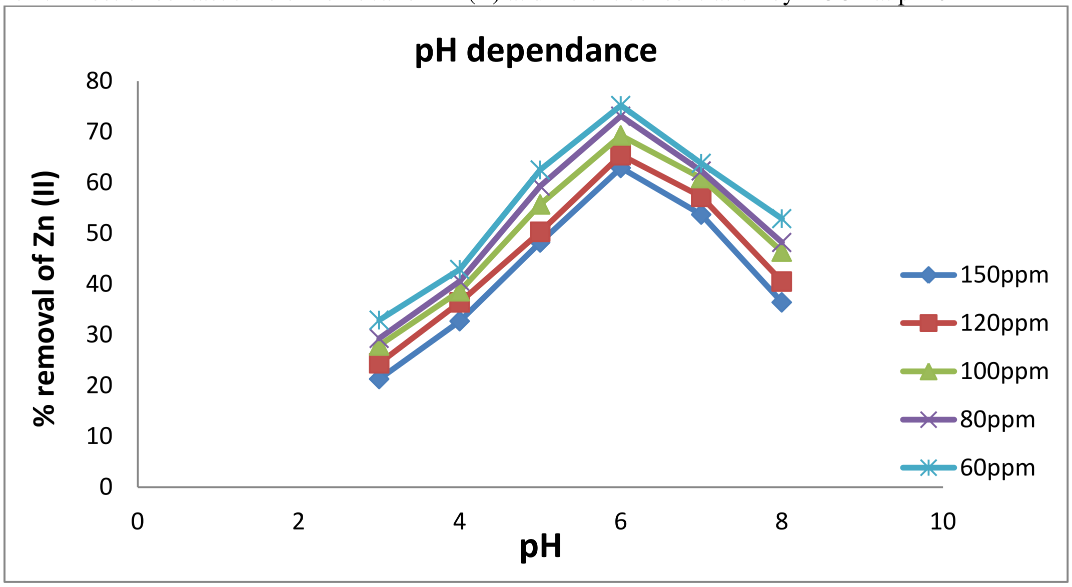

Figure 2: Effect of pH on removal of Zn (II) at different concentrations by 15g/L of ACCP at constant contact time 105 min.

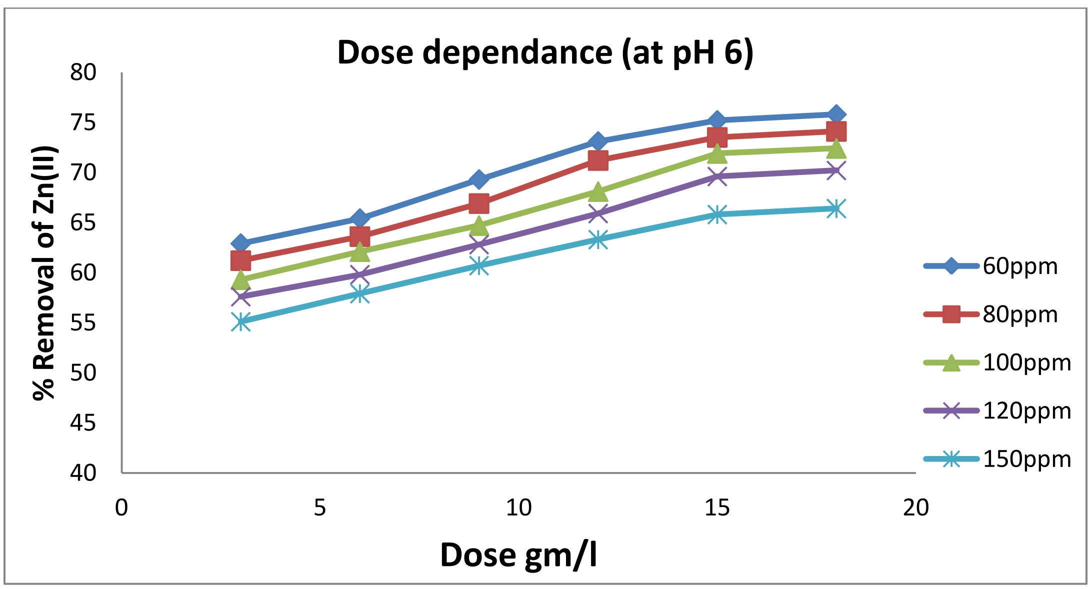

Figure 3 : Effect ACCP dose on percent removal of Zn(II) at equilibrium contact time 105 min. and effective at pH 6.

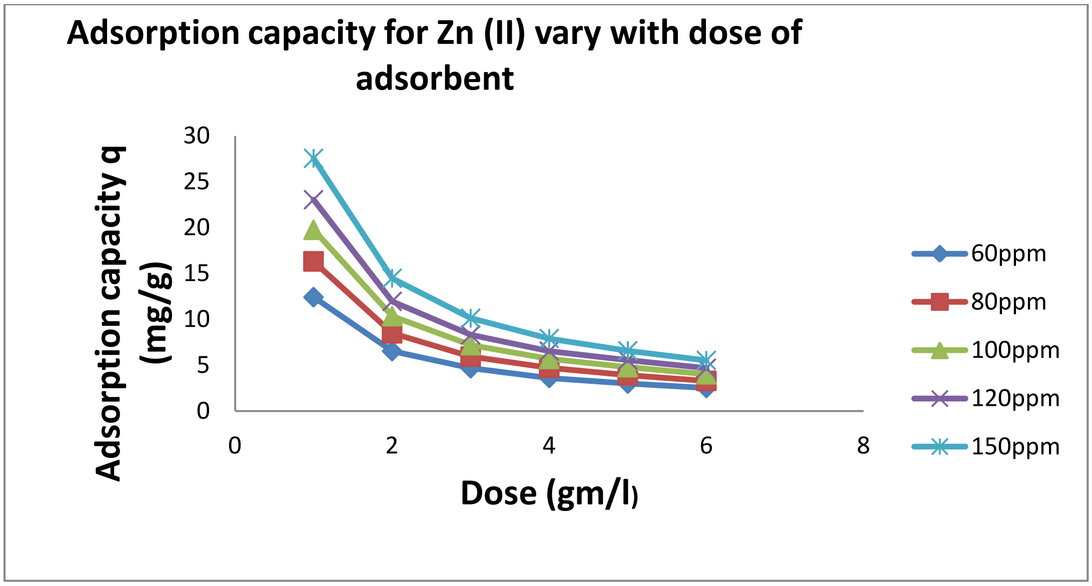

Figure 4: Effect of dose of adsorbent on adsorption capacity at equilibrium contact Time 105 and effective pH 6.

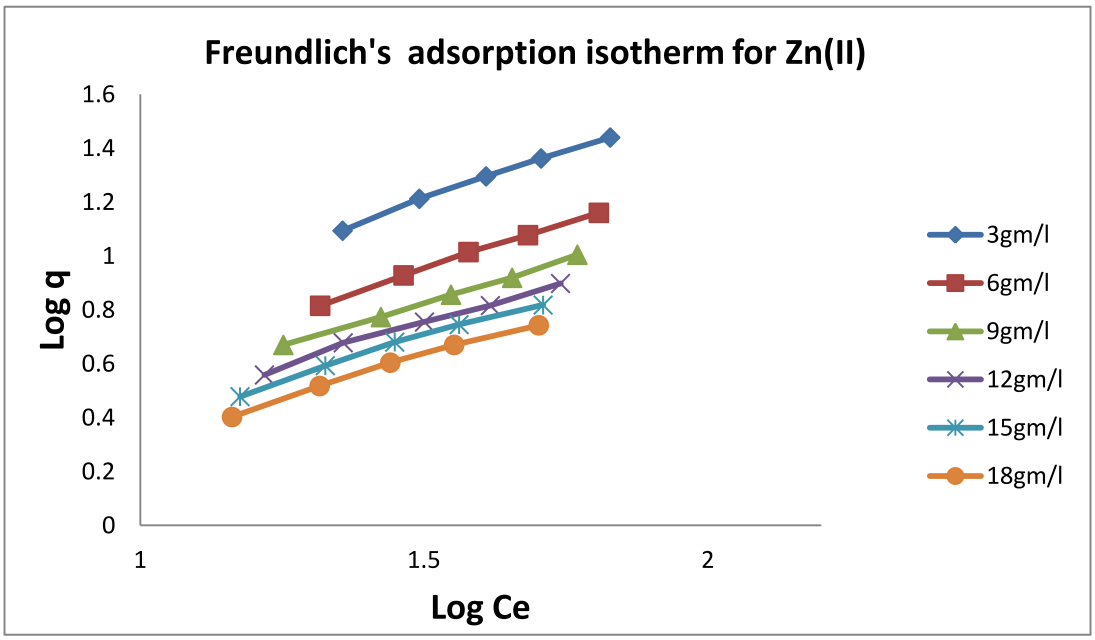

Figure 5: Freundlich Isotherm plot for Zn (II) adsorption by ACCP at optimum conditions

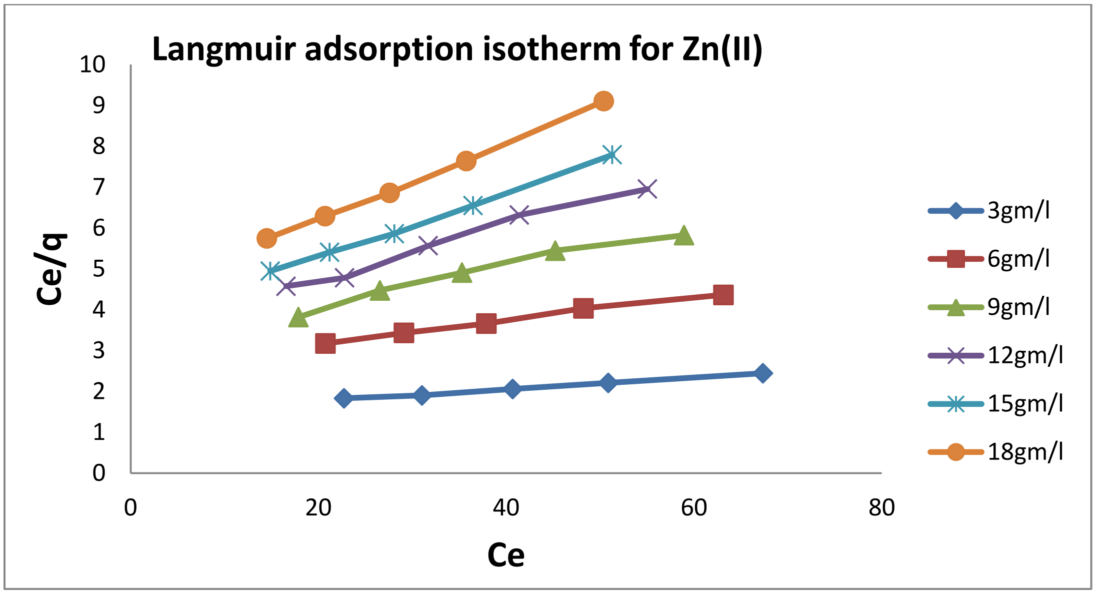

Figure 6: Langmuir Isotherm plot for Zn (II) adsorption by ACCP at optimum conditions.

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