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# Adsorption Studies of Zn (II) ions from Wastewater using Calotropis procera as an Adsorbent

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## Abstract

*Increased industrialization and human activities have impacted on the environment through disposal waste containing heavy metals. The presence of heavy metals in the environment can be detrimental to a variety of living species. Metals can be distinguished from other toxic pollutants, because these are non biodegradable, may undergo transformation, and can have a large environmental, public health, and economic impact. The presence of toxic heavy metal contaminants in aqueous streams, arising from the discharge of untreated metal containing effluents into water bodies, is one of the most important environmental issues. Zinc is an essential mineral, but too much is not beneficial. Symptoms of zinc toxicity include nausea/vomiting, fever, cough, diarrhea, fatigue, neuropathy and dehydration. Adsorption technique is one of the most important technologies for the treatment of polluted water from zinc, but seeking for the low-cost adsorbent is the target of this study. Removal of zinc studied using adsorbent prepared from poly vinyl activated charcoal of calotropis procera leaves (PVAC-CP). Batch adsorption experiments performed by varying adsorbent dose, pH of the metal ion solution and contact time. Adsorption of zinc is highly pH dependent and the results indicate that the maximum removal (85.8%) took place at dose 15gm/l in the pH range of 6 and initial concentration of 60 ppm. Kinetic experiments reveal that the dilute zinc solution reached equilibrium within 105 min. the adsorbent capacity was also studied the zinc adsorption followed both the Langmuir and Freundlich equation isotherms. Comprehensive characterization of parameters indicates that PVAC-CP to be an excellent material for adsorption of zinc ion to treat wastewater containing low concentration of the metal.*

**Keywords:** Wastewaters, adsorption isotherms, calotropis procera.

## Introduction

Industrial activities and mining operations have exposed man to the toxic effects of metals[1]. Heavy metals are present in the soil, natural water and air, in various forms and may become contaminants in food and drinking water[2]. Heavy-metal adsorption reactions, in a competitive system, are important to determine heavy-metal availability to plants and their mobility throughout the soil. It is now well established that the free metal ion concentration, which is of relevance in metal bioavailability and toxicity studies, often controlled by metal ion binding to natural organic matter[3,4]. Although zinc compounds have been use for at least 2,500 years in the production of brass, zinc wasn't recognized as a distinct element until much later. Metallic zinc first produced in India sometime in the 1400s by heating the mineral calamine ($ZnCO_3$) with wool.

Andreas Sigismund Marggraf rediscovered zinc in 1746 by heating calamine with charcoal. Today, most zinc is produced through the electrolysis of aqueous zinc sulfate ($ZnSO_4$). Treatment processes for heavy metal removal from wastewater include precipitation, membrane filtration, ion exchange, adsorption and co precipitation adsorption. Studies on the treatment of effluent bearing heavy metal have revealed adsorption to be a highly effective technique for the removal of heavy metal from waste stream and activated carbon has been widely used as an adsorbent[5,6,7]. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. 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[8].

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[9,10].

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

## Material and Methods

**Preparation of Poly Vinyl Activated Charcoal from Calotropis Procera (PVAC-CP):** The naturally dried leaves of the plant Caltrops procera obtained locally. It cut into small pieces. The leaves treated with concentrated sulphuric acid (five times its volume) and kept in oven at 150°C for 24 hours. It filtered and washed with distilled water repeatedly to remove sulphuric acid (washings tested with two drops of barium chloride solution) and finally dried. The adsorbent sieved to 40-60-mesh size and heated at 150 °C for 2 hours. 1 gm of PVA dissolved in 10ml hot water (10% solutions) as a result gel formation occurs.

Now 2.5gm of furnace black added in it to form a thick paste. This paste mixed with activated carbon obtained from the leaves of the plant Caltrops procera. Now the thick paste obtained, and then dried to form lumps. The lumps further ground into fine powder. This powder used as an adsorbing material. When 2.5gm furnace black used the results were better.

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

**Sorption isotherms:** Equilibrium studies that give the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorb ate described by adsorption isotherms which are usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. Freundlich and Langmuir isotherms are the earliest and simplest known relationships describing the adsorption equation. These two isotherms model used to assess the different isotherms and their ability to correlate experimental data.

**Langmuir Model:** The Langmuir equation derived from simple mass-action kinetic, assuming chemisorptions. This model based on two assumptions that the forces of interaction between adsorbed molecules are negligible, once a molecule occupies a site, and no further sorption takes place[11]. The saturation value reached beyond which no further sorption takes place. The saturation monolayer represented by the expression:

$$C_e/q_e = 1/Q_o b + C_e/Q_o$$

Where, $C_e$ is equilibrium concentration (mg/I), q is the amount at equilibrium time per unit adsorbent (mg/g) and Q and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively.

The essential characteristics of a Langmuir isotherm expressed in terms of a dimensionless constant separation factor or equilibrium parameter $R_L$. It defined by

$$R_L = 1/(1+bC_o)$$

Where $C_o$ is the initial adsorb ate concentration (mg/l) and b is the Langmuir constant (mg/l). Values of Dimensionless equilibrium parameter $R_L$ (0.99614) show the adsorption to be favorable ($0< R_L<1$). More ever the higher correlation coefficient value ($R^2$=0.982) confirmed the suitability of the modal.

**Freundlich Adsorption Isotherm:** The Freundlich isotherm model chooses for estimate the adsorption intensity of the sorbent towards the adsorbent[12]. It is an empirical equation employed to describe the isotherm data given by:

$$Qe = K_F (Ce)^{1/n}$$

The linear form of the equation or the log form is Log $q_e$ = log $k_f$ + 1/n log $C_eK_F$ 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 $K_F$ value, then greater adsorption intensity. The value of 1/n, less than unity obtained mostly for the PVAC-CP. Also the $K_f$ value, the greater the adsorption intensity. Present study verifies value of 1/n (0.39400) and value of $K_f$ (1.458814) from table-1.

The equilibrium concentration was calculated using following formula

$$C_e = C_0 - (\% \text{ adsorption} \times C_0 / 100)$$

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

$$q = (C_0 - C_e) \times V / m$$

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 (0.997) & Langmuir (0.982) obtained from table-2. Therefore for the present adsorption study that Freundlich and Langmuir adsorption equations found to be better fitted. ($R^2 \approx 0.999$)

## Results and Discussion

**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 (at 120 min). Thus the effective contact time (equilibrium time) 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 influence pH of solution on the extent of adsorption of adsorbent material used shown in figure-2.

The removal of metal ions from solution by adsorption is highly dependent on the pH of the solution. It was found that 85.8 % removal of Zn (II) achieved at pH 6 and thereafter the percent removal decreases with increases in pH as 7 and 8. Thus the optimum adsorption pH for Zn (II) removal 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 PVAC-CP increase with increase in the PVAC-CP dose up to 15gm/l and thereafter further increase in dose the increase in removal was very small. Thus the effective dose 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 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[12]. In conclusion, PVAC-CP could be use as potential adsorbent for the removal of Zn (II) from aqueous solutions. The optimium data found from this adsorption studies given below in table-1

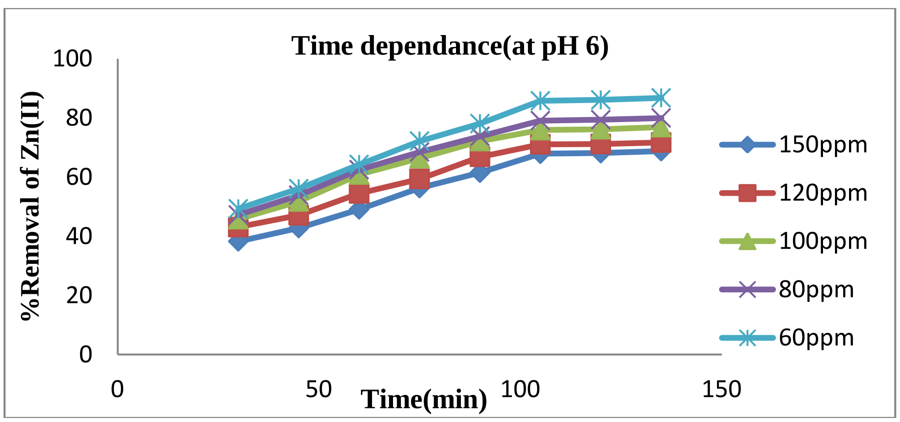


**Figure-1**
**Effect of contact time on removal of Zn (II) at different concentration by PVAC-CP at pH 6**

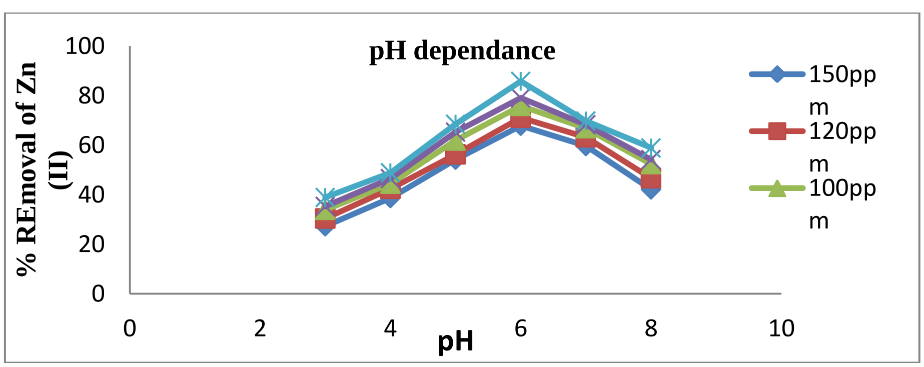


**Figure-2**
**Effect of pH on removal of Zn (II) at different concentrations by 15gm/l of PVAC-CP at constant contact time 105 min.**

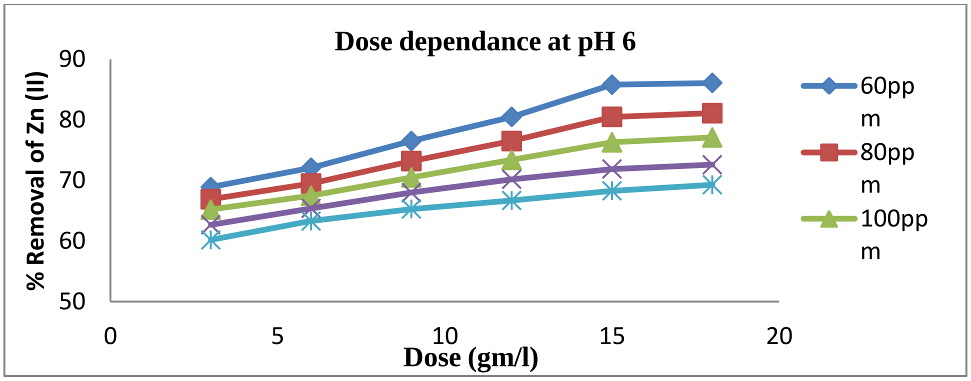


**Figure-3**
**Effect PVAC-CP dose on percent removal of Zn (II) at equilibrium contact time 105 min. and effective at pH 6.**

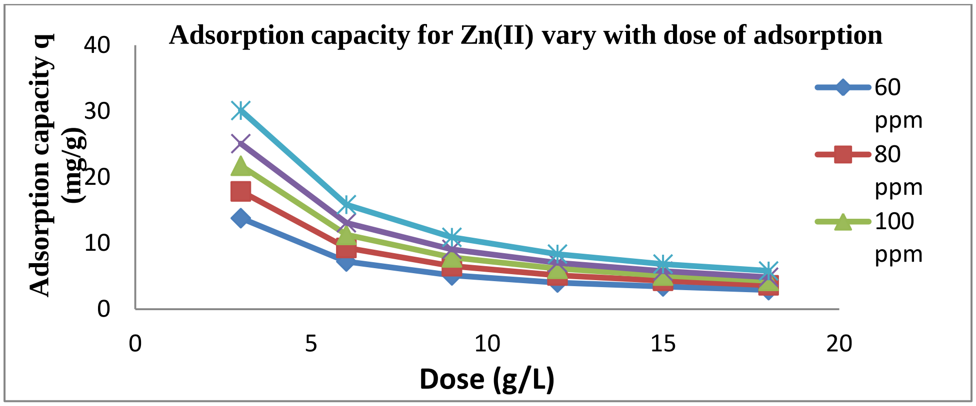


**Figure-4**
**Effect of dose of adsorbent on adsorption capacity at equilibrium contact Time 105 min and effective pH 6.**

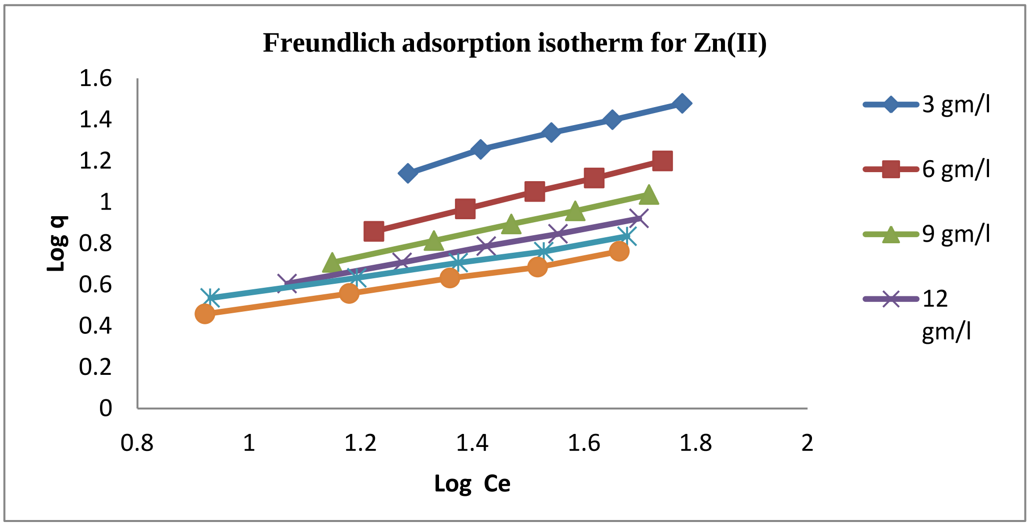


**Figure-5**
**Freundlich Isotherm plot for Zn (II) adsorption by PVAC-CP at optimum conditions**

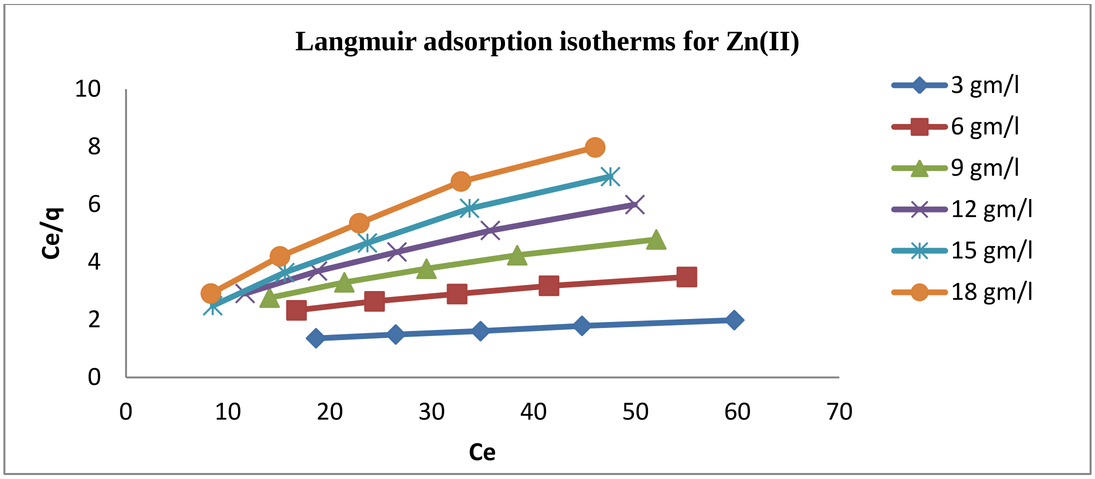


**Figure-6**
**Langmuir Isotherm plot for Zn (II) adsorption by PVAC-CP at optimum conditions.**

**Table-1**

| Sr No. | Particular | Optimium data (PVAC-CP) |
|---|---|---|
| 1 | Time (min.) | 105 min |
| 2 | pH | 6 |
| 3 | Dose (gm/l) | 15 gm/l |
| 4 | Max. % removal of Metal (Zn) | 85.8% |

**Table -2**

**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=0.394x+0.164 | y=0.0114x+1.771 | 0.997 | 0.982 |

**Table -3**

| Dose (gm/l) | Freundlich constants | | | Langmuir constants | | |
|---|---|---|---|---|---|---|
| | Kf | n | 1/n | Qm (mg/g) | b (l/ mg) | $R_L$ |
| 15 | 1.458814 | 2.53807 | 0.39400 | 8.77193 | 0. 06437 | 0.99614 |

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