ISOTHERMAL AND KINETIC STUDY OF ZINC (II) REMOVAL FROM THE AQUEOUS SOLUTION USING COUROUPITA GUIANENSIS FRUIT SHELL CARBON. (J.K. AUBLET)

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ABSTRACT

The presence of heavy metals in a trace amount in the water is highly toxic, which affects the living organism. It is mainly due to industrial and agricultural activities. Many researchers work on various methods for the removal of heavy metals from waste water. Adsorption is the effective and the low-cost method for the removal of heavy metals. The Couroupita guianensis fruit shell was acid treated and used as an adsorbent. The batch adsorption mode operation has been done using acid activated Couroupita guianensis shell carbon for the removal of Zinc (II) from the synthetic solution to investigate pH, initial concentration, contact time and adsorbent dosage. The adsorption isotherm was tested with Freundlich isotherm and Langmuir isotherm. It favours the Langmuir adsorption isotherm of R^2 is 0.9955. The adsorption Kinetics of Zinc (II) was carried out using different kinetic models and linearity was calculated. Pseudo Second order kinetics model was found to be fit in to the experimental data as calculated.

Keyword:- *Couroupita guianensis, Activated carbon, Zinc (II), Isotherm, kinetics.*

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1. INTRODUCTION

The rapid industrialization increases various chemicals and its amount discharged into the water bodies the toxic heavy metals present in the water causes several problems. Adsorption onto activated carbon has been found to be superior to other technologies. The toxic heavy metals discharged into the environment by the various industries and agricultural activities. The discharged wastewater percolates and enters into the surface and groundwater-stream and make into unfit for the domestic and drinking purposes. The discharged water which contains heavy metals greatly responsible for the serious threat to the environment and it becomes a major issue in the removal and reduction of heavy metal toxic levels. The heavy metals greatly affect the plants, animals, human beings. Many researchers used various plant materials as a low-cost adsorbent for the removal of heavy metals from the wastewater using different methods. [1]. Zinc is an essential element for all the living organisms in minute quantity, when Zinc (II) exceeds, it is highly toxic. Zn (II) is non –biodegradable in nature and accumulates on the higher level of trophic structure of an ecosystem and changes the physical and psychological order in the living organisms and also it reduces the activity of soil fertility. [2]. Therefore the removal of heavy metals discharge is the major global issue to reduce the toxic levels. The World Health Organization stated that The permissible range of Zn (II) in drinking water is 5 mg Zn^{2+}/L. [3]. *Couroupita guianensis* fruit shell was acid activated and used as an adsorbent for the removal of *Zn (II)* from the synthetic aqueous solution was carried out in this study [4]. There are various methods to remove heavy metals before discharging into the environment. Adsorption is the cost effective and eco-friendly and selective method for the removal of zinc ions from the waste waters even at very low concentration. In this study, the use of *Couroupita guianensis* acid activated carbon as a low-cost adsorbent for the effective removal of Zinc (II) from the aqueous solution its adsorptive capacity was done. [5] [6]. The influence of batch sorption parameters, such as contact time, initial metal ion concentration, adsorbent dosage, and pH. The sorption process has been described using the Freundlich and

Langmuir models. Further, the kinetics of heavy metal adsorption on the activated carbons was investigated using first-order, Pseudo first- order, Pseudo-second-order, and intraparticle diffusion model.

2. MATERIALS AND METHODS

2.1 Activated Carbon Preparation:
In this present study, *Couroupita guianensis* was used as a adsorbent for the removal of Zn (II) ions from aqueous solutions. *Couroupita guianensis* fruits were collected from the temple campus and washed with distilled water. The fruit was dried in sunlight for two weeks the shell was taken and smashed into small pieces. The dried pieces were grounded into a very fine powder in a domestic machine to increase the surface area. The finely powdered material was chemically activated by treating with the 98% concentrated Sulphuric acid and kept aside until all the fumes escapes and charred. The acid treated material carbon was kept in a hot air oven for more than 6 hrs, and then cooled. The carbonized material obtained was washed with distilled water for several times until the acid is removed .The chemically activated carbon was dried in hot air oven for 8 hours at 105 -110^oC for the removal of moisture present in it. The prepared activated carbon was grounded well and sieved in the mesh size of 250 µm. The chemically activated fine powder of carbon was put in an air tight bottle for the batch processes and kinetic studies.

2.2 Adsorbate:
Dissolving 0.4404 g of analytical grade (Merck) $ZnSO_4.7H_2O$ and 5ml of 1:1 HNO_3 using distilled water1000ppm aqueous solution of adsorbate was prepared. The concentrations of required quantity for the experiments were made from the prepared aqueous stock solution. The experiment was conducted by mixing the calculated amount of acid activated carbon for the isothermal and kinetic study.

2.3 Adsorption experiment:
The experiment was done using a magnetic stirrer at a definite temperature, and regular interval of time until the equilibrium was achieved. The solution was filtered with what man paper No 42. The filtrate was analyzed, to evaluate the concentration of Zinc (II) ions in the supernatant solution. The percentage removal of Zn (II) from the aqueous solution was calculated with the equation given below **[7].**

$$\% \text{ removal} = Ci - Cf/\, Ci \ x\ 100 \quad \text{------------------------------------} \ (1)$$

Where C_i (mg/L) the initial concentration, Cf (mg/L) the final concentration.
The adsorption of metal was calculated using the following equation:

$$qe = (Ci - Cf)V\ /\ 1000\ W \ . \quad \text{------------------------------------} \ (2)$$

Where qe (mg/g) is the adsorption capacity. V(L) is the volume of solution taken at time t, and W(g) is the adsorbent dosage, C*i* (mg/L) the initial concentration and *Cf* (mg/L) the final concentration. The extent of adsorption by the effect initial concentration of Zinc (II) from 50 mg/L to 400 mg/L. The adsorbent dosage experiments were conducted in different dosages from 0.05 to 0.6 g. and the pH of the solution varied from 2 to 8, pH was adjusted using 0.1M HCl and 0.1M NaOH solutions. The adsorption isotherm experiments were conducted at the temperature of 35^oC with the concentration of 50mg/L and pH 6.0and dosage of 600mg.

2.4 Adsorption isotherms:

Adsorption isotherms give the idea of adsorption capacity of the adsorbent and give the relationships between adsorbent and adsorbate concentration at the fixed 35^oC temperature.

Freundlich Model: This model based on the multilayer formation on the adsorbent, The first layer forms the strong bond with the adsorbent and the above layer forms vanderwaals bond. [8]. Freundlish adsorption isotherm is an empirical method has been used by the following linear equation.

$$log\ qe = log\ K + 1/n\ log\ Ce \ . \quad \text{-----------------------------------} \ (3)$$

Where *qe* = amount of metal ion adsorbed, (mg/g) *Ce* = equilibrium concentration of adsorb ate (L). The graph is plotted between *log qe* Vs *log Ce* from the intercept and slope. K and n was found out. K is the Freundlich adsorption capacity constant and n is the Freundlich adsorption intensity constant are calculated.

Langmuir Model: This model is based on the monolayer on the adsorbent. [9]. The Langmuir isotherm model equation has been used by the following equation.

$$Ce/qe = 1/Qob + Ce/Qo \quad \text{--} \ (4)$$

Where, Ce = equilibrium concentration (mg/L), qe = the equilibrium amount per unit adsorbent (mg/g).

b and Qo are Langmuir constants. The graph is plotted between Ce/Qe Vs Ce from the slope and intercept, *b* and Qo constants are calculated. R^2 value of Zinc (II) onto activated carbon was found out. The maximum adsorption capacity of Langmuir follows the isotherm model [10].

The adsorption process are confirmed by R_L factor

$$R_L = 1/\ (1 + b\ Ci) \quad \text{--} \ (5)$$

Here, b is the Langmuir constant, C_i is the initial concentration.

3. RESULT AND DISCUSSION

3.1 Effect of contact time:
The Chart-1. Showed that there was an appreciable increase in percentage removal of Zinc (II) up to 30 min. hereafter further increase in contact time, the increase in removal was very small (at 50min) maximum removal of 92 %was achieved. Thus the contact time (equilibrium time) taken as 75 min duration was ideal. The adsorption process is faster at the beginning due to the availability of more vacant spaces on the surface of the adsorbent. When the equilibrium was achieved there was no progressive increase in adsorption. The adsorption increased until equilibrium was achieved the similar reports was given [11].

3.2 Effect of adsorbent dosage:
Adsorption process depends on the amount of adsorbent required and extent of adsorption takes place. Chart-2. Showed that the Zinc (II) removal increases with the increase in adsorbent dosage from 50-600mg, this is mainly due to the greater availability of adsorbent. The percentage of removal from 65 to 89 % acquired by the increase of adsorbent dosage. [12].

3.3 Effect of initial concentration:
The results are showed in the Chart-3 percentage removal of Zinc verses initial concentration.. The initial concentration from 50 mg/L to 400 mg/Land the corresponding removal of Zinc adsorption decreased from 80% to 52%. The curve is constant after 400 mg/L showed adsorption sites were saturated. [13].

3.4 Effect of pH:
pH plays the vital role in the influence of heavy metal ion adsorption from the aqueous solutions. It greatly affects the adsorbent surface and the heavy metal ionization in the aqueous solutions. Chart-4. Zinc (II) adsorption is noted to be maximum at pH 6 with 90%. After that the adsorption capacity decreases from 6 to 9. The adsorption at pH 2-9 was observed, It is low adsorption at the initial due to the higher mobility of [H+] ions. [14].

3.5 Freundlich Isotherm:
Chart -5. Freundlich Isotherm for adsorption of Zn (II) at various temperatures. The linearity that confirmed and favors the process of adsorption.The1/n value is less than one indicates the unfavorable nature of Freundlich isotherm for Zn (II) onto *Couroupita guianensis* activated carbon. Table-1 shows that the 'n' (intensity of adsorption) value lies between 1and 10 shows the favorable adsorption.

3.6 Langmuir Isotherms:
Langmuir describes the layer of molecules formed on the surface as a function of concentration of liquid phase, in which it is in contact. Chart-6. Langmuir Isotherms for adsorption of Zinc (II) at various temperatures. The formation of unimolecular layer of adsorb ate on adsorbent was verified. The values are correlated well, and then R_L factor is less than one. The value R^2 0.9955 in Table-1, reveals that the process is favorable for the Langmuir adsorption isotherm. The solubility of Zinc depends on temperature and pH of the water in aqueous solutions.

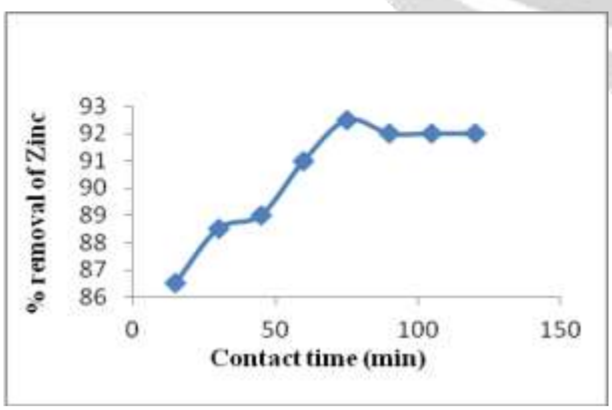

Chart – 1 Effect of contact time

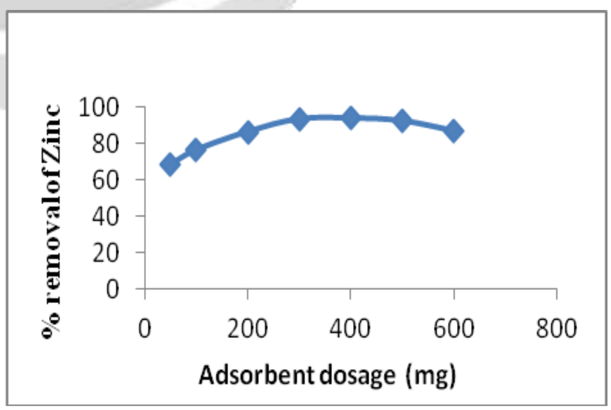

Chart – 2 Effect of adsorbent dosage

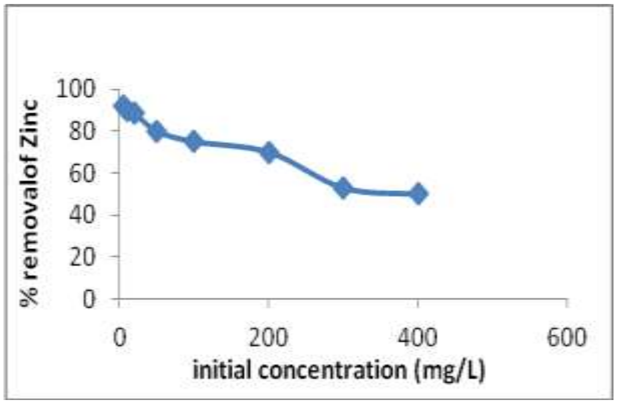

Chart – 3 Effect of initial concentration

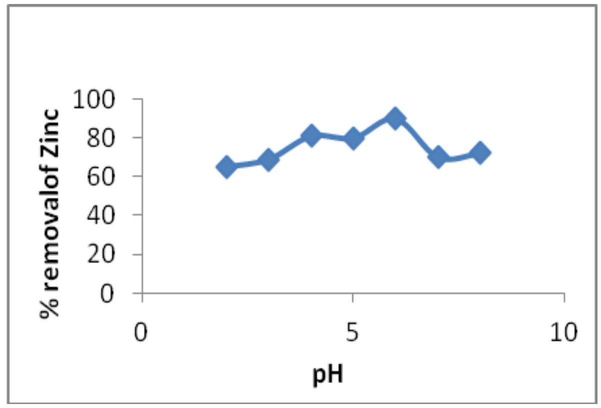

Chart – 4 Effect of Ph

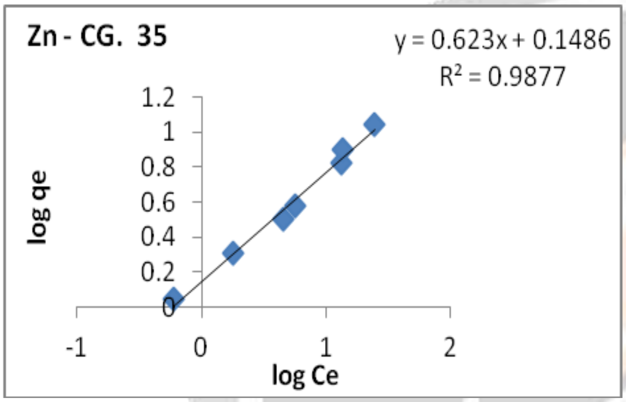

Chart - 5 . Freundlich Isotherm

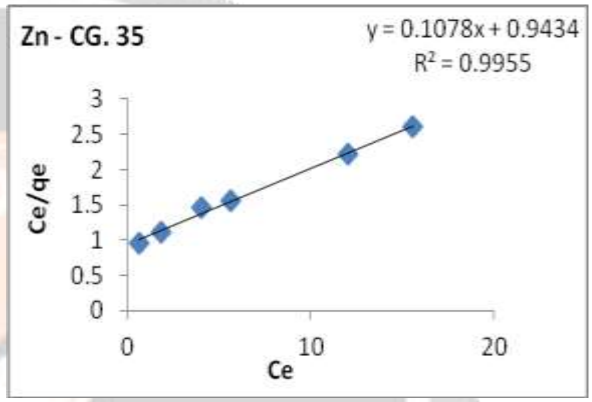

Chart - 6 Langmuir Isotherm

Table-1. Isothermal study result

Model - Freundlich Isotherm					Model - Langmuir isotherm			
Temp(K)	n	1/n	K_f	R^2	Temp(K)	R^2	q_{max}	b
308	1.6051	0.623	308	0.9877	308	0.9955	19.2	0.114

3.7 Kinetic Models:

Adsorption kinetics of Zinc (II) on *Couroupita guianensis* fruit shell activated carbon was undergone for first- order , pseudo first- order, pseudo second order, and intraparticle diffusion model. Batch experiments at the regular interval of time were calculated and the results were tabulated in Table-2. The uptake of Zn (II) is higher in the beginning and thereafter the adsorption rate was reduced.

The kinetics of Zinc (II) adsorption followed by Langergren's equation:

$$\text{Log } (qe\text{-}qt) = \log qe - k_1 p / 2.303\ t. \quad \text{----------------------- (6)}$$

A linear plot of log (qe –qt) against time (minutes) allows one to obtain the rate constant showed in Chart-7 If the plot was found to be linear with good correlation coefficient, indicating that Lagergren's equation is appropriate to Zinc (II) ions sorption on to adsorbate. So, the adsorption process is a pseudo first-order process, The Lagergren's first order rate constant (k_1) and qe determined from the graph are presented in Table-2 along with the corresponding correlation coefficients. It was observed that the pseudo-first-order model did not fit well. It was found that the calculated qe values do not agree with the experimental qe values. This suggests that the adsorption of Zinc (II) ions does not follow pseudo First-order kinetics.

(2) First order:
To describe the kinetics the first order kinetics is used and the plot of ln C versus time is drawn in Figure-8. The model rate equation: [15].

$$\ln C_i/C_t = k_1 t \quad (7)$$

Where k_1 is the rate constant of first-order adsorption (min^{-1}).

(3) Pseudo-second order:
The linear form of pseudo second order kinetics was plotted using the second – order equation: [16].

$$t/q_t = 1/k_2qe_2 + t/q_e \quad (8)$$

Where k_2 is the rate constant of pseudo seconded equation ($gmg^{-1}min^{-1}$) The regression coefficient R^2 was correlated well with the plot of t/q versus time (min) in Chart- 9. qe (experimental) value had the high degree of correlation with qe data . Hence Zinc (II) allows pseudo second order kinetic; the value of h, qe are calculated from the model and tabulated. (Table-2).This shows the heavy metal adsorption on *Couroupita guianensis* activated carbon by chemisorptions. [17].

(4) Adsorption Mechanism:
Adsorption mechanism is used to predict the rate limiting step. Intra-particle diffusion Model is important to identify the diffusion mechanism. [18]. The kinetic results were analyzed by the intraparticle diffusion model for Zinc (II) to define the diffusion mechanism**.** The mechanism model is expressed as Weber Morris Equation:

$$q_t = k_{id} t^{1/2} + C. \quad (9)$$

Where k_{id} is the intraparticle diffusion rate constant (mg/g) $t^{1/2}$ can be found from the slope of the linear plot of Weber-Morris q_t Vs $t^{1/2}$ and C is the intercept Chart-10. The calculated kid (Table-2) [19]. has the similar report .

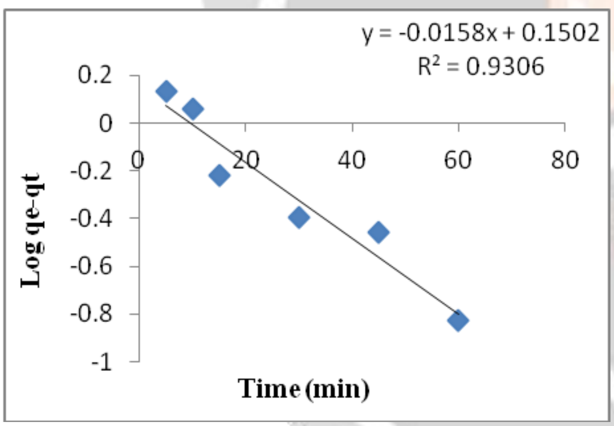

Chart - 7. Pseudo first order

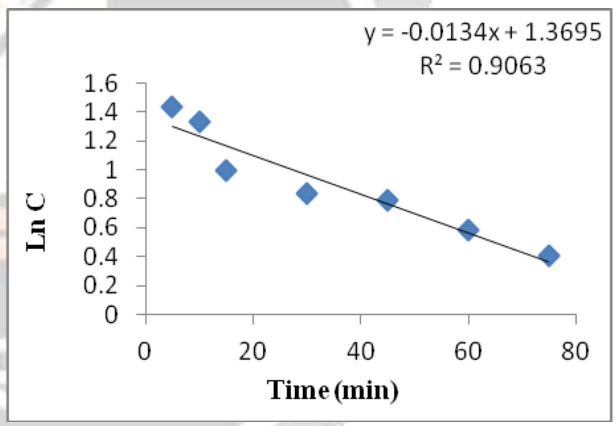

Chart - 8. First order

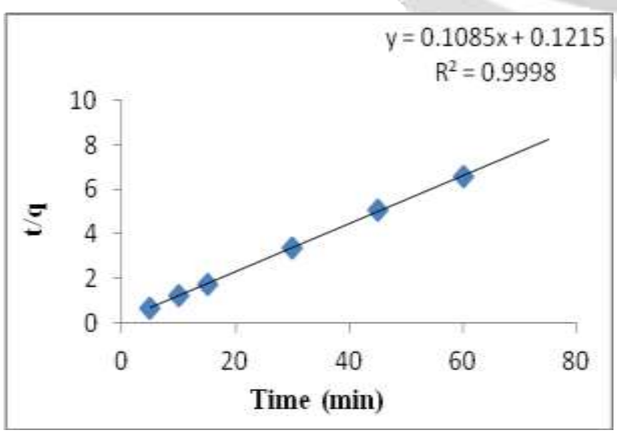

Chart -9. Pseudo second order

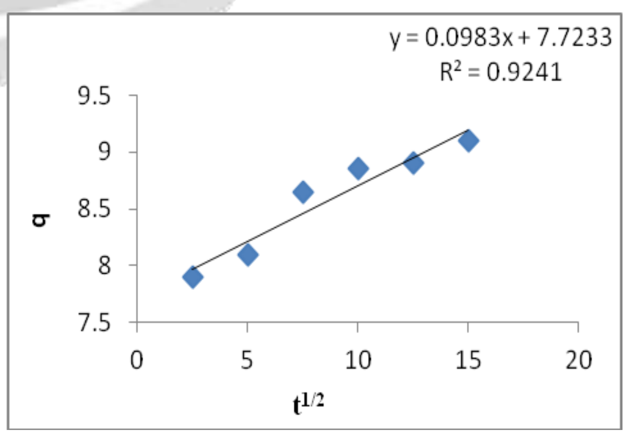

Chart -10. Intra particle diffusion

Table -2 . Kinetic study result

Metal Ion – Activated Carbon		Pseudo First Order			Pseudo second order				Intra particle diffusion		First Order	
A C . Metal ion	qe (exp)	k_1 min^{-1}	qe_1 mg/g	R^2	qe_2 mg/g	k_2 gmg^{-1} min^{-1}	h mg/g^{-1}	R^2	kid	R^2	k	R^2
Zn - CG.	9.25	0.035	1.41	0.93	9.26	0.096	8.23	0.999	7.723	0.92	1.369	0.906

4. CONCLUSION

Couroupita guianensis acid activated carbon was the effective adsorbent , for the removal of Zn (II) from the aqueous solution , It reached the absorption of 85% at 35^{o}C.The adsorption efficiency is high at pH 6. The removal of Zn (II) decreases by increasing the initial concentration and temperature. The Langmuir adsorption isotherm model is the better model than Freundlich adsorption isotherm model. The adsorption of Zn (II) was reliable with *Couroupita guianensis* with the R_L factor which is less than one. The kinetics of pseudo second order Zn (II) adsorption on the *Couroupita guianensis* experimental value was found to be fit with the calculated value. This present work reveals that *Couroupita guianensis* carbon as the best material for the removal of Zinc metal ions from the aqueous solutions.

5. REFRENCES

[1]. Ekpete O.A. and Horsfall M. JNR Preparation and Characterization of Activated Carbon derived from Fluted Pumpkin Stem Waste (Telfairia occidentalis Hook F Res.J.Chem.Sci Vol. 1(3) **(2011)**

[2]. Francis Amala Rejula and Masilamai Dhinakaran. Removal of Zinc (II) by Non Living Biomass of Agaricus Bisporus Vol. 1(9), 13-17, September Res.J.Recent Sci. **(2012)**

[3]. World Health Organization, Geneva, Guidelines for drinking Water Quality, **(1984)**

[4]. Resmi, G.; Thampi, S. G.; Chandrakaran, S.,. A novel bio-sorbent for removal of lead fromwastewater. Int. J. Environ. Res., 4 (2), 281-288 **(2010)**

[5]. Metcalf and Eddy, Wastewater Engineering: Treatment and Reuse In: McGraw Hill series in civil and environmental engineering,4th. Ed. 1149 - 1819 McGraw-Hill, New york. **(2003)**

[6]. APHA, AWWA Standard Methods for Examination of water and wastewater 10th Edition Washington DC **(1994)**

[7]. S. D. Deosarkar, S. P. Hangirgekar Cu(II) Adsorption from Aqueous Solution by Punica granatum L. Husk Journal of Chemical and Pharmaceutical Research, 4(10):4651-4656 **(2012)**.

[8]. Freundlich, H.; Hatfield, H., Colloid and Capillary Chemistry. Methuen and Co. Ltd., London. **(1926).**

[9]. Langmuir, I., The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc., 40 (8), 1361-1403 **(1918).**

[10]. Dash, S. Nand Satya Sagar, P, Adsorption of Zn metal from paper mills waste water by activated carbon prepared from Shorea Robusta leaf litter, J. Nat. Environ. Pollu. Techno,. 7(1): 117-122. **(2008).**

[11]. Vaishnav Vinod, Daga Kailash, Chandra Suresh and Lal Madan Adsorption Studies of Zn (II) ions from Wastewater using Calotropis procera as an Adsorbent .Res.J.Recent.Sci Vol. 1(ISC-2011), 160-165 **(2012)**.

[12]. Y. B. Onundi; A. A. Mamun; M. F. Al Khatib; Y. M. Ahmed Adsorption of copper, nickel and lead ions from synthetic semiconductor industrial wastewater by palm shell activated carbon Int. J. Environ. Sci. Tech., 7 (4), 751-758, Autumn **(2010)**.

[13]. Wan, M.W., Wang, C.C. and Chen, C.M., The adsorption study of copper removal by chitosan-coated sludge derived from water treatment plant. International Journal of Environmental Science and Development, 4(5), pp. 545-551. **(2013)**.

[14]. D. Mohan, K.P. Singh**.** Single-and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste. Water Research. 36: 2304-2318. **(2002)**

[15]. Bernard E., Jimoh A. and Odigure J.O. Heavy Metals Removal from Industrial Wastewater by Activated Carbon Prepared from Coconut Shell Res. J. Chem. Sci Vol. 3(8), 3-9, **(2013)**

[16]. Shrivastava A.K, Sorption of Zinc (II) on to point of use granular activated carbon from coke (POU-GACFC) Impregnated with waste tea leaves carbons (WTAC) from water/waste H2O, Indian Journal of Environmental protection, 30(1): 34-39. **(2010).**

[17]. Kannan, N and Veemaraj, T, Kinetics of Adsorption for the Removal of Zinc (II) ions from Aqueous solution using indigenously prepared Jack fruit seed and Commercial activated carbons, *Indian Journal of Environmental protection*, 30(5): 366-373. **(2009).**

[18]. Lodeiro, P. Herrero, R and Sastre de Vincente, E.M. *Environ. Chem* 3:400-418. **(2006).**

[19]. Igwe, J.C. Abia, A.A and Ibeh, C.A *Int. J. Environ Sci. Tech*. 5(1) 83-92. **(2008)**.