

# Fixed Column Study for the Removal of Zinc (II) Ions from Waste Water by Bone Char Rice Husks Ash and Water Hyacinth Composite-Mixture

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**Abstract:** *The adsorption potential of animal charcoal (BC/RHA/WH composite mixture to remove Zinc (II) ions from industrial wastewater was investigated using a fixed bed column was investigated. The effects of bed height (2 - 10) cm, flow rate (5 - 10) ml/min and feed concentration (diluted in the ratio 1:1 and 1:2) on the break through characteristics were determined. The highest bed capacity of 476.2 mg/g mg/g was obtained using 10 cm bed height, 1:2 feed concentration and 5 ml/min flow rate. The results indicate that adsorption capacity increased with increase in the inlet ion concentration and bed height and decreased with increase in flow rate. Adsorption data was fitted to Adam-Bohart, Thomas and Yoon-Nelson models.*

**Keywords:** Adsorption; Bone char; Breakthrough curves; fixed bed column; Rice husks ash; Wastewater, Zinc (II) ions

## 1. Introduction

Due to rapid industrialization, pollution caused by industrial wastewater has become a common problem in many countries. In Kenya the local National Environment Management Authority (NEMA) set the minimum limit of zinc (II) in the industrial effluents at 0.5mg/l [1].

Traditional methods used to remove heavy metal residues from industrial effluents include, chemical precipitation, biological bacterial uptake and reverse osmosis [2, 3]. These technologies are however expensive. Development of efficient and more affordable clean-up technologies for the treatment of large volumes of water contaminated with these metals is of major interest [4, 5]. Materials such as, water hyacinth [6], charcoal dust [7], bone charcoal [8,9], spent bleaching earth ash [10] coffee grounds [11] and rice husks [12] have been investigated and found to have the capacity to adsorb heavy metals. More investigations need to be conducted on the use of these materials singly and in combination with a view of optimizing on their uptake capacity of effluent pollutants. Batch experiments provide an easier way of categorizing the adsorbent materials. In terms of the actual applicability, they are not very useful. Adsorbent materials column experiments are more resourceful. The potential of a mixture of adsorbents in a column should be investigated. This will help to exploit various qualities of different adsorbents. Moreover this may improve the adsorptivity of the adsorbents and prevent the clogging of the column based on pulverized adsorbents. Furthermore, some of the industrial water treatment plants use activated charcoal-sand mixture in their treatment columns in various proportions. In this study, real industrial waste rather

than usual simulated water was used. This offered the practical adsorption potential of the adsorbent. It may, in the end of this on-going investigation, lead to construction of an effluent clean up stream(s) that could offer a desired solution to discharge of industrial effluent for our local industries.

## 2. Modeling and Analysis of Column Data

The prediction of breakthrough curve is required for the successful design of a column-sorption process. The maximum adsorption capacity of an adsorbent is also needed for design purposes. Various mathematical models can be used to describe the fixed-bed adsorption. Among these, the Thomas model, Yoon-Nelson and Adams –Bohart models have been widely used by several investigators starting at concentration ratio,

$\frac{C_t}{C_0} > 0.1$  to  $\frac{C_t}{C_0} > 0.90$  considering the safe water quality

standards and operating limit of mass transfer zone of a column [12]. The Thomas model mathematical expression is given as equation 1

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{Th} q_0 m}{Q} - k_{Th} C_0 t \dots\dots\dots (1)$$

Where,  $k_{Th}$  is the Thomas rate constant,  $m$  is mass of the adsorbent in the column,  $q_0$  is equilibrium adsorbate uptake capacity,  $C_t$  is the effluent concentration,  $C_0$  influent concentration and  $Q$  is the total flow time (min). A plot of

$\ln\left(\frac{C_0}{C_t} - 1\right)$  against  $t$  gives  $k_{Th}$  as the slope while  $q_0$  is obtained from the intercept [13].

The Yoon-Nelson model not only has a more simple form than other models, but also requires less detailed data concerning the characteristics of the adsorbate and adsorbent, as well as the parameters of the fixed bed. The adsorption data was also analyzed based on this model in the form:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN}t - t_{1/2}k_{YN} \dots\dots\dots (2)$$

Where  $C_t$  is the effluent concentration,  $C_0$  is the influent concentration,  $k_{YN}$  (L/min) is Yoon-Nelson rate constant,  $t_{1/2}$ (min) is the time required for 50 % adsorbate breakthrough [14].

Adams-Bohart models gives a simple and comprehensive approach for evaluating column dynamics, its validity, however, is limited to the range of condition used. The breakthrough data was fitted to the Adams-Bohart model in the form:

$$\ln\left(\frac{C}{C_0}\right) = k_{AB}C_0t - k_{AB}N_0\frac{z}{u} \dots\dots\dots (3)$$

where,  $C_0$  and  $C$  are the inlet and outlet of metal concentrations,  $z$  is the bed depth in,  $u$  the linear flow rate, is  $k_{AB}$  the adsorption rate constant  $t$  is the time and  $N_0$  is the saturation concentration mg/L [13].

Linear plots of  $\ln\left(\frac{C}{C_0}\right)$  against time,  $t$  at different flow rates, bed heights and initial cation concentrations are plotted [16]

### 3. Experimental

#### 3.1 Preparation of the adsorbent

##### 3.1.1 Bone Char (BC)

The bones, as obtained from various sampling sites, butcheries in Farmer's choice <sup>TM</sup>, Kahawa west and industrial area in Kenya. They were boiled to remove the flesh and fats for 10 hours. 1 kg of the bones was impregnated with 100 ml of 10 M KOH. They were then placed in a thermostat vacuum oven model Townson & Mercer (Ltd) Croydon England at 550°C for 5 hours in a partial vacuum created by pumping out air from the carbonizing chamber. After which they were cooled in desiccator and later crushed into powder. The activated carbons obtained were thoroughly washed with excess distilled water

until a pH of 6.5 to 7 was obtained and finally dried at 110°C. The resultant activated carbon was subjected to adsorption tests [8, 9, 10]

##### 3.1.2 Rice husks ash (RHA)

Rice husks were washed in excess tap water and thereafter in 0.01M Nitric acid. They were then rinsed with distilled water until a pH between 6.5 and 7 is obtained. They were dried at room temperature and later calcined in a furnace at 500 - 600°C for 24 hours. They were ground, sieved through a 250 µm mesh and stored in an air-tight glass bottle prior to use [14].

#### 3.2 Preparation of Water Hyacinth

The WH was sorted in the laboratory to remove the rotten ones. They were washed with running water and rinsed with de-ionized water. They were then activated by soaking them in 0.01M phosphoric acid for 1 hour. The activated WH was rinsed several times with deionized water until a pH of around 6.5 was obtained. The samples were then sun dried for 2 weeks. The resultant dry biomass was crushed using mortar and a pestle then sieved to 0.5 mm mesh. The material was packed and stored in plastic bottles. The resultant WH was subjected to FTIR, ash and moisture content analysis.

#### 3.3 Preparation of AC/RHA/WH composite (mixture)

Ground activated Bone Char (BC) was mixed well with rice husk ash (RHA) and water hyacinth (WH) at the AC -to -RHA -to-WH mass ratio of 2:1.:1 A predetermined amount of the mixture was placed in the column until the desired height was obtained.

#### 3.4 Effluent

The effluent used was obtained from a local manufacturing firm in Nairobi Kenya. The pH of the effluent was determined on the spot using potable pH meter. The physico - chemical characteristics which included biological oxygen demand (BOD), carbon oxygen demand (COD), turbidity and pH of the effluent were determined using standard analytical methods [15]. The concentration of lead (II) ions was analyzed using atomic absorption spectroscopy (AAS).

#### 3.5 Adsorption Studies

Three columns were packed with a known quantity of BC/RHA/WH mixture to the desired height. The pH of the industrial effluent was adjusted to 6.5 -7.0. Before being fed into the column the concentration of the effluent was varied between raw effluent which was diluted in the ratio 1:1 and finally diluted in the ratio 1:2. A variable peristaltic pump model, A. 85.S/E Charles Auston pump (Ltd) was used to pump the effluent through the column in the upward direction. The aliquot of the effluent at the outlet of the column was collected at regular time intervals. Column effluent samples were analyzed by AAS. The bed height was 2.0, 5.0 and 10.0 cm and

the flow rate was adjusted to 5, 7.5 and 10 ml/min. The data obtained was subjected to, Thomas model, Yoon-Nelson and Adams –Bohart models [12].

**3.6 Desorption**

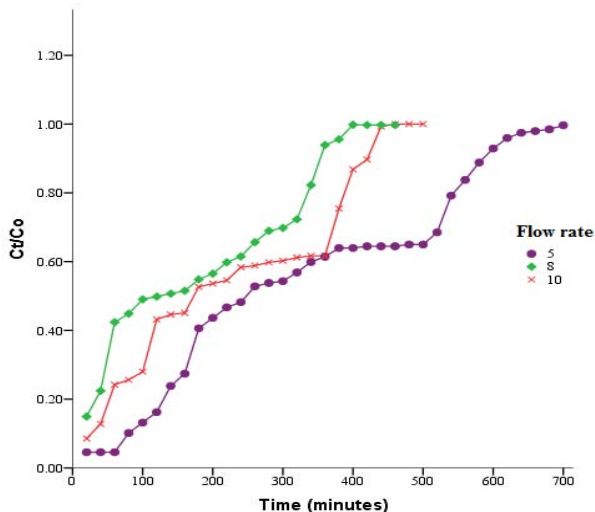
Desorption experiments were performed using 0.01 M HNO<sub>3</sub> as an eluting agent at flow rate of 5ml/min for 12 hours. There after the column was rinsed with distilled water until the pH was between 6.0 and 7.0.

**4. Results and Discussion**

**4.1 Column Studies**

**4.1.1 Effect of flow rate**

The effect of flow rate for the adsorption of zinc (II) ions using BC/RHA/WH was studied at various flow rates of 5, 7.5 and 10 ml/min as shown in Figure 1. It is observed that there is rapid uptake of metal ion at the initial stages, later on the rate decreases slowly and finally it reached saturation. The results indicate that breakthrough time for Zinc (II) uptake by BC/RHA/WH decrease with increasing flow rate. Ahmad and Alrozi [16] suggested that the residence time distribution of influent concentration in the adsorbent is greater in lower flow rate. According to Nasehir *et al.* [12] the front of the adsorption zone quickly reaches the top of the column and the column is saturated faster when the flow rates are high. This could be because of the reduced contact time which causes a poor distribution of the liquid inside the column, which leads to a lower diffusivity of the solute through the adsorbent particles [17].

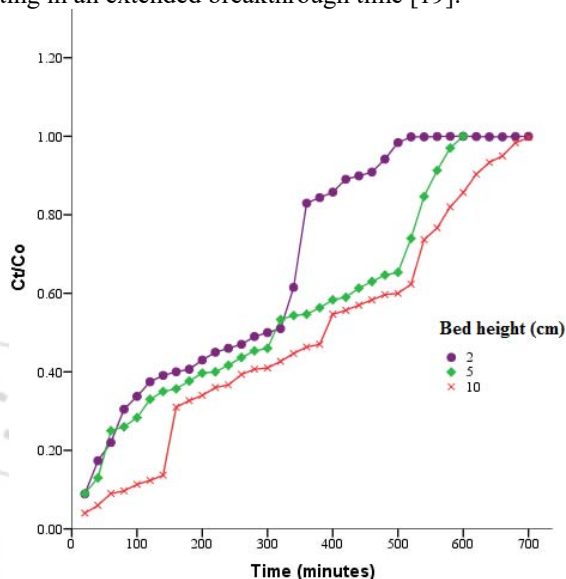


**Figure 1:** Effect of flow rate on the adsorption of zinc (II) ions

**4.1.2 Effect of bed height**

Figure 2 shows, that the breakthrough time was decreased with decreasing bed height of the adsorption column the adsorption of zinc (II) ions. A higher zinc (II) uptake was achieved at higher bed height due to the increase in the amount of the

BC/RHA/WH mixture which provided more binding sites for the metal ions. Altenor *et al.* [18] observed that the increase in bed height also increase the mass transfer zone. Hence in a fixed bed system, an increase in bed height would create a longer distance for the mass transfer zone to reach the exit resulting in an extended breakthrough time [19].



**Figure 2:** Effect of bed height on the adsorption of zinc (II) ions

**4.1.3 Effect of Feed Concentration**

The effect of feed concentration on the adsorption of zinc (II) ions is reported on figure 3. The results show that the breakthrough point for raw and diluted effluent, in the ratios, 1:1 and 1:2 were 80 min, 120 min and 240 min respectively. The breakthrough curve for raw effluent was achieved earlier due higher concentration of zinc (II) ions. Faster saturation of the available binding sites for zinc (II) ions led to the decreased breakthrough time. Conversely, dilution of the feed effluent led to slower transport of zinc (II) ions through the column. According to [20], lower concentration leads to decrease in mass transfer coefficient. This may result in a late breakthrough curve. It may be deduced that, at a lower inlet concentrations, more breakthrough time is required to remove zinc (II) ions from the effluent.

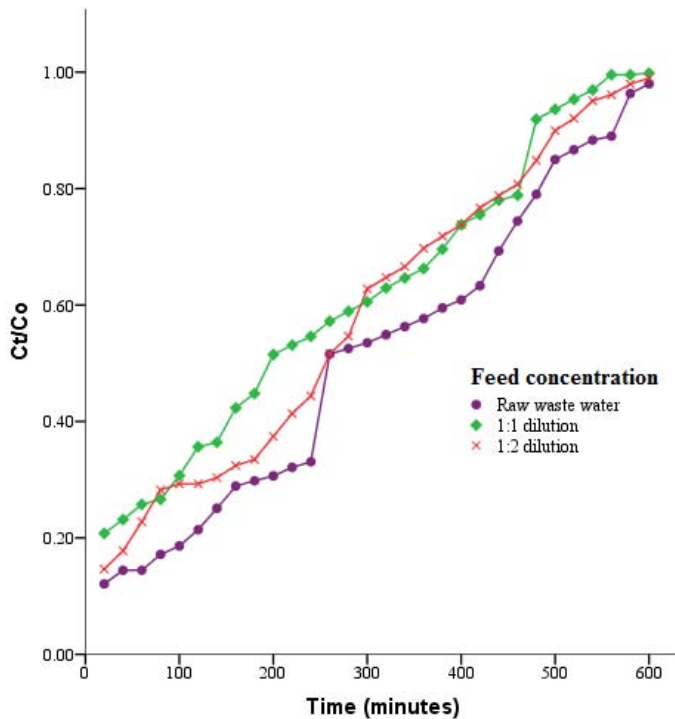


Figure 3: Effect of feed concentration on the adsorption of zinc (II) ions

#### 4.2 Modeling and analysis of column data

The prediction of breakthrough curve is required for the successful design of a column-sorption process. The maximum adsorption capacity of an adsorbent is also needed for the design. Various mathematical models can be used to describe the fixed-bed adsorption. Among these, the Thomas model [15], Yoon-Nelson [17] and Adams-Bohart [14, 19] models have been widely used by several investigators to characterize sorption processes in fixed phase experiments. The results are given in Table 1.

##### 4.2.1 Thomas Model

The values of Thomas rate constant  $k_{Th}$  increased with the increasing flow rate whereas the maximum adsorption  $q_0$  decreased. As the bed height is increased, the values of  $q_0$  increased [21]. The high fit of the experimental data with the Thomas model indicate that the external and internal diffusion will not be the rate limiting step [9, 22]. The breakthrough curve analysis from continuous adsorption studies reveals that the slower breakthrough time reached for lesser initial concentration, slower flow rate, and higher bed height [23, 24].

##### 4.2.2 Yoon-Nelson Model

The values of Yoon-Nelson rate constant  $k_{YN}$  decreased with decreasing bed height whereas the values of  $t_{1/2}$  increased with increasing bed height. At a higher bed height the adsorbate molecules have more time to travel through the column. The rate constant  $k_{YN}$  increased with the increase in the initial

metal ion concentration. This may be due to increase of competition between the adsorbate molecules for the adsorption sites which results in increased uptake. The rate constant was found to increase with the increase in flow rate. At a high flow rate the number of metal ion passing through a particular adsorbent is more which increases the rate. [12].

##### 4.2.3 Adams Bohart Model

Adams-Bohart rate constant  $k_{AB}$  increased with increase in bed height and flow rate, but decreased with initial concentration. The sorption capacity  $N_0$  increased for increasing initial concentration, flow rate, and bed height. Although, Adams-Bohart models gives a simple and comprehensive approach for evaluating column dynamics, its validity is limited to the range of condition used. The  $R^2$  values are lower compared to Thomas and Yoon-Nelson models. Thus the poor correlation coefficient reflects less applicability of this model [18,25]

#### 4.3 Comparing the effect of AC/sand and BC/RHA/WH adsorbents

The results in figure 4 show that the breakthrough curve for AC/Sand came earlier than that of BC/RHA/WH. The maximum adsorption for AC/Sand column was found to be 378.93 mg/g whereas that of BC/RHA/WH was 476.2 mg/g. One way ANOVA revealed that, at 95 percent confidence limit ( $p > 0.005$ ) the breakthrough and exhaust time differed significantly. It is clear from the test that BC/RHA/WH is a promising adsorbent than the industrial AC/Sand composite mixture

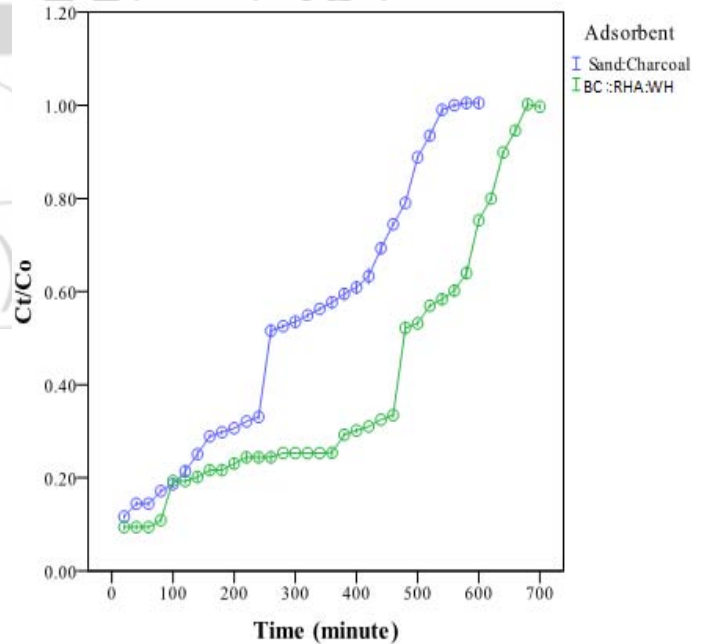


Figure 4: Comparison of AC/sand and BC/RHA/WH adsorbents

## 5. Conclusion

BC/RHA/WH mixture is a better adsorbent than AC/Sand mixture used in the industry. The fixed-bed adsorption system was found to perform better with lower Zinc (II) ions inlet concentration, lower feed flow rate and higher BC/RHA/WH bed height. The column experimental data were fitted well to the Thomas and Yoon-Nelson models with the correlation coefficient,  $R^2$  values were between 0.86 and 0.98 but Adams-Bohart was  $R^2 \geq .095$ . Thomas model reveals the monolayer adsorption. The maximum adsorption capacity for AC/sand column was found to be 378.93 mg/g whereas that of BC/RHA/WH was 476.2 mg/g. The change in percentage regeneration efficiency was minimal after three cycles. The result demonstrates that AC/RHA/WH is a good adsorbent for heavy metal ions.

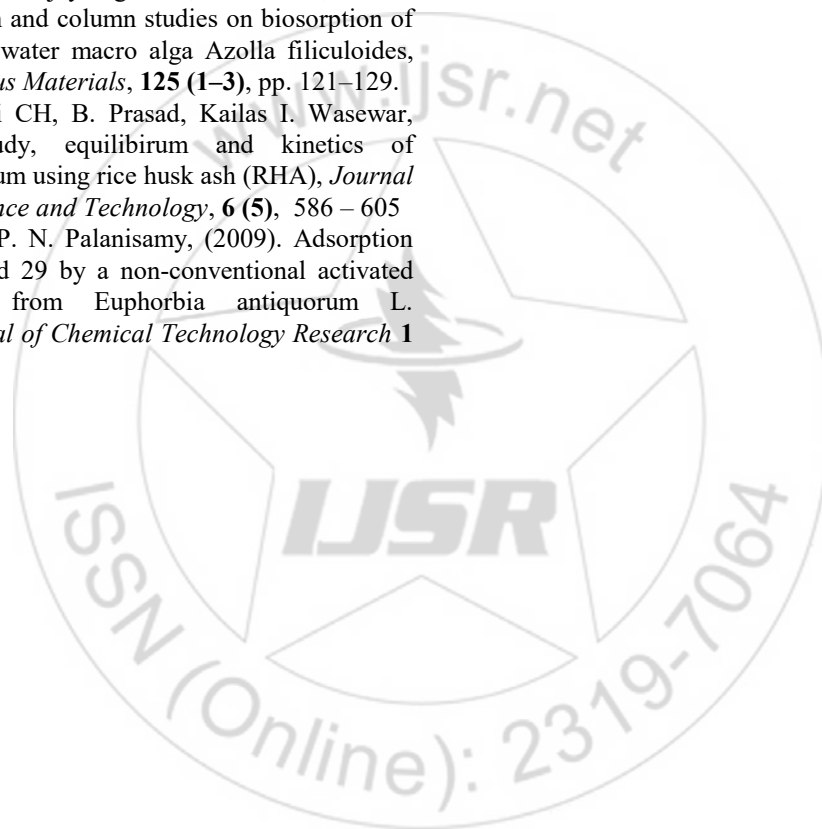
## 6. Acknowledgements

The authors of this work would like to thank ICRAF, Kenyatta University ICRAF, Geology and mines and Jomo Kenyatta university of Agriculture and Technology for the technical support in their laboratories

## References

- [1] Environmental management and co-ordination (water quality) regulations, (2006) Kenya Gazette supplement No 6829 (Legislative supplement No. 36) Third schedule, legal notice no. 120, 11-13, Nairobi, Kenya
- [2] Volesky, B. (1990). Biosorption and biosorbent. In: Volesky, B. (Ed.), Biosorption of heavy metals. CRC Press, Inc., Boca Raton, pp 3-5.
- [3] Li, X., Tang, Y., Cao, X., Lu, D., Luo, F., Shao, W. (2008). Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium zinc, cobalt and nickel. *Colloids and Surfaces A: Physicochemical Approach Engineering Aspects*, **317**, 512.
- [4] Goyer, R.A. (1991). Toxic effects of metals, in: Amdur, Doull, Klaassen (Eds.), Casarett and Doull's toxicology: The basic science of poisons, Pergamon, New York, pp.623-680. Argun, E. M., Dursun, S. (2008). A new approach to modification of natural adsorbent for heavy metal adsorption, *Bioresource Technology*, **99**, 2516.
- [5] Schwartz, C., Gerard, E., Perronnet, K., Morel, J.L. (2001). Measurement of ions in phyto extraction of zinc by spontaneous metallophytes growing on a former smelter site, *Science Total Environment*, **279**, 215.
- [6] Murithi, G, Onindo, C.O., Muthakia, G.K., (2011), Kinetic and Equilibrium study for the sorption of Pb (II) ions from aqueous phase by water hyacinth. *Bull chemical society Ethiopia*, **26 (2)**, 181- 193
- [7] Mohammad-Khah .A and Ansari. R (2009). Activated Charcoal: Preparation, characterization and Applications : A review article, *International Journal of Chemical Technology Research*, **1 (4)**, 859-864
- [8] Ghader. G., Mohammad-Taghi. G., Ghorban. A. (2013), Application of Bone Char as an Adsorbent for Purification of Water Contaminated with Hexavalent Chromium, *Qom University of Medical Sciences Journal*, **7(2)**, 1-3
- [9] Slimani R, A. Anouzla , Y. Abrouki , Y. Ramli, S. El Antri. Mamouni, S. Lazar, M. El Haddad, (2011), Removal of a cationic dye -Methylene Blue- from aqueous media by the use of animal bone meal as a new low cost adsorbent, *Journal of Material and Environmental Science*, **2 (1)**, 77-87
- [10] Wambu E.W, Muthakia G.K, Karanja Wa -Thiong'o J.K., Shiundu P.M. (2009). Kinetics of copper desorption from regenerated spent bleaching earth and its adsorption of Cu (II) ions from solutions, *American –Eurasian journal of scientific research* , **4(4)**, 317-323
- [11] Tokimoto, T., Kawasaki, N., Nakamura, T., Akatugawa, J., And Tanada, S. (2005). Removal of Lead Ions in Drinking Water by Coffee Grounds as Vegetable Biomass. *Journal of Colloid and Interface Science*, **281**, 56.-61
- [12] Nasehir Khan E M Yahaya, Ismail Abustana, Muhamad Faizal Pakir Mohamed Latiffa, Olugbenga Solomon Bello, Mohd Azmier Ahmad (2011) Fixed-bed column study for Cu (II) removal from aqueous solutions using rice husk based activated carbon, *International Journal of Engineering and Technology*, **11(1)**, 248-252
- [13] Mohan.S and Sreelakshmi G. (2006), Fixed bed column study for heavy metal removal using phosphate treated rice husk, *Journal of Hazardous Materials*, **153 (1-2)**, 75–82
- [14] Tangjuank .S, Insuk.N, Tontrakoon. J, Udeye. V. (2009), Adsorption of Lead(II) and Cadmium(II) ions from aqueous solutions by adsorption on activated carbon prepared from cashew nut shells, *World Academy of Science, Engineering and Technology*, **3**, 4-28
- [15] Saravanan A, Uvaraja Nishanth, Soundarajan Krishnan (2012), Column Study on the Removal of Metals from Industrial Effluents using the biomass *Sargassum sp*, *International Journal of Applied Research in Mechanical Engineering*, **2**, 2231–5950,
- [16] M.A. Ahmad, R. Alrozi, (2010) Optimization of preparation conditions for mangosteen peel-based activated carbons for the removal of Remazol Brilliant Blue R using response surface methodology, *Chemical engineering Journal*. **165**, 883-890.
- [17] Negrea, L. Lupa, M. Ciopec and P. Negrea (2011) Experimental and Modelling Studies on As (III) Removal from Aqueous Medium on Fixed Bed Column *Chemical Bulletin "POLITEHNICA" University (Timisoara)*, **56 (70)**, 2.
- [18] Altenor S, Carene B, Emmanuel E, Lambert J, Ehrhardt JJ, Gaspard S (2009). Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation, *Journal of Hazard Materials*, **165 (1-3)**, 1029–1039.
- [19] Bohart. G, E.Q. Adams, (1920), some aspects of the behaviour of charcoal with respect to chlorine, *Journal of America Chemical. Society*. **42**, 523-544.

- [20] Z. Z. Chowdhury, S. M. Zain, A. K. Rashid, A. A. Ahmed, and K. Khalid (2012), Application of response surface methodology (RSM) for optimizing production condition for removal of Pb (II) and Cu (II) Onto kenaf production condition for removal of Pb (II) and Cu (II) Onto Kenaf, *Research Journal of Applied Sciences, Engineering and Technology*, **4 (5)**, pp. 458–465.
- [21] Ghribi and M. Chlendi (2011), Modeling of fixed bed adsorption: application to the adsorption of an organic dye, *Asian Journal of Textile*, **1(4)**, pp. 161–171.
- [22] V.C. Taty- Costodes, H. Fauduet , C. Porte, Y.S. Ho (2005), Removal of lead (II) ions from synthetic and real effluents using immobilized *Pinus sylvestris* sawdust : adsorption on a fixed column, *Journal of Hazardous Material*, **123**, 135 -144
- [23] T. V. N. Padmesh, K. Vijayaraghavan, G. Sekaran, and M. Velan, (2005) Batch and column studies on biosorption of acid dyes on fresh water macro alga *Azolla filiculoides*, *Journal of Hazardous Materials*, **125 (1–3)**, pp. 121–129.
- [24] Sekhararao gulipalli CH, B. Prasad, Kailas I. Wasewar, (2011), batch study, equilibrium and kinetics of adsorption of selenium using rice husk ash (RHA), *Journal of Engineering Science and Technology*, **6 (5)**, 586 – 605
- [25] Sivakumar, P. and P. N. Palanisamy, (2009). Adsorption studies of basic Red 29 by a non-conventional activated carbon prepared from *Euphorbia antiquorum* L. *International Journal of Chemical Technology Research* **1 (3)**, 502-510.



Thomas model									
Parameters	Flow rate (ml/min)			Bed height(cm)			Initial [ ] mg/L		
	5	7.5	10	2	5	10	R	1:1	1:2
$k_{Th}$ (ml/min/mg)	0.18	0.035	0.030	0.022	0.028	0.030	0.033	0.013	0.029
$q_0$ (mg/g)	68.48	49.38	6.40	15.52	16.29	18.18	14.43	34.61	16.65
$R^2$	0.92	0.98	0.96	0.90	0.79	0.96	0.96	0.93	0.96
Yoon-Nelson model									
$k_{YN}$ (L/min)	0.0029	0.0063	0.0079	0.006	0.0047	0.0065	0.0072	0.0063	0.0056
$t_{1/2}$ (min)	5355.9	152.94	40.82	195.6	313.53	366.08	292.90	254.52	239.18
$R^2$	0.95	0.98	0.91	0.96	0.96	0.86	0.95	0.94	0.96
Adams- Bohart model									
$k_{AB}$ (L/mg.min)	0.0094	0.011	0.013	0.016	0.0170	0.0110	0.018	0.013	0.013
$N_0$ (mg/L).	427.17	293.26	220.08	7.328	7.51	10.3	7.09	9.42	9.57
$R^2$	0.75	0.84	0.86	0.90	0.79	0.84	0.79	0.83	0.84