Treatment of Industrial Effluent Containing Metal Ions With Rubber Seed Coat Based Activated Carbon

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Abstract—Activated carbon derived from rubber seed coat has been employed in the removal of heavy metals from an industrial wastewater. The rubber seed coat was washed, dried, grounded, carbonized at 300oC, activated using hydrochloric acid and used to carry out adsorption process. The activated rubber seed coat was then used to carry out adsorption of heavy metal from waste water collected from the refinery. The adsorption studies indicated that rubber seed coat based activated carbon (RSCAC) was effective in removing 85.417% of copper and 70.986% of iron. The batch isotherm studies showed that the adsorption data were described by the Langmuir and Freundlich model. Freundlich isotherm fitted better for Fe removal, and Langmuir isotherm fitted better for removal of copper and zinc. The result in this study indicated that activated carbon from rubber seed coat was an attractive adsorbent for the removal of metal from industrial effluent.

Index Terms— Activated carbon, adsorption, isotherm, heavy metals, rubber seed coat.

1 Introduction

HEAVY metals such as lead, iron, zinc, cadmium etc. can often be found in industrial wastewater and their discharge to the environment poses a serious threat due to their acute toxicity to aquatic and terrestrial life which includes humans. As a result of increasing industrialization more heavy metals are being continually released to the environment and this has prompted environmental engineers and scientists to investigate methods by which heavy metal-bearing wastewaters can be treated effectively and economically.

There exist numerous techniques for the removal of heavy metals from wastewater and these include chemical precipitation, ion exchange, adsorption, electrolytic recovery, electro dialysis, solvent extraction, reverse osmosis, membrane separation, ultra filtration, ozonation, foam floatation, vapour recovery, gamma irradiation, freeze crystallization, and photochernical methods [1],[2],[3],[4],[5],[6],[7],[8].

Although some of these treatment methods can be successfully used for treating most wastewaters, others are quite limited in use. The application of chemical precipitation to dilute solutions (low concentration) can be difficult unless the addition of flocculating agents such as lime, caustic and sodium carbonate is employed. However, a bulky sludge is produced and the disposal constitutes a problem [7], [9],[10],[11],[12]. Ion exchange and activated carbon adsorption are quite expensive and require recharge of resin or spent activated carbon as well as the disposal of substantial volume of used regeneration solution. In addition to the fact that membrane technology is expensive, membranes are susceptible to attack by microorganisms, likewise other methods mentioned require elaborate and considerably high operation costs.

In general, factors to be considered in the choice of a method to be adopted for the treatment of heavy metal-bearing wastewater should include: high rate of removal, economic feasibility in terms of labour, materials, equipment and energy, applicability to small, intermediate and large scales, low productivity of highly enriched spent materials and capability of reducing heavy metal ion concentration to levels below established regulatory standards.

Adsorption process has been revealed as an effective process for heavy metal removal and adoption of economic and easily available adsorbents will make the process a considerably promising option by meeting the criteria stated above. However, the high cost of activated carbon has resulted in limitation of its use as an adsorbent and thus the need to explore other cheaper adsorbents. The use of inexpensive adsorbents had been demonstrated to be effective in removing heavy metals from wastewater and such materials include: rice husk [8],[9],[11],[12],[13], peat moss [1], coconut husk [12], sugarcane bagasse [13], [14], sawdust [6],[9], crab shell, fly ash, zeolite, bentonite, rubber seed shell, corn cob and discarded automotive tyres [15],[16],[17],[18],[19].

Literature has reported that rubber seed coat activated carbon has been used in the treatment of textile waters to remove dyes [9], but to the best of our knowledge, it has not been used in the removal of heavy metals from waste water. Rengaraj et al. [16] reported that activated carbon prepared from rubber seed coat is 2.25 times more efficient compared to commercial activated carbon for phenolic wastewater treatment. Hence, the feasibility of applying activated carbon from rubber seed coat towards the removal of heavy metals from industrial effluent is being approached. The main objective of the work is to investigate the effectiveness of rubber seed coat activated carbon in the removal of heavy metals in industrial effluent. The study includes adsorption as a function of time, adsorbent dose and concentration of effluent solution. The isotherm studies were fitted for Langmuir and Freundlich adsorption isotherm.

1.1. Adsorption Isotherms

Adsorption isotherms relate the amount of a substance adsorbed at constant temperature to its concentration in the equilibrium solution. The adsorption equilibrium relates equilibrium concentration of adsorbable species in solid adsorbent q, which is the mass of species adsorbed per unit mass of adsorbent, to the equilibrium concentration of adsorbable species in solution C. It has been found that for most of the cases of importance in wastewater treatment the function q = f(C) takes the form of one of the following isotherms:- Langmuir isotherm, Brauner-Emmet-Teller (BET) isotherm; and Freundlich isotherm [7],[20].

The Langmuir isotherm is an empirical isotherm derived from a proposed kinetic mechanism based on the following assumptions:

(i) The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
(ii) Adsorbed molecules do not interact
(iii) All adsorption occurs through the same mechanism
(iv) At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

$$q = \frac{q_m K_A C}{1 + K_A C} \qquad (1)$$

Where: qm = maximum adsorbable value of q, KA = constant (function of enthalpy of adsorption and temperature), and C=equilibrium concentration

The Langmuir isotherm can be rearranged to give a straight-line plot of C/q vc C:

$$\frac{C}{q} = \frac{1}{K_A q_m} + \frac{1}{q_m} C \qquad (2)$$

The Freundlich equation can be mathematically represented by:

$$q = K_F C e^{1/n} \qquad (3)$$

Where: KF = constant (function of energy of adsorption and temperature), n = constant and Ce = equilibrium concentration. The freundlich isotherm can also be rearranged to give a straight-line logarithmic plot:

$$log q = log K_F + \; - log C \qquad (4)$$

2 EXPERMINTAL

Rubber seed coat was collected in a farmland at Obomkpa in Aniocha North local Government of Delta State, the effluent (wastewater) was collected from Indorama Eleme Petrochemical Limited, Port Harcourt, Nigeria. The atomic absorption spectrophotometry (AAS) employed for metal analysis was conducted at Anal concept ltd, Elimgbu Port Harcourt. Grinding machine used in the study was obtained at a nearby market. 0.5M of hydrochloric acid (HCl) was prepared for the activation by adding 175ml of concentrated HCl into a 4000ml Erlenmeyer flask that was half filled with distilled water. More distilled water was added into the flask to make it up to the 4000ml mark.

2.1. Adsorbent Preparation

Rubber seed coat was collected in a farmland at Obomkpa in Aniocha North local Government of Delta State. The rubber seed coat collected was thoroughly washed with water, dried in an oven at a temperature 100oC for 2hours and allowed to cool for 2hours after drying. The dried rubber seed coat was grinded in order to reduce the bulkiness and increase the surface area of contact. The grinded rubber seed coat was sieved to a sieve size of 4mm.

2.2. Carbonization

The grounded rubber seed coat was weighed and the total weight was 1051.977g. The sample was loaded in a crucible (in batches) and carbonization was carried out using a muffle furnace at a temperature of 300oC (573K) for 1hr. The carbonized rubber seed coat (rubber seed coat carbon, (RSCC)) was weighed and the weight was 329.3012g.

2.3. Activating the Rubber Seed Coat Carbon (RSCC)

200g of RSCC was weighed and poured into 1000ml beaker. The RSCC was then poured into a 4000ml volumetric flask and 4000ml of 0.5M HCl was added to it. The mixture was heated on a hot plate for 8hrs until it dries off. Another 125g of RSCC was weighed and poured into a 4000ml volumetric flask and 2000ml of 0.5M HCl was poured into the flask and heated on a hot plate for 4hrs when the mixture dries off. The rubber seed coat activated carbon (RSCAC) was poured into a funnel with a filter paper and washed with distilled water to pH of 5. The RSCAC was dried in the oven at a temperature of 80oC for 5hrs. The RSCAC was then grounded with a small grinding machine and sieved to a sieve size of 1mm.

2.4. Batch Adsorption Experiments

The adsorption study was carried out in batches. The dosages of the RSCAC (adsorbent) taken were 2g, 4g, 6g, 8g and10g respectively. The different dosages were mixed with 150ml of the effluent (refinery wastewater) in the sample bottles and closed tightly. The bottles were clamped to a shaker. The equipment was switched on and timed for 2hrs for proper agitation. After shaking, the mixture was filtered into a vacuum flask, using a filter paper and funnel. A clear solution was not gotten which lead to the use of a centrifuge. The centrifuge tube was filled with the filtrate of the different dosages starting with the 2g dosage. The centrifuge was set to operate at a speed of 2000rpm for 5mins after which the clear solution was decanted. Same was done for the other dosages. The concentration of the metals in the refinery wastewater before and after adsorption was determined using atomic absorption spectrophotometer. The percentage removal and the amount adsorbed (q_e) at equilibrium were calculated by the equations below;

$$Removal\,(\%) = \frac{(Co - Ce)}{Co} \times 100 \quad (5)$$

and

$$Amount\ adsorbed\ (q_e) = \frac{(Co - Ce)V}{m} \quad (6)$$

Where, q_e is the adsorption capacity/amount adsorbed of the adsorbent (mg adsorbate/g adsorbent); C_o is the initial concentration of metal (mg/L); C_e is the final concentration of metal after adsorption had taken place over a period of time t (mg/l); V is volume of metal solution in shake flask (l) and m is mass of adsorbent (g).

3 Results and Discussion

3.1 Effect of Adsorbent Dosage

Effect of adsorbent dose plays an important role in standardizing the adsorption process with quantification of adsorbate solution and the adsorbent. The effects of variation of RSCAC dosage on the concentration of the metals present in the wastewater are shown in the Figs 1 – 6 below. It follows a trend of increment in removal of Fe in the wastewater. The removal was maximum at the 8g dosage after which further increment resulted in lesser removal of Fe. For Cu removal, it recorded a maximum reduction in concentration of the metal present in the wastewater at the 3g dosage. Further increase lead to lesser removal. It was different in Zn, where increase in adsorbent dosage resulted in increase in concentration of the metal in the wastewater.

The concentration of zinc in the refinery wastewater increased with increase in adsorbent dosage from 2g to 4g and then decreased. Further increment in dosage resulted in increase in concentration of zinc in the refinery wastewater (effluent) as shown in Table 2. This means that the adsorbent contains some amount of zinc in it.

The contact time used for this study was 2 hours. The rubber seed coat based activated carbon (RSCAC) dosage was also an important factor. It was observed that the affinity of Fe for the adsorbent was higher making it reach equilibrium concentration at the adsorbent dosage of 8g. Affinity of Cu for the adsorbent reached equilibrium at 4g dosage. The removal efficiency for Fe increased from 41.9% to 75.7% when the rubber seed coat based activated carbon (RSCAC) dosage was increased from 2 g to 8g and reduced to 71.0% at 10 g at pH value of 5 as shown in fig 4.8. The % removal and the amount adsorbed of Fe were highest at 8g dosage with values of 75.7%, 0.178 mg/g (equilibrium adsorbance) as shown in Figs 2 and 4. The removal efficiency for Cu also increased from 12.5% to 85.4% when the rubber seed coat based activated carbon (RSCAC) dosage was increased from 2 g to 4g at pH value of 5, increasing the dosage further resulted in a decrease to 81.3% at 6g dosage and later reduced to 70.8% at 10g as shown in Figs 3 and 5. Evident also is the fact that the % removal and the amount adsorbed of Cu were highest at 4g dosage recording 85.4% and 1.54 x10-3 (mg/g).

Their adsorption varied also with the type of metal. The results obtained from the analysis of the effluent (wastewater) before and after adsorption are presented. Table 1 contains the result of the metals initial concentrations in the refinery wastewater before adsorption while Table 2 contains results of % Removal and amount adsorbed for the metals calculated using equations 5 and 6 above.

The advantages of using RSCAC for the removal of metal (Cu, Fe and Zn) include: simplicity in system design, effectiveness and it is relatively cheap. Batch adsorption studies have shown that rubber seed coat based activated carbon (RSCAC) can effectively remove Fe and Cu from refinery wastewater and unsuitable for removal of Zn as shown in the results presented in Table 1 and Figs 1 - 6.

Table 1. Initial Concentration Co of the Metals Before Adsorption

Metal	Co, (mg/L)	Mean Absorbance
Zn	0.094	0.0166
Cu	0.048	0.0079
Fe	12.549	0.0739

Table 2. Effect of adsorbent dosage on the adsorption of metals

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Dosage, (g)	% Removal			Amount Adsorbed qe (mg/g)		
	Cu	Fe	-Zn	Cu x 104	Fe	-Zn x103
2	12.5	41.9	139.4	4.5	0.394	9.83
4	85.4	54.7	223.4	15.4	0.257	7.88
6	81.2	64.9	147.9	9.75	0.204	3.48
8	47.9	75.7	383.0	4.31	0.178	6.75
10	70.8	71.0	387.2	5.10	0.134	5.46

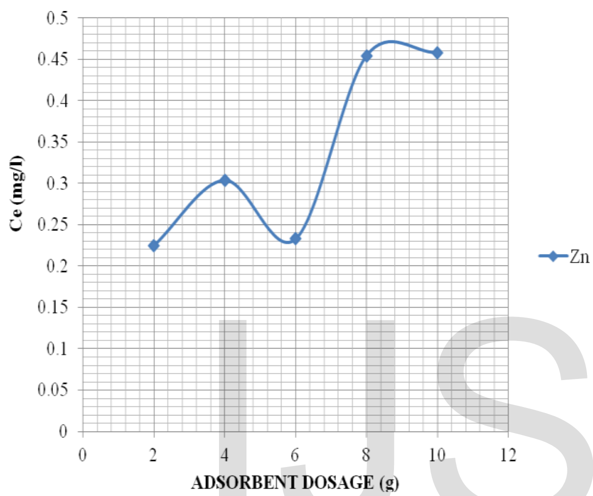

Fig. 1. Final concentration of Zn vs adsorbent dosage after adsorption

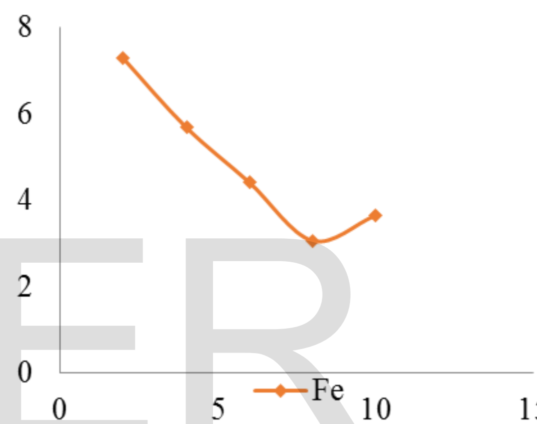

Fig. 2. Final concentration of Fe vs adsorbent dosage after adsorption

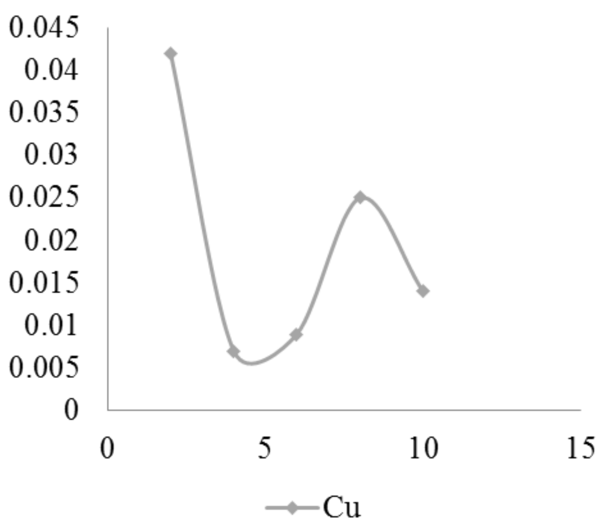

Fig. 3. Dependence of final concentration of Cu on adsorbent dosage after adsorption.

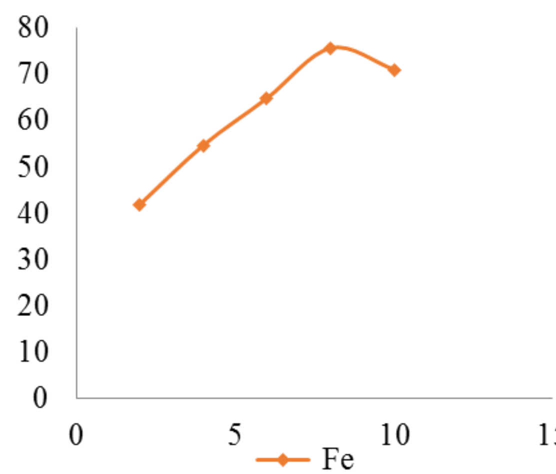

Fig. 4. Dependence of adsorbent dosage on the %Removal of Cu from industrial effluent.

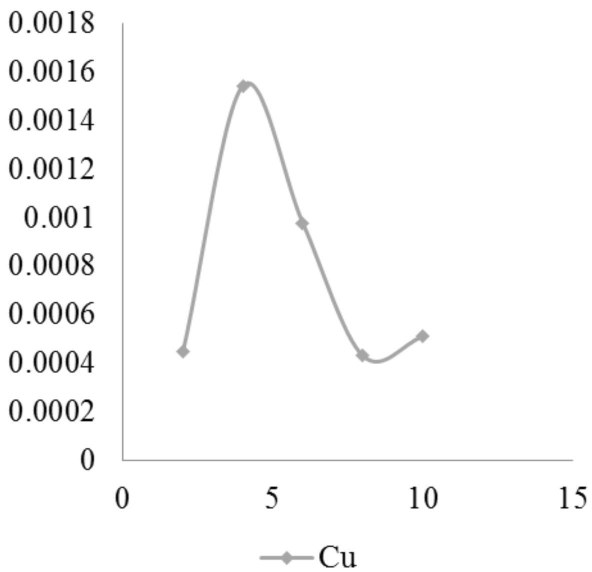

Fig. 5. Effect of adsorbent dosage on the amount of Cu adsorbed at pH 5, contact time 2hrs

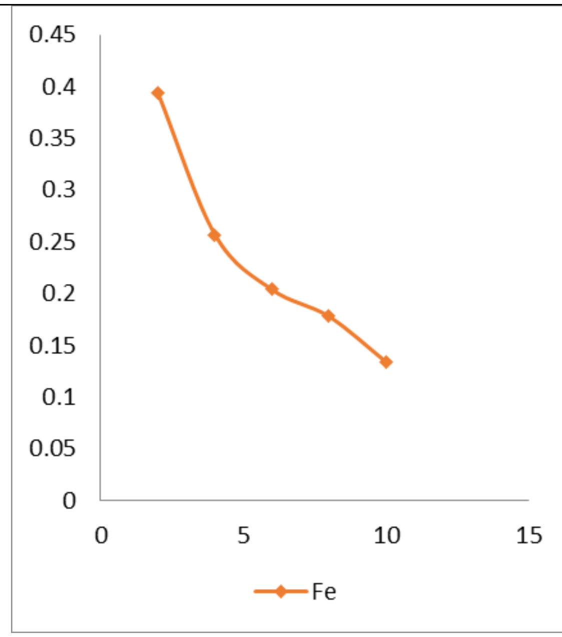

Fig. 6. Effect of adsorbent dosage on the amount of Fe adsorbed at pH 5, contact time 2hrs

Table 3 and Figs 7 and 8 present the results of the Langmuir and Freundlich isotherms calculated using equations 2 and 4. It is clearly evident that metal adsorption varied also with the type of metal. Freundlich and Langmuir isotherms were used in this work. For the adsorption of Fe on RSCAC, a fairly good fit was obtained with the Freundlich isotherm yielding a coefficient of determination (R^2) of 0.81, while Langmuir isotherm indicated absolutely no fit. The reverse was the case when Zn adsorption was investigated and fitted by these two generally acceptable adsorption isotherm models. A poor but moderately fair fit (R^2 value of 0.48) was obtained from the plot of the Langmuir isotherm, while Freundlich isotherm indicated absolutely no fit, with R^2 values of 0. Upon the adsorption of Cu, however, it was observed that both isotherms provide good fits with the Langmuir isotherm perfectly fitting the dependence (R^2 = 0.99), far better as compared to Freundlich isotherm (R^2 = 0.77) (Table 3).

Table 3. The coefficient of determination (R^2) obtained for Langmuir and Freundlich adsorption isotherm plots upon the adsorption of various metals on RSCAC

Metal	R^2	
	Langmuir	Freundlich
Zn	0.48	0
Fe	0.05	0.81
Cu	0.99	0.77

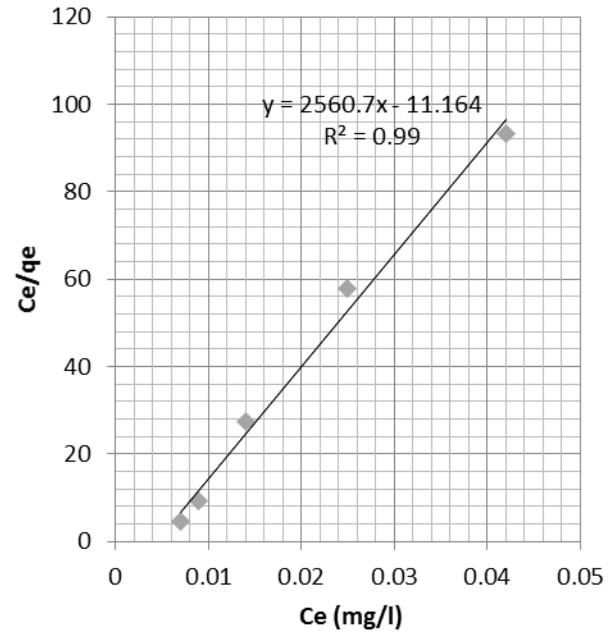

Fig. 7. Langmuir adsorption isotherm plot for Cu adsorption on RSCAC

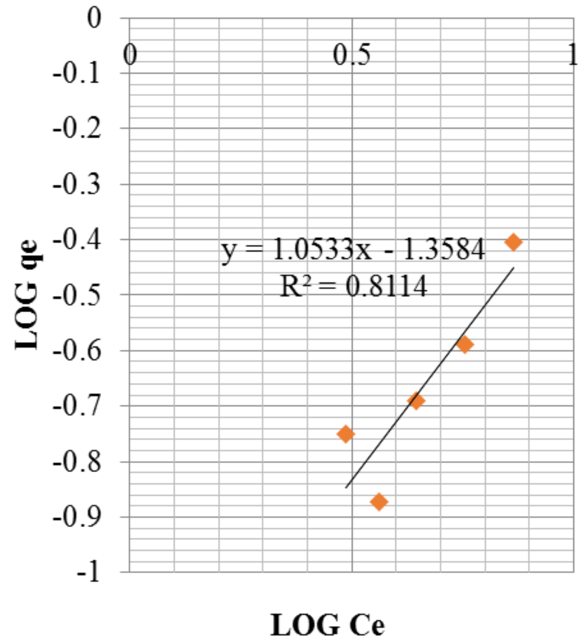

Fig. 8. Freundlich adsorption isotherm plot for the adsorption of Fe on RSCAC

4. Conclusion

In conclusion we have demonstrated that activated carbon derived from rubber seed coat could be successfully employed for the removal of heavy metals, especially Cu and Fe, from an industrial wastewater. The adsorption of Zn and Cu could be better described by means of Langmuir isotherms while that of Fe was better fitted with the aid of Freundlich isotherm. The trend of adsorption capacity was observed to be dependent on the adsorbent dosage and also influenced by the type of metal in the trend Fe>Cu>Zn.

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6. References

[1] A. Akinbiyi, R. Saskatchewan, *Removal of lead from aqueous solutions by adsorption using Peat Moss,* University of Regina, Canada, 2000.

[2] M. Ajmal, R.A.K. Rao, and B.A. Siddiqui, Studies on Removal and Recovery of Cr (VI) from Electroplating Wastes. *Water Res. 30(6):* 1996. 1478-1482.

[3] K. C. Khulbe1 and T. Matsuura, Removal of heavy metals and pollutants by membrane adsorption techniques, Applied Water Science 8:19, 2018. 1-30, https://doi.org/10.1007/s13201-018-0661-6

[4] J. Zhongmin, L. Siyue, W .Li, Assessment of soil heavy metals for eco-environment and human health in a rapidly urbanization area of the upper Yangtze Basin. *Natureresearch scientific reports 8, 3256*, 2018,1-14, DOI:10.1038/s41598-018-21569-6.

[5] B. W. Atkinson, F. Bu, and H. C. Kasan, Considerations for application of biosorption technology to remediate metal-contaminated industrial effluents. *Water SA*, *24*, 1998, 129 - 135.

[6] M.A. Renu and K. Singh, Heavy metal removal from wastewater using various adsorbents: a review, *Journal of Water Reuse and Desalination, 07.4*, 2017, 387-419.

[7] Z. Guixia, Wu Xilin, Tan Xiaoli and Wang Xiangke Sorption of Heavy Metal Ions from Aqueous Solutions: A Review. *The Open Colloid Science Journal, 4*, 2011, 19-31.

[8] M. H. Zia, M. J. Watts, A. Niaz, D. R. S. Middleton, and A. W. Kim, Health risk assessment of potentially harmful elements and dietary minerals from vegetables irrigated with untreated wastewater, *Environmental Geochemistry and Health,* 2017, **39**, 707–728, https://doi.org/10.1007/s10653-016-9841-1.

[9] P.K. Malik, Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics, *J. Hazard. Mater.113*, 2004, 81-88.

[10] H.N.M.E. Mahmud, A.K.O. Huq, and R. Yahya, The removal of heavy metal ions from wastewater/aqueous solution using polypyrrole-based adsorbents: a review. *RSC Adv 18:*2016, 14778–14791.

[11] M. Subhan and IIDR Pardeep Study to Adsorbent of Rice Husk and Saw Dust (Agriculture waste and Timber waste), *Int. Journal of Research in Science and Technology, Vol. 1(III)*, (2011).

[12] O. O. Kehinde, T. A. Oluwatoyin and O. O. Aderonke, Comparative analysis of the efficiencies of two low cost adsorbents in the removal

of Cr (VI) and Ni (II) from aqueous solution, *African Journal of Environmental Science and Technology, Vol.3 (II),* 2009, 360 – 369.

[13] W.S. Peternele, A.A. Winkler-Hechenleitner, , and Pineda, E.A.G., Adsorption of Cd(II) and Pb(II) onto Functionalised Formic Lignin from Sugar Cane Bagasse. *Biresource Technology 68,* 1999, 95-100.

[14] M.O. Smart, O.A. Fawole, O.A. Adesida, A.A. Olunloyo, Assessment of Heavy Metals in Soils and Sugarcane around Cement Factories of Ewekoro Area, South West Nigeria, *International Journal of Scientific & Engineering Research Volume 10, Issue 9,* 2019, 12-21.

[15] Upendra Kumar, Agricultural products and by-products as a low-cost adsorbent for heavy metal removal from water and wastewater: A review. *Scientific Research and Essay, Vol. 1 (2)*, 2006, 033 – 037.

[16] S. Rengaraj, S.H. Moona, R. Sivabalan, B. Arabindoo, V. Murugesan, Removal of phenol from aqueous solution and resin manufacturing industry wastewater using an agricultural waste: rubber seed coat, *J. Hazard. Mater. B 89*, 2002, 185–196.

[17] E. L. Thackston, D. J. Wilson, J. S. Hanson, and D. L. Miller, Lead removal with adsorbing colloid floatation, *Journal Water Pollution Control Federation, 52,* 1980, 317 - 328.

[18] Y. L. Yu, Y. T. Zhuang, X. Y.Song, & J. H.Wang, Lyophilized carbon nanotubes/graphene oxide modified cigarette filter for the effective removal of cadmium and chromium from mainstream smoke. *Chemical Engineering Journal 280,* 2015, 58–65.

[19] R.K. Vempati, S.C., Musthyala, Y.A. Molleh, and D.L.Cocke,, Surface Analyses of Pyrolysed Rice Husk using Scanning Force Microscopy. *Fuel*, *74(11)*, 1995, 1722-1725.

[20] K.K. Wong, C.K. Lee, K.S. Low, M.J. Haron, Removal of Cu and Pb by Tartaric Acid Modified Rice Husk from Aqueous Solution. *Chemosphere* 50, 2003, 23-28.