

## Effects Variation of Some Factors on Adsorption of Cd<sup>2+</sup> onto Modified Agricultural waste

\*Musah, M., <sup>1</sup>Elele, U. U., <sup>1</sup>Umar, M. T. and <sup>2</sup>Umar, A.

<sup>1</sup>Department of Chemistry, Ibrahim Badamasi Babangida University, Lapai, Nigeria

<sup>2</sup>Department of Chemistry, Niger State College of Education, Minna, Nigeria

### ABSTRACT

The effects of variation of time, adsorbent dosage, concentration and solution pH on the adsorption of Cd<sup>2+</sup> from aqueous solution were determined using standard methods of analysis. Results indicate that 83.49 % of Cd<sup>2+</sup> was adsorbed after 30 minutes interaction time and 0.2 g adsorbent dosage with concentration and pH kept at 10 mg/dm<sup>3</sup> and 4 respectively. Similarly, 92.11 % Cd<sup>2+</sup> was removed from solution when adsorbent dosage was increased to 1.0 g while time, concentration and pH remained unchanged. The effect of adsorbent dosage on adsorption of Cd<sup>2+</sup> positive and high (7.438) while the effects of concentration and pH were -6.622 and -4.532 respectively (negative effect). The experimental and calculated (predicted) value for each run were close to the straight line with residual value of  $\leq 2.00$  indicating a good fit of the model.

**Keywords:** Adsorption, time, dosage, concentration, pH, Agricultural Waste

### INTRODUCTION

Heavy metals enter the environment through natural processes or through human activities. These metals are known to persist in the environment creating problems of inaccessibility to clean water as result of contamination. The high cost of water treatment to remove heavy metals has necessitates the need for activated carbon prepared from low cost viable agricultural materials or wastes to meet the increasing need for heavy metal removal from wastewater.

In Nigeria as in most other developing countries, most industries discharge their wastewaters without treatment and there seem to be very little or no supervision by relevant authorities on how the wastewater is discharged into the environment (Babatunde *et al.*, 2014).

The utilization of agricultural by-products for removal of heavy metals from aqueous solutions is getting much attention these days. Natural biopolymers are industrially attractive because of their capability of lowering transition metal ion concentration to parts per billion concentrations and may have potential to be used as low-cost adsorbents, as they represent unused resources, widely available and are environmentally friendly (Ahmad *et al.*, 2014). The best known and most famous of such solids known is activated carbon (AC). AC is a microcrystalline carbonaceous material that has highly developed porosity and internal surface area of more than 500 m<sup>2</sup>/g. It consists of an irregular array of interconnected micro crystallite, each consisting of fused hexagonal ring of carbon similar in structure to graphite. It is predominantly an amorphous solid with large internal surface area and pore volume (Siki *et al.*, 2012). AC is one of the best discoveries that man ever made in technological advancement. It has been

recognized as one of the most widely used adsorbent in wastewater treatment (Bhatnagar *et al.*, 2013).

Adsorption has now become an important phenomenon in sensing and separation of ions and molecules. Any sorbent that has high adsorptive capability and good selective ability is very important in separation through adsorption. This study was aimed at determining the effects of factor variation and contribution on the efficiency of adsorption of Cd<sup>2+</sup>.

### MATERIALS AND METHODS

Cadmium Stock Solution (1000 mg/dm<sup>3</sup>) was prepared by dissolving 2.036 g of 99 % cadmium nitrate tetrahydrate (Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O) in 1000 cm<sup>3</sup> volumetric flask with distilled then made up to mark. The working solutions of 10, 20, 30, 40 and 50 mg/dm<sup>3</sup> were prepared by appropriate dilutions of the stock solution. Adsorbent used for adsorption experiment was prepared from *Bombax buonopozense* Calyx using the two step method with H<sub>2</sub>SO<sub>4</sub> as activating agent. In this method, five (5) grams of the precursor was carbonized in a muffle furnace at 400 °C for 30 minutes then washed thoroughly with distilled water to remove ash before drying. Five (5) grams of the carbonized sample was mixed with 5 cm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> allowed to stand for two hour followed by activation at 800 °C (Abdul-Khalil *et al.*, 2013).

### Factorial design of the adsorption experiment

A 2<sup>4</sup> factorial design was employed to study the adsorption of Cd<sup>2+</sup> on activated carbon (Sheibani and Zera-Khormini, 2012). Table 1 shows the low and high levels of the variables for the adsorption of Cd<sup>2+</sup>. Factorial design reduces the total number of experiments to be performed in

\*Corresponding author. E-mail: mail: mkkoro22@gmail.com

order to achieve maximum optimization (Musah, *et al.*, 2018). It also reduces time and cost of overall process and

better response is obtained (Geyikci and Buyukungov, 2013).

**Table 1:** Factor levels of variables for the adsorption of  $\text{Cd}^{2+}$

Factors	Low level	High Level
Time (min.)	30	150
Dosage (g)	0.2	1.0
Concentration ( $\text{mg}/\text{dm}^3$ )	10	50
pH	4	8

The rate of agitation was kept constant at 250 rpm.

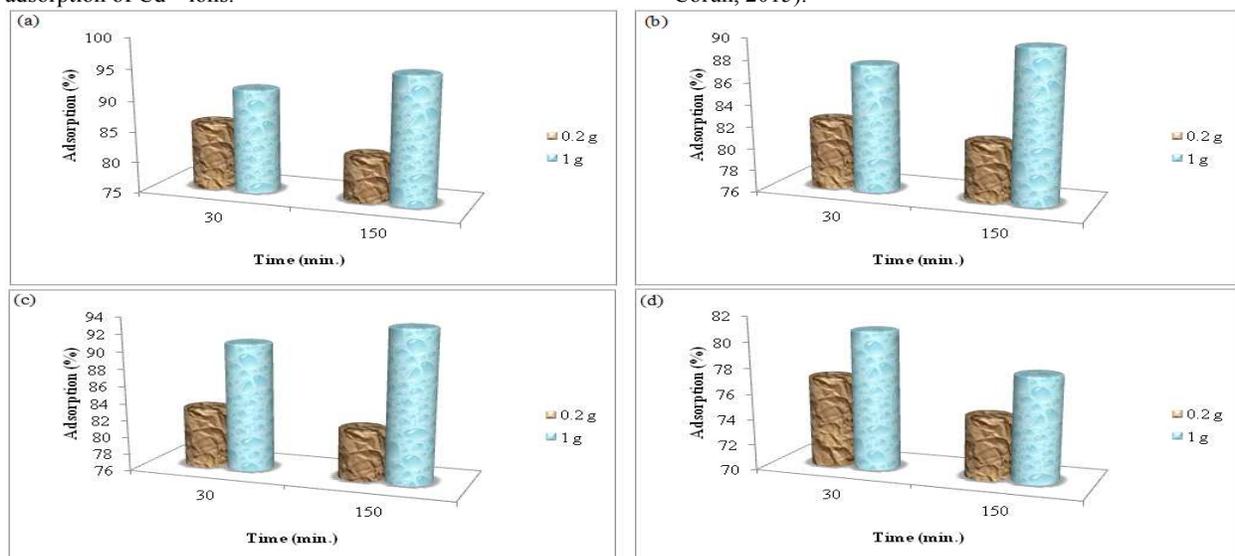
Mathlab 2013A was employed to design the number and order of runs for the factorial experiment for time, adsorbent dosage, concentration and pH with their two-way interactions (Musah *et al.*, 2016). It was also used to determine the predicted response of Cd (II) ion removal in comparison to the actual percent removal obtained from laboratory results. Graphs for variation of adsorption factors were plotted using Microsoft spreadsheet for windows 10.

## RESULTS AND DISCUSSION

### Effect of Factor Variation on Adsorption of $\text{Cd}^{2+}$

Figures 1 – 4 present graphical representation of how change in two experimental conditions at a time (with other parameters kept constant) can simultaneously affect the adsorption of  $\text{Cd}^{2+}$  ions.

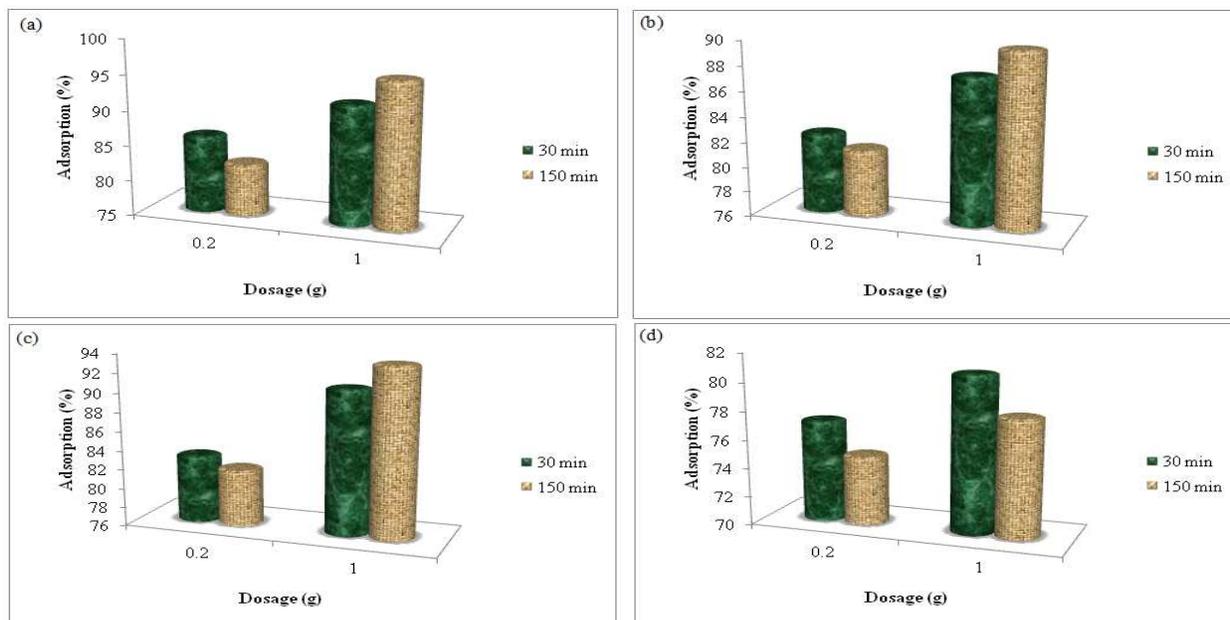
Figure 1 shows the effect of simultaneous variation of time of interaction and adsorbent dosage on adsorption of  $\text{Cd}^{2+}$  while concentration and pH were kept unchanged. At 30 minutes interaction time and 0.2 g adsorbent dosage with concentration and pH held at  $10 \text{ mg}/\text{dm}^3$  and 4.0 respectively, 83.49 % of  $\text{Cd}^{2+}$  was adsorbed; while 92.11 % was adsorbed at 30 minutes when adsorbent dosage was increased to 1.0 g. The increase in adsorption was due increase in number of adsorbing sites resulting from increased adsorbent dosage not the time of interaction. When time was increased to 150 minutes and adsorbent dosage varied between 0.2 and 1.0 g, there was a corresponding increase in adsorption as dosage was increased from 0.2 to 1.0 g. These observations were similar to those reported for the removal  $\text{Pb}^{2+}$  (Tibet and Coruh, 2015).



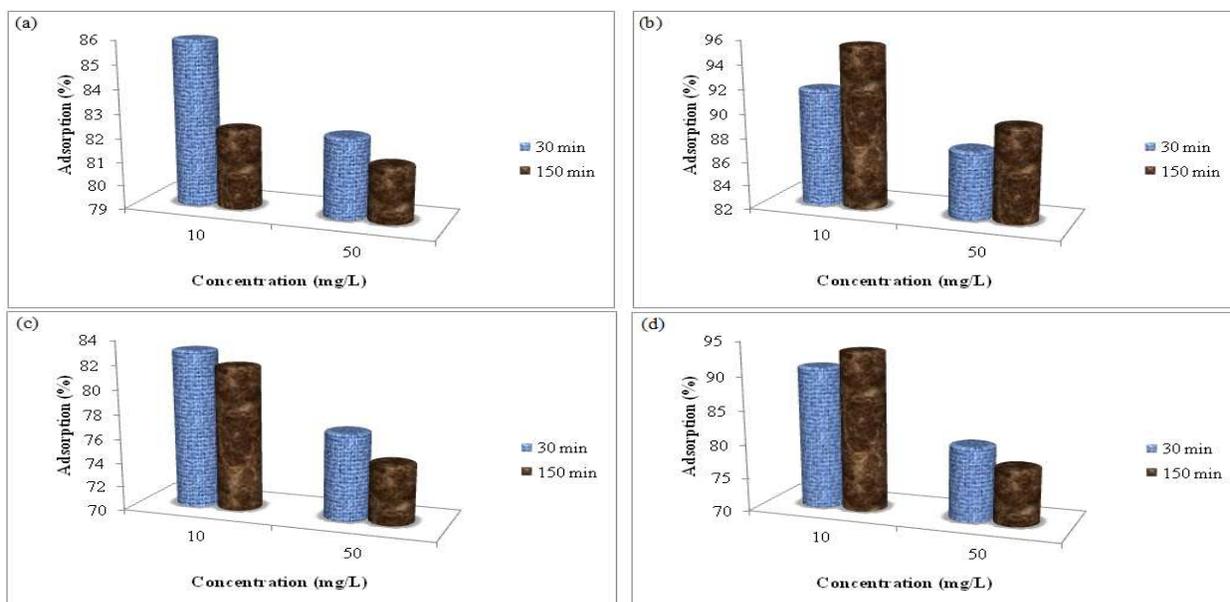
**Figure 1:** Effect of Time on adsorption of  $\text{Cd}^{2+}$  (a) conc. of  $10 \text{ mg}/\text{dm}^3$  and pH of 4, (b) conc. of  $50 \text{ mg}/\text{dm}^3$  and pH of 4 (c) conc. of  $10 \text{ mg}/\text{dm}^3$  and pH of 8 (d) conc. of  $50 \text{ mg}/\text{dm}^3$  and pH of 8

Concentration of adsorbate is an important factor in adsorption. Varying concentration ( $10\text{-}50 \text{ mg}/\text{dm}^3$ ) of solution and time of interaction (30-150 minutes) while keeping dosage and pH constant at 0.2 g and 4.0 respectively, significant adsorptions of  $\text{Cd}^{2+}$  were observed when concentration was  $10 \text{ mg}/\text{dm}^3$  at 30 minutes as seen in figure 2a. On the other hand, when concentration was increase from 10 to  $50 \text{ mg}/\text{dm}^3$  at 30 minutes interaction time, there was a reduction in the amount of  $\text{Cd}^{2+}$  adsorbed. This is due to increased competition for the available

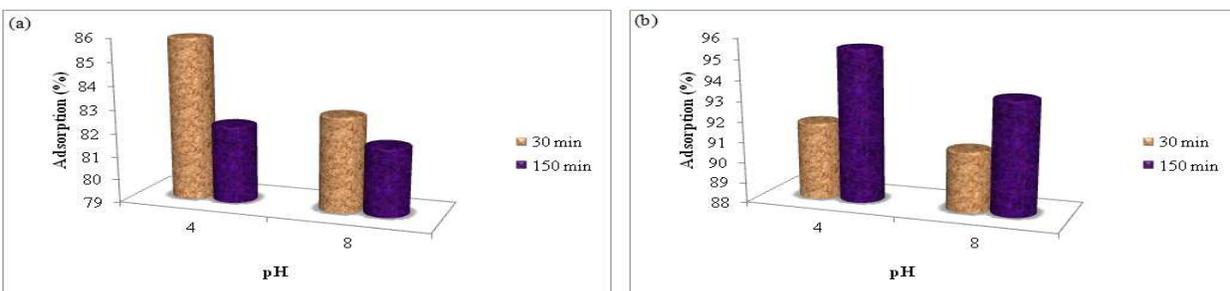
binding sites on the adsorbent as more ions are present in  $50 \text{ mg}/\text{dm}^3$  solution competing for sites available in 0.2 g. The amount of  $\text{Cd}^{2+}$  adsorbed at concentration of  $50 \text{ mg}/\text{dm}^3$  and interaction time of 150 minutes when adsorbent dosage and pH are kept constant (0.2 g and 4.0) was lower than adsorption of  $10 \text{ mg}/\text{dm}^3$  at 30 minutes. With limited binding sites and increased concentration, time of interaction may not significantly enhance the adsorption of  $\text{Cd}^{2+}$  from the solution.

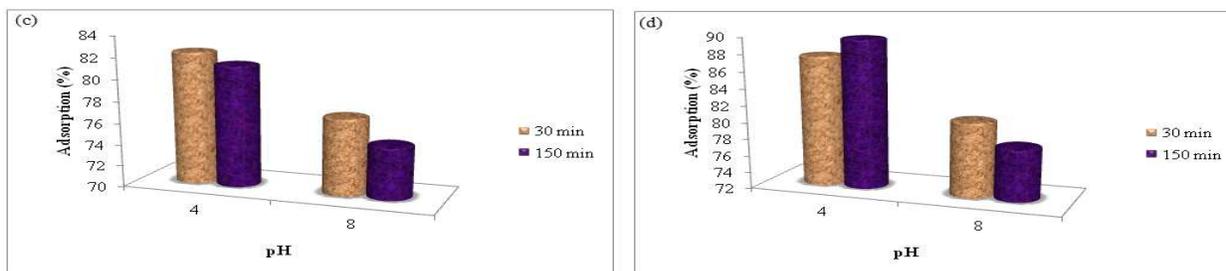


**Figure 2:** Effect of Dosage on adsorption of Cd<sup>2+</sup> (a) conc. of 10 mg/dm<sup>3</sup> and pH of 4, (b) conc. of 50 mg/dm<sup>3</sup> and pH of 4 (c) conc. of 10 mg/dm<sup>3</sup> and pH of 8 (d) conc. of 50 mg/dm<sup>3</sup> and pH of 8



**Figure 3:** Effect of concentration on adsorption of Cd<sup>2+</sup> (a) Dosage of 0.2 g and pH of 4, (b) Dosage of 1 g and pH of 4 (c) Dosage 0.2 g and pH of 8 (d) Dosage of 1 g and pH of 8





**Figure 4:** Effect of pH on adsorption of Cd<sup>2+</sup> (a) conc. of 10 mg/dm<sup>3</sup> and Dosage of 0.2 g (b) conc. of 50 mg/dm<sup>3</sup> and Dosage of 0.2 g (c) conc. of 10 mg/dm<sup>3</sup> and Dosage of 1 g (d) conc. of 50 mg/dm<sup>3</sup> and Dosage of 1 g

**Effect and Contribution of Factors on Adsorption Efficiency**

The effects and percent contributions of each factor and interaction of factors on adsorption of Cd<sup>2+</sup> ions are presented in Tables 2. While adsorbent dosage had the highest positive effect on the adsorption of Cd<sup>2+</sup> from solution, concentration on the hand had the highest negative effect (-6.622). pH of solution also showed negative effect (-4.532) on sorption. The negative values mean an increase in the parameter will cause a decrease in adsorption of Cd<sup>2+</sup> (Santuraki and Muazu, 2015). Adsorbent dosage gave significant positive effect (7.438). This could be due increased surface area and pore volume in the adsorbent. An increase in adsorbent dosage would lead to a corresponding increase in the amount adsorbate removed as more surfaces become available and competition for adsorption sites was reduced (Shalna and Yogamorthi, 2015; Adie *et al*, 2012).

**Table 2:** Effect and Contribution of Factors on the % Adsorption of Cd<sup>2+</sup>

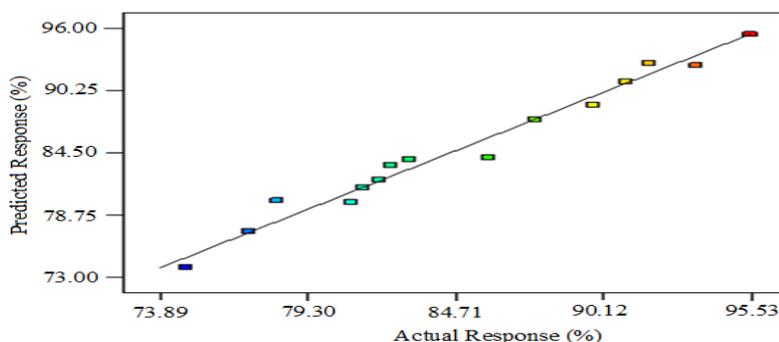
Term	Effect	Sum of Square	Contribution (%)
Time (A)	-0.287	0.340	0.060
Dosage (B)	7.438	221.040	39.060
Concentration (C)	-6.622	175.230	30.970
pH (D)	-4.532	82.040	14.500
AB	1.733	11.950	2.110
AC	-0.678	1.820	0.320
AD	-0.602	1.430	0.250
BC	-2.227	19.780	3.500
BD	-0.768	2.330	0.410
CD	-2.992	35.670	6.300

The percentage contribution of adsorbent dosage to adsorption of Cd<sup>2+</sup> ion is 39.06 % and significantly higher than that of time, concentration and pH.

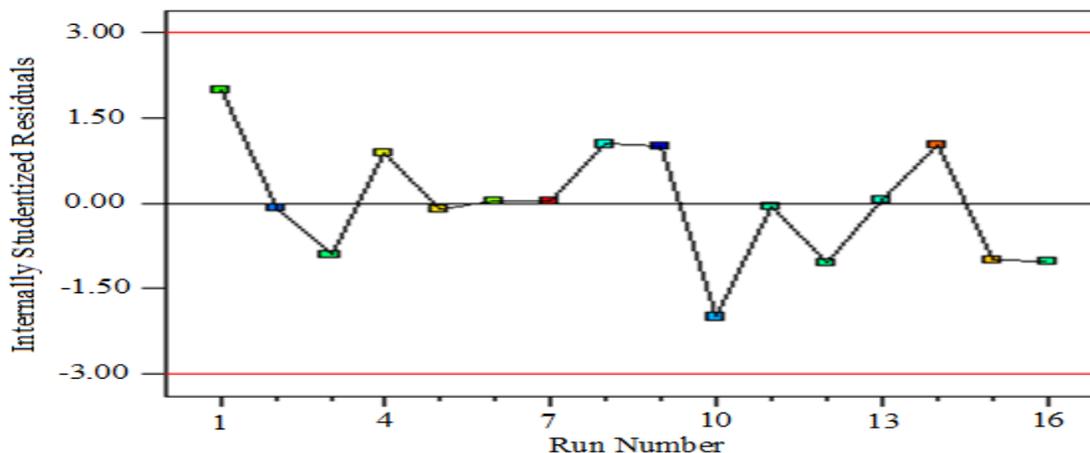
**Verification of Model**

Performance of adsorbents can be visualized by observing the plots of actual (experimental) response versus predicted response and residuals versus run number for the sorption of Cd<sup>2+</sup> as depicted in figures 5 – 6. Figure 5 presents values of plots of actual versus predicted responses of the

adsorption of Cd<sup>2+</sup>, it shows that experimental and predicted values fall close to the straight line and their residuals are within ± 2.00. This suggests the suitability of the models and also indicates a good fit for the experimental data of the sorption of Cd<sup>2+</sup>. The closer the actual and predicted values are to the line, the lower the residual value and the better the fit of the model. Similarly, Davarnejad *et al.* (2015) reported a good fit of model to experimental data using plots of actual versus predicted values.



**Figure 5:** Predicted vs Actual Responses of Adsorption of Cd<sup>2+</sup>



**Figure 6:** Residual vs Number of Run Response for Adsorption of  $Cd^{2+}$

Plot of residuals versus experimental run order (figure 6) showing randomly scattered residual values can also be used to validate the model. Residuals are the difference between experimental and predicted values (Turan and Ozgonenel, 2013). Residual values obtained for the sorption of  $Cd^{2+}$  are within  $\pm 2.00$  which is an indication of a good fit of the model to experimental data. Result of plot for the removal of  $Cd^{2+}$  was lower than the residuals scattered around  $\leq \pm 3.00$  reported for the adsorption of  $Pb^{2+}$  and  $Cu^{2+}$  onto Kenaf fiber based activated carbon (Chowdhury *et al.*, 2012).

### CONCLUSION AND RECOMMENDATION

The influence of adsorption factors on the removal of  $Cd^{2+}$  from aqueous solution was studied. Application of factorial design experiment enhanced the adsorption of  $Cd^{2+}$  and results of analysis indicate that adsorbent dosage had greater influence on sorption  $Cd^{2+}$ , hence the application of factorial design in removal ions from aqueous solution is recommended.

### REFERENCES

- Abdul-Khalil, H.P.S., Jawaid, M., Firoozian, P., Rashid, U. Islam, A. and Akil, H.M. (2013). Activated carbon from various agricultural wastes by chemical activation with KOH: Preparation and characterization. *Journal of Biobased Materials and Bioenergy*, 7:1-7
- Adie, D. B. Okuofu, C. A. and Osakwe, C. (2012). Comparative analysis of the adsorption of heavy metals in wastewater using *Borrassu aethiopicum* and *Cocos nucifera*. *International Journal of Applied Science and Technology*, 2(7): 313-322.
- Ahmad, S. Ali, A. and Ashfaq, A. (2016). Removal of Cr (VI) from aqueous metal solution using roasted China clay. *International Journal of Current Microbiology and Applied Sciences*, 5(5):171-185.
- Babatunde, A. I., Bamgbola, E. P. and Oyalola, O. T. (2014). The pharmaceutical effluents on the quality of groundwater: a case study of Ikeja industrial area of Lagos, Nigeria. *International Journal of Medical Resources and Health Science*, 4(1):1-8.
- Bhatnagar, A., Hogland, W., Marques, M. and Sillanpa, M. (2013). An overview of the modification methods of activated carbon for its water treatment applications. *Chemical Engineering Journal*, 219: 449-511.
- Chowdhury, Z. Z., Zain, S. M., Khan, R. A., Arami-Niya, A. and Khalid, K. (2012). Process variables optimization for preparation and characterization of novel adsorbent from lignocellulosic waste. *BioResource*, 7(3): 3732-3754.
- Davarnejad, R., Moraveji, M. K. and Havaie, M. (2015). Integral technique for evaluation and optimization of Ni (II) ions adsorption onto regenerated cellulose using response surface methodology. *Arabian Journal of Chemistry*. Retrieved from [www.sciencedirect.com/science/article/pii/S187535215001707](http://www.sciencedirect.com/science/article/pii/S187535215001707) doi.org/10.1016/j.arabjc.2015.05.022
- Geyikci, F. and Buyukgungor, H. (2013). Factorial experimental design for adsorption of silver ions from water onto montmorillonite. *Acta Geodyn.Geometer*, 10(3):363-370.
- Musah, M., Yisa, J., Suleiman, M. A.T., Mann,A. and Shaba, E. Y. (2018). Factorial design analysis for the sorption of chromium (VI) ion on modified calyx of gold coast bombax. *FUW Trends in Science & Technology Journal*, 3(1): 223-229.
- Musah, M., Yisa, J., Suleiman, M. A.T., Mann,A. and Auta, M. (2016). Application of factorial design to the adsorption Cd (II) ion from aqueous solution onto chemically modified *Bombax buonopozense* Calyx. *Journal of Scientific and Engineering Research*, 3(3):188-193.

- Santuraki, A. H. and Muazu, A. A. (2015). Assessing the potential of *Lonchocarpus laxiflorus* roots (LLR) plant biomass to remove cadmium (II) ions from aqueous solutions: Equilibrium and kinetic studies. *African Journal of Pure and Applied Chemistry*, 9(5):105-112.
- Shalna. T. and Yogamoorthi, A. (2015). Preparation and characterization of activated carbon from used tea dust in comparison with commercial activated carbon. *International Journal of Recent Scientific Research*, 6(2): 2750-2755.
- Sheibani, A. and Zera-Khormini, M. (2012). Application of factorial design for adsorption of Thallium (III) ion from aqueous solution by pistachio hull. *Indian Journal of Chemical Technology*, 19: 48-51
- Siti, K. C. O., Siki, F. C. O., Misnon, N. A. and Hanim, F.K. (2012). Utilization of sugarcane bagasse in the production of activated carbon for groundwater treatment. *International Journal of Engineering and Applied Science*, 1(2):76-85.
- Tibet, Y. and Coruh, S. (2015). Lead release from lead-acid batteries slag using waste materials: Full factorial design analysis. Proceeding of the 14<sup>th</sup> International Conference on Environmental Science and Technology, Rhodes, Greece
- Turan, N. G. and Ozgonenel, O. (2013). Study of montmoillonite clay for removal of copper (II) by adsorption: Full factorial design approach and cascade forward neural network. *The Scientific World Journal*, 1-11.