



## REMOVAL OF HEAVY METAL IONS FROM WASTE WATER USING GROUNDNUT SHELL AND CLAY SOIL AS NATURAL ADSORBENTS

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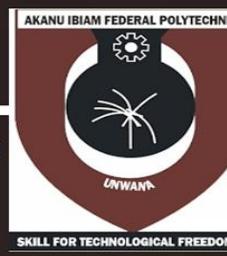
### Abstract

This study was on the use of groundnut shell and clay soil as natural adsorbents for the removal of heavy metals. Groundnut shell and clay soil were used as natural adsorbents for the removal of heavy metals in waste water effluent. The effluent was treated with activated charcoal from groundnut shell and clay soil. The heavy metal concentrations in the effluent, activated charcoal and clay soil after the treatment and purification were determined using Atomic Absorption Spectrophotometer (AAS). The results were compared with WHO Drinking Water Standard. The results showed that the effluent before the treatment recorded Cu  $0.05 \pm 0.01$ mg/L, Fe  $2.20 \pm 1.19$ mg/L, Ni  $0.27 \pm 0.03$ mg/L, Pb  $0.02 \pm 0.00$ mg/L, Zn  $5.37 \pm 0.23$ mg/L, Cd  $0.05 \pm 0.02$ mg/L, and Cr  $0.03 \pm 0.02$ mg/L. The treated effluent with activated charcoal from groundnut shell Cu  $0.05 \pm 0.01$ mg/L, Fe  $0.9 \pm 0.01$ mg/L, Ni  $0.12 \pm 0.01$ mg/L, Pb  $0.02 \pm 0.00$ mg/L, Zn  $0.98 \pm 0.03$ mg/L, Cd  $0.01 \pm 0.00$  mg/L and Cr  $0.01 \pm 0.00$  mg/L, treated with clay soil Cu  $0.34 \pm 0.03$ mg/L, Fe  $1.13 \pm 0.09$ mg/L, Ni  $0.44 \pm 0.26$ mg/L, Pb  $0.00 \pm 0.00$ mg/L, Zn  $3.48 \pm 0.18$ mg/L, Cd  $0.05 \pm 0.02$ mg/L and Cr was not detected. The results showed that Cu and Cr were lower than WHO Drinking Water Standard while the other parameters were higher. The analyses also shows that the clay soil was a better adsorbent than the activated charcoal from a groundnut shell.

**Keywords:** Adsorbents, Heavy metal, Effluent, Treatment, Spectrophotometer

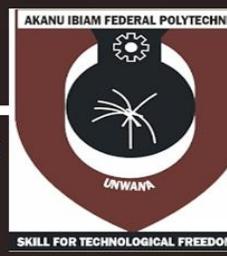
### Introduction

One of the most essential components of human nutrition is water which serves both directly as drinking water or indirectly as constituent of food (Akpen *et al*, 2018). Water can be obtained from a number of sources, among which streams, lakes, rivers, ponds, are rain springs and wells as well as boreholes (Okonko *et al*, 2008) including waste water from industrial effluents. It serves as an important nutritional requirement for promoting healthy living. Maintains personal hygiene, prevents disease and improves quality of life (Dinrifo *et al*, 2010; Adegoke *et al*, 2012; Taiwo *et al*, 2023). In addition to its essential role in human nutrition, in everyday



life, water functions both directly as drinking water directly as constituent of food (Akpen *et al*, 2018). Water is a well-known universal solvent, which consist of hydrogen and oxygen atom chemically combined together to form a molecular substance; hence the molecular formula is  $H_2O$  (Olubanjo *et al*, 2019). With respect to water encyclopedia Britannica, a 2020 report by Zumdahl buttressed that water is an inorganic, transparent and nearly colourless chemical substance made up of hydrogen and oxygen. In its pure form, Olubanjo *et al* (2019) added that water is a colourless, odourless and tasteless liquid but can exists in three physical states; liquid, gaseous and solid states. About 71% of the earth surface is covered by water and less than 3% of the earth's water resources are freshwater with only one-hundredth of a percent of this is adapted for human consumption (Olubanjo *et al*, 2019); Yu and Rong, 2020). Interestingly, over decades, access to portable water has become a daily challenge for many people in Nigeria and other parts of Africa (Hamad *et al*, 2018; Duru *et al*, 2019). Nowadays in Nigeria, the major sources of water are reported to be protected wells, nearby streams and long narrow wells drilled to access groundwater referred to as boreholes (Duru *et al*, 2019). In 2020, Boadi *et al* reported that factors such as location, climate, soil and rock types through which the water moves can affect the quality of water while the reports of Grant and Dietrich (2017), Pitt *et al* (2019) and Abugu *et al* (2021) separately revealed that anthropogenic factors such as disposal of chemical, industrial effluents and microbiological material on landfill sites, waste burning or even directly injecting of waste into the groundwater can later he water natural composition and quality, especially due to heavy metals.

Global environmental pollution by heavy metals has over the years constituted an issue of great concerns due to their non-biodegradability, bio-accumulative nature and adverse effects on the ecosystems as well as the general public health. In 2019, Engwa *et al*. reported that metals which are mainly natural constituents that exist in the ecosystem, are found all over the earth including the atmosphere, earth crust, eater bodies, and can also accumulate in biological organisms including plants and animals. There has been an increased awareness about the health effects of toxic and other trace metals subsequent to environmental exposure (Alizadeh *et al*, 2017; Abdullah and Ibrahim, 2013). In several environmental media, metals are mainly found in ionic form (Moi, 2016). The heavy metals play an important role in environmental pollution as their concentrations in the soil; air and water are continually increasing due to anthropogenic activities (Moi, 2016). Heavy metal contamination is a major environmental concern due to their toxicity carcinogenicity and mutagenicity even at low concentration (Iiechukwu and Okonkwo, 2012). They added that these metals can cause damage to practically all organs of the body (Iiechukwu and Okonkwo, 2012). Heavy metals constitute a very heterogeneous group of elements widely varied in their chemical properties and biological functions and are kept under environmental pollutant category due to their toxic effects on plants, animals and human being (Rajeswari and Namburu, 2014). Majorly, the contamination of soil and water by heavy metals often result from anthropogenic as well as natural activities; but the main anthropogenic activities such as mining, smelting operation. Industrial effluents discharge an agriculture chemicals have locally increased the levels of heavy metals such as Cd, Co, Cr, Pb, As and Ni in the environment up to dangerous levels which ends up exhibiting



harmful effect on biological systems and do not undergo biodegradation (Rajeswari and Namburu, 2014).

Generally, industrially used water is one of the major sources of aquatic pollution and among the aquatic pollutants; heavy metals have gained relatively more significance in view of their persistence, bio-magnification and toxicity (Kadivelu *et al.* 2001). A 2012 report by Sulaymon *et al.* buttressed that the main sources of toxic metals are industrial wastes from processes such as electroplating, metal finishing and chemical manufacturing. From the foregoing it is obvious that the environment is polluted with some heavy metals which can be detrimental to a variety of living species. Again, since there is a water shortage in the world, wastewater treatment and water reuse have become significant. Hence, the elimination of heavy metals from the environment and particularly from water and wastewater plays significant role to public health (Sulaymon *et al.* 2012) since water remains an inevitable essential requirement for life. In the past decades, chemical precipitation, membrane filtration, ion exchange and adsorption are some of the common techniques for the removal of metals from contaminated water and wastewater with adsorption process being the most effective method for removing dissolved metal ions from wastes, have been deployed (Corapcioglu and Huang, 1985; Aalam *et al.*, 2004). Understanding the mechanism of metal ions interaction, specifically, adsorption with a hydrous solid surface is significant to the control of heavy metals in aquatic systems (Corapcioglu and Huang, 1985). Previous literature have shown that the application of activated carbon, a cheap and economically viable approach, can effectively remove heavy metals in water treatment (Aluyor and Oboh, 2009; Jusoh *et al.*, 2007; Gbeju and Miulescu, 2008). Consequently, in the recent decades, efforts have been channeled to wards the use of cheap and commonly available agricultural wastes such as groundnut shell, coconut shell, orange peel, rice husk, peanut husk and sawdust etc., as natural adsorbents in the remediation of these toxic metals from different environmental media and particularly, from wastewater. In 2012, Sulaymon *et al.*, reported that activated carbon has been widely used as an adsorbent with great success. For instance, Bernard *et al* (2013) observed that activated carbon produced from coconut shell (ACS) was used as adsorbent to remove  $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Zn^{2+}$  and  $Pb^{2+}$  ions from electroplating industrial wastewater. Their findings revealed that the optimum adsorbent dosage stirring rate and Ph. Were found to be a 1 g, 350 rpm and pH 6 respectively, while pseudo second-order reaction best fits the kinetic studies, indicating that activate carbon prepared form coconut shell can be efficiently used as low accost alternative for the removal of metal ions from waste water (Benard *et al*, 2013). Similarly, a 2020 study by Ajala and Ali revealed that groundnut shell-based activated charcoal prepared using xing chloride as a chemical activating agent had best iodine adsorption capacity at  $1.0 \text{ moldm}^{-3}$  while the activator's concentration with adoption capacities significantly correlated with iodine value, porosity and surface area. Since heavy metals ions are toxic pollutant and their contaminations of water including waste water constitute a world-wide environmental challenge. This study aims to explore the use of groundnut shell and clay as natural adsorbents for the removal of heavy metal ions from waste water.



### Sample Collection

Groundnut shell and clay soil samples were collected from groundnut fruits selling source and farm land in Afikpo respectively. The clay soil was collected from 15 cm depth using a plastic spoon and a polyethylene bag. The waste water sample was obtained from seven up company effluents located at nine-mile, Enugu, Enugu State, Nigeria. All the samples collected were transported to the Chemistry Research Unit of the Department of Science Laboratory Technology, Akanu Ibiam Federal Polytechnic, Unwana, for pretreatment and were further taken to Home Water Research Laboratory, Abakaliki for the analysis.

### Sample Pre-Treatment

Extraneous materials in the groundnut materials in the groundnut shells and clay soil obtained were removed and were repeatedly washed with deionized water to remove other impurities. They were sun-dried for 3 to 5 days. The dried samples were pulverized and particle size of 500  $\mu\text{m}$  were collected using a mesh, then crushed with a gun and crusher to further reduce their sizes and then stored in an air-tight container for further analyses.

### Adsorbent preparation

The adsorbents were prepared following the method of Ajala and Ali (2020). Exactly 250g of each of the pretreated samples were carbonized at 400°C for 15 minutes and then subsequently activated using 1.0 M  $\text{ZnCl}_2$  at 500°C for two to three hours. They were then brought out of the muffle furnace and cooled in a desiccator until a constant weight was obtained. On cooling, each of the adsorbent prepared was washed several times with deionized water until a pH range between 6 and 7 was obtained. The adsorbent was then dried in an oven at 105°C for a period of 24 hours, removed and allowed to cool and then used for the selected heavy metal ions present in the waste water sample.

### Sample Digestion

A 50 ml of each water sample was transferred into a 250 ml conical flask and 3 ml of a nitric acid ( $\text{HNO}_3$ ) and perchloric acid ( $\text{HClO}_4$ ) in the ratio 3:1 was added to each of the sample. The mixture was placed on a hot plate and digested down to 50ml. It was allowed to cool and filtered through a Whatman no. 42 filter paper into a 50ml volumetric flask. The test samples filtrates were used for metal analysis Varian Spectra AA 55B Atomic Absorption Spectrometer using appropriate cathode lamp.

### Determination of Heavy Metal Ions in the Waste Water

The heavy metal (Pb, Cd, Ni, Cu, Cr, Fe and Zn) ions concentrations in the waste water sample were analyzed using standard analytical methods of APHA (1998). Determinations were carried out before and after adsorption with adsorbents prepared.



### AAS Technique

Atomic absorption spectrophotometer makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires standard solutions to establish the relationship between measured absorbance and the analyte concentration, and relies of Beer-Lambert law. It is commonly used for determining the concentration of a particular metal element in a sample. In their elemental form, metals were made to absorb ultraviolet light and get excited. Each metal has a characteristic wavelength that will be absorbed. The AAS instrument looks for a particular metal by focusing a beam of UV light at a specific wavelength through a flame and into a detector. The sample of interest was aspirated into the flame. If that metal is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity. A computer data system converts the change in intensity into an absorbance.

### Determination of Heavy Metal Ions Adsorption Capacity

Adsorption capacity was determined using the Atomic Absorption Spectrophotometer in accordance with the method of Bernard et al (2013). Adsorption experiment was performed by measuring 100ml of the wastewater sample and poured into a 250 ml conical flask. A 0.5 g of the previously prepared activated carbon was added to the wastewater. The conical flask containing the adsorbent and the wastewater was placed on a rotary shaker and shook at 150 rpm at a room temperature of 32°C for a period of 120 min to ensure equilibrium. The suspension was filtered using Whatman filter paper no. 40. Atomic adsorption spectrophotometer (AAS) was used to analyze the concentrations of the different metal ion present in the filtrate. The amount of metal ions adsorbed by the adsorbent, that is, the equilibrium concentrations,  $C_e$ , of heavy metals ions in the waste water (mg/L) was then evaluated using the expression below:

$$C_e = \frac{(C_0 - C_t) V}{W}$$

Where,

$C_0$  = Initial concentrations (mg/L) of the heavy metal ions present in the waste water before adsorption;

$C_t$  = final concentrations (mg/L) of the heavy metal ions present in the waste water after adsorption for a period of time (t)

$V$  = Volume (ml) of wastewater used, and

$W$  = represent the mass (g) of the adsorbent used.

The percentage of metals ions removed.  $R$  (%) was equally calculated from the equation shown below:



$$R (\%) = Ce = \frac{(Co - Ct)100}{W}$$

### Statistical Analysis of Data

Experimental data were expressed in terms of mean and standard deviation values and percentage composition and were presented in Tables and Graph for each of the adsorption model.

The results of the analysis for the removal of the heavy metal ions in waste water before and after adsorption, using groundnut shell charcoal (GSC) and clay soil charcoal (CSC) as natural adsorbents, are presented in Tables 1 - 6. The results were expressed as mean of standard deviation.

**Table 1: Heavy Metal Concentrations in Untreated Waste Water (sample A), Groundnut shell (Sample B) and Clay Soil (Sample C)**

| Sample | Cu, ppm | Fe, ppm | Ni, ppm | Pb, ppm | Zn, ppm | Cd, ppm | Cr, ppm |
|--------|---------|---------|---------|---------|---------|---------|---------|
| A      | 0.85    | 2.20    | 0.27    | 0.12    | 5.37    | 0.05    | 0.201   |
| B      | 0.03    | 0.89    | 0.12    | 0.02    | 2.88    | 0.01    | 0.01    |
| C      | 0.34    | 1.13    | 0.44    | 0.00    | 3.48    | 0.05    | Nd      |

**Table 2: The Results of the Heavy Metal Concentrations in Purified Waste Water (Sample A) before the Treatment**

| Parameter | 1 <sup>st</sup> | 2 <sup>nd</sup> | 3 <sup>rd</sup> | Mean | Std Dev |
|-----------|-----------------|-----------------|-----------------|------|---------|
| Cu        | 0.04            | 0.04            | 0.06            | 0.05 | 0.01    |
| Fe        | 2.13            | 2.00            | 2.46            | 2.20 | 0.19    |
| Ni        | 0.30            | 0.24            | 0.28            | 0.27 | 0.02    |
| Pb        | 0.10            | 0.15            | 0.11            | 0.12 | 0.02    |
| Zn        | 5.67            | 5.10            | 5.34            | 5.37 | 0.23    |
| Cd        | 0.03            | 0.04            | 0.07            | 0.05 | 0.02    |
| Cr        | 0.20            | 0.22            | 0.19            | 0.20 | 0.01    |

**Table 3: The Results of the Heavy Metal Concentrations in Purified Waste Water with Clay Soil (Sample B)**

| Parameter | 1 <sup>st</sup> | 2 <sup>nd</sup> | 3 <sup>rd</sup> | Mean | Std Dev |
|-----------|-----------------|-----------------|-----------------|------|---------|
| Cu        | 0.02            | 0.01            | 0.06            | 0.03 | 0.02    |
| Fe        | 0.90            | 0.88            | 0.91            | 0.89 | 0.01    |
| Ni        | 0.12            | 0.11            | 0.14            | 0.12 | 0.01    |
| Pb        | 0.01            | 0.02            | 0.02            | 0.02 | 0.00    |
| Zn        | 0.95            | 0.96            | 1.02            | 0.98 | 0.03    |
| Cd        | 0.01            | 0.02            | 0.01            | 0.01 | 0.00    |
| Cr        | nd              | 0.01            | 0.01            | 0.01 | 0.00    |

**Nd = Not detected**

**Table 4: The Results of the Heavy Metal Concentrations in Purified Waste Water with Activated Charcoal from Groundnut Shell (Sample C)**

| Parameter | 1 <sup>st</sup> | 2 <sup>nd</sup> | 3 <sup>rd</sup> | Mean | Std Dev |
|-----------|-----------------|-----------------|-----------------|------|---------|
| Cu        | 0.3             | 0.33            | 0.39            | 0.34 | 0.03    |
| Fe        | 1.17            | 1.00            | 1.22            | 1.13 | 0.09    |
| Ni        | 0.21            | 0.31            | 0.80            | 0.44 | 0.26    |
| Pb        | 0.00            | 0.00            | 0.01            | 0.00 | 0.00    |
| Zn        | 3.57            | 3.63            | 3.22            | 3.48 | 0.18    |
| Cd        | 0.42            | 0.08            | 0.04            | 0.18 | 0.17    |
| Cr        | Nd              | Nd              | Nd              | Nd   | Nd      |

**Table 5: Summary of the Results of the Heavy Metal Concentrations in Waste Water after Purification with Sample A, B and C expressed as Mean Concentration±Standard Deviation**

| Parameter | Sample A  | Sample B  | Sample C  |
|-----------|-----------|-----------|-----------|
| Cu        | 0.85±0.01 | 0.03±0.02 | 0.34±0.03 |
| Fe        | 2.20±1.19 | 0.89±0.01 | 1.13±0.09 |
| Ni        | 0.27±0.03 | 0.12±0.01 | 0.44±0.26 |
| Pb        | 0.12±0.02 | 0.02±0.00 | 0.00±0.00 |
| Zn        | 5.37±0.23 | 0.98±0.03 | 3.48±0.18 |
| Cd        | 0.05±0.02 | 0.01±0.00 | 0.05±0.02 |
| Cr        | 0.20±0.01 | 0.01±0.00 | Nd        |

The results obtained as shown in Tables 1, 2, 3, 4 and 5 revealed varying concentrations of the metal ions in the selected waste water sample with the activated charcoal while Nd means not detected

**Table 6: Results of the Selected Metal Ions Adsorption Capacity and Percentage Removal**

| Meta<br>1<br>l<br>Waste<br>r | Initial<br>Conc.<br>Of<br>Waste<br>r | Conc. After<br>GSC<br>Purificatio<br>n | Adsorptio<br>n Capacity<br>of GSC<br>(mg/g) | R % of<br>GSC    | Conc. after<br>CSC<br>Purificatio<br>n | Adsorptio<br>n Capacity<br>of CSC<br>(mg/g) | R%<br>of CSC   |
|------------------------------|--------------------------------------|--|---|------------------|--|---|----------------|
| Cu                           | 0.018                                | 0.34                                   | -0.064                                      | -<br>1788.8<br>9 | 0.03                                   | -0.002                                      | -<br>66.6<br>7 |
| Fe                           | 2.134                                | 1.13                                   | 0.20  | 47.74            | 0.89                                   | 0.249                                       | 58.2<br>8      |



|    |       |      |        |         |      |        |      |
|----|-------|------|--------|---------|------|--------|------|
| Ni | 0.304 | 0.44 | -0.027 | 100.00  | 0.12 | 0.037  | 60.5 |
| Pb | 0.102 | 0.00 | 0.02   | 0       | 0.02 | 0.016  | 80.3 |
| Zn | 0.672 | 3.48 | -0.562 | -417.86 | 0.98 | -0.062 | -    |
| Cd | 0.28  | 0.18 | -0.03  | -542.86 | 0.01 | 0.004  | 64.2 |
| Cr | 0.201 | ND   | 0.04   | 100.00  | 0.01 | 0.038  | 95.0 |

**GSC = Groundnut Shell Charcoal, CSC = Clay Soil Charcoal**

### Discussion

Tables 1- 5 show the results of the heavy metal concentrations in untreated waste water (Sample A), Clay soil (Sample B) and Activated Groundnut shell charcoal (Sample C) studied. All the metals: Pb, Cd, Ni, Cu, Cr, Fe and Zn, investigated were present in the studied samples at varying concentrations except Cr that was not detected in Sample C. Heavy metal concentrations in Sample A for Cu was  $0.085 \pm 0.01$  ppm, Fe  $2.20 \pm 1.19$  ppm, Ni  $0.27 \pm 0.03$  ppm, Pb  $0.12 \pm 0.02$  ppm, Zn  $5.37 \pm 0.23$  ppm and Cr  $0.20 \pm 0.01$  ppm. Similarly the concentrations of the heavy metals in Samples B for Cu was  $0.03 \pm 0.02$ , Fe  $0.89 \pm 0.01$  ppm, Ni  $0.12 \pm 0.01$  ppm, Pb  $0.09 \pm 0.00$ , Zn  $0.98 \pm 0.03$  ppm, Cd  $0.01 \pm 0.00$  ppm and Cr  $0.01 \pm 0.00$  ppm. The study recorded the mean concentrations in Sample C for Cu as  $0.34 \pm 0.03$  ppm, Fe  $1.13 \pm 0.09$  ppm, Ni  $0.44 \pm 0.26$ , Pb  $0.00 \pm 0.00$  ppm, Zn  $3.48 \pm 0.18$  ppm, Cd  $0.05 \pm 0.02$  ppm and Cr was not detected in Sample C. The results in Table 1 further revealed that the trends of the metal contents in the sample A, B and C are Zn > Fe > Cu > Ni > Cr > Pb > Cd; Zn > Fe > Ni > Cu > Pb > Cd = Cr and Zn > Fe > Ni > Cu > Cd > Pb > Cr, respectively.

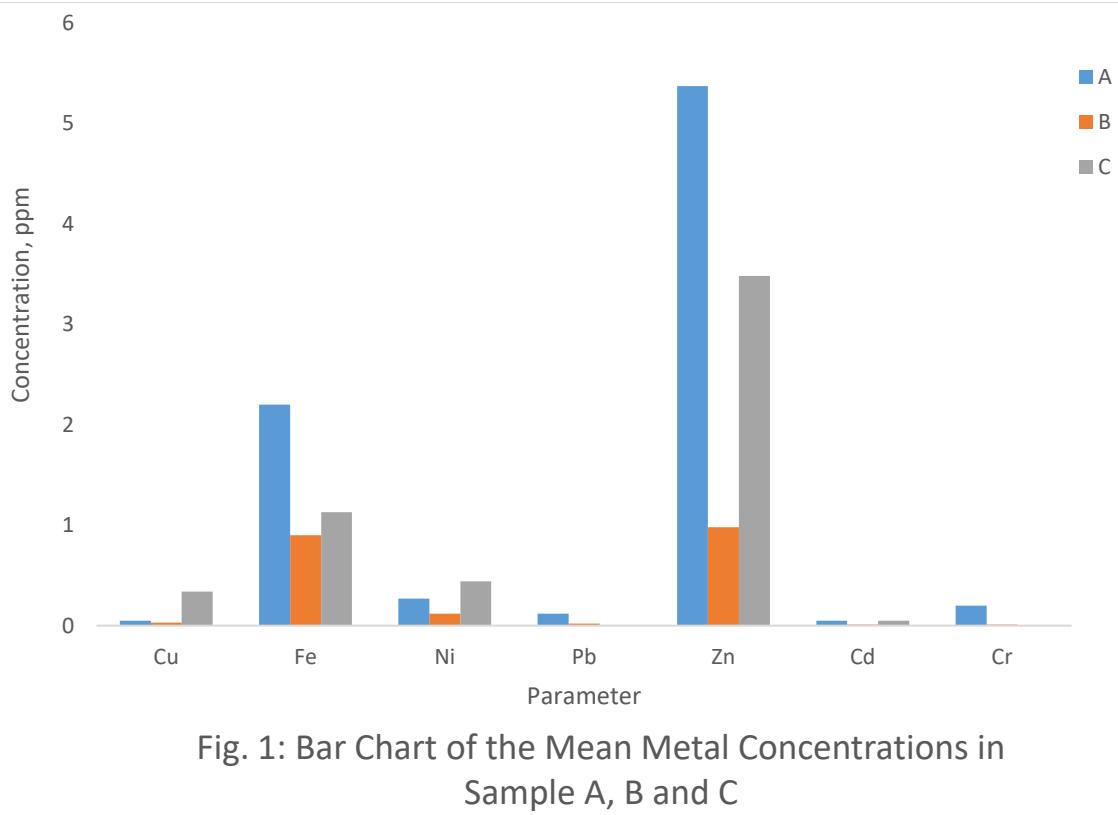


Fig. 1: Bar Chart of the Mean Metal Concentrations in Sample A, B and C

Comparing with the untreated waste water metal contents in Table 1, the results showed that Sample A recorded the highest Cu while Sample B had the lowest value. The value of Fe in Sample A was higher than Sample B and Sample C. The same trend goes for Ni, Pb, Zn, Cd and Cr as all the heavy metal concentrations were higher than all the heavy metals submitted in Sample B and Sample C. The study showed that Clay soil have a higher absorption capacity than the activated groundnut shell. The concentrations of other metals were found to have increased significantly. For instance, Zn shows a rise from 0.672, ppm to 5.37 ppm while Cu, Cd and Pb increased from 0.85 ppm, 0.028 ppm to 0.018 ppm to 0.05 ppm and 0.102 ppm to 0.12 ppm, respectively. Thus, adding waste water to treated waste water can increase its metal contamination level.

In Table 2, the data obtained show the results of heavy metal concentrations in purified waste water using activated clay as a natural adsorbent. On adsorption of the metals with activated carbon made with clay soil, the waste water metal concentrations were found to range from Zn > Fe > Ni > Cu > Pb > Cd and Cr; indicating that the highest and lowest metal values were recorded for Zn  $0.98 \pm 0.03$  ppm and  $0.01 \pm 0.00$  ppm. The results show that while Fe, Ni, Pb, Cd and Cr decreased significantly from their initial concentrations, the concentrations of Cu and Zn rather show an increase their initial values. Cu shows a rise in concentration from 0.018 ppm to 0.03 ppm while Zn rises from 0.672 ppm to 0.98 ppm. The results reveal that using clay carbon as a natural adsorbent; there is a significant adsorption of the metal concentrations in the treatment of contaminated waste water.



The data presented in Table 4 show the results of the heavy metal concentration in purified waste water with groundnut shell activated charcoal. On adsorption of the metals with activated charcoal prepared with groundnut shell. The results in Table 3 reveal a significant decrease in the amounts of Fe, Pb and Cr in the waste water sample, while the concentration of the other metals Cu, Ni, Zn and Cd were significantly increased. The results reveal that groundnut shell activated charcoal is significantly efficient in the removal of Fe, Pb and Cr metal ions showing the metal adsorption trend OF Cr > Pb > Fe.

In addition, the data in Table 5 represent a summary of the results of the heavy metal concentrations in waste water after purification with clay and groundnut shell activated charcoal expressed as mean concentration  $\pm$  standard deviation. On purification of the waste water with samples A, B and C, the results obtained as shown in Table 5 above revealed varying concentrations of the metal ions in the selected waste water sample with the activated charcoal while ND indicates that parameter not detected. The results also show that Cu, Fe, Ni, Pb, Zn, Cd and Cr concentrations, respectively ranged from Sample B  $0.03 \pm 0.02$  ppm – Sample C  $0.34 \pm 0.03$  ppm, Sample B  $0.90 \pm 0.01$  PPM – Sample A  $2.20 \pm 1.90$  ppm, Sample B  $0.12 \pm 0.01$  ppm, Sample C  $0.98 \pm 0.03$  ppm – Sample A  $5.37 \pm 0.23$  ppm, Sample B  $0.01 \pm 0.00$  ppm - sample A and C  $0.05 \pm 0.02$  ppm and C ND – Sample A  $0.20 \pm 0.01$  ppm. The results in Table 5 further reveal that using different activated charcoal, different metal ions concentrations can be significantly added or removed from waste water sample.

The adsorption capacity studies and percentage removal of the selected metal ions were investigated.. The adsorption capacity studies and percentage removal were performed and verified under conditions of 100 m<sup>3</sup> of the waste water, 0.5 g of the adsorbent prepared, room temperature of 32°C and shaking time of 150 rpm. In this study, the results of the adsorption capacity investigated were presented in Table 6. The results revealed that GSC rather resulted in desorption of some of the metal ions Cu, Ni, Zn and Cd from the adsorbent surface, indicating negative adsorption capacities for the metals whereas Fe, Pb and Cr show positive adsorption capacities with removal percentages of 47.05%, 100% and 100%, respectively. This implies that the GSC has greater tendency for adsorption of Pb and Cr followed by Fe when compared with other selected metals under investigation. Similarly, the results of the adsorption capacity of CSC revealed that Cu, Zn were rather desorbed, increasing the metallic concentrations by 66.67% and 45.83%, respectively, while the percentage concentrations of Fe, Ni, Pb, Cd and Cr removed using CSC were 58.29%, 60.53%, 80.39%, 64.29% and 95.02%, respectively. Thus the trend of heavy metal removal by groundnut shell charcoal (GSC) is Cr = Pb > Fe, while for clay soil charcoal (CSC), it is Cr > Pb > Cd > Ni > Fe. In addition, the results revealed that some metallic contaminants are rather desorbed than adsorbed during purification with some adsorbents, indicating adsorbent selectivity. The results of this study agree also with the findings of Kadirvelu *et al* (2001) and compare well with the findings of Bernard *et al* (2013).



## Conclusion

Activated carbon produced from groundnut shell and clay soil are good natural adsorbents for the removal of heavy metals but are more effective for the removal of Cr, Pb and Fe. The results also revealed high percentage removal of Cr and Pb (100%) for GSC and Cr 95.02% for CSC from waste water sample. Since groundnut shell (a waste) and clay (a natural and free substance) are inexpensive and readily available, thus this study provide a cost effective means for removing metals ions from contaminated water or effluents.

## Recommendations

Based on the results of the study, the following are hereby recommended:

- i. That carbonized biomass such as plant shells should be modified and used in the treatment of waste water, and adsorption of pesticides, dyes and heavy metals;
- ii. Other new technologies involving the applications of carbonized ion mass should be developed for the decontamination of other environmental contaminants;
- iii. Government should encourage and support mass production of activated charcoal for several other industrial and domestic uses; and
- iv. More research in the area of functional properties and adsorption kinetics of activated groundnut shell and clay should be carried out.

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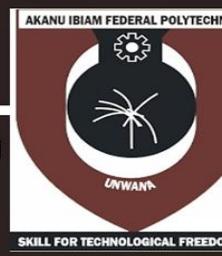
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