PREPARATION, CHARACTERISATION AND APPLICATION OF ACTIVATED CARBON FROM *Terminalia avicennioides* PODS FOR THE REMOVAL OF SELECTED HEAVY METALS FROM AN ELECTROPLATING EFFLUENT

K. A. Abdulkadir[1], J. Yisa[2], E. Y. Shaba[2], J. T. Mathew[3*], and M. Musah[3]

[1]Department of Pure and Industrial Chemistry, Faculty of Physical Sciences, Nnamidi Azikiwe, Awka.
[2]Department of Chemistry, Federal University of Technology, Minna, Niger State
[3]Department of Chemistry, Ibrahim Badamasi Babangida University, Lapai, Niger State
*Corresponding author: ka.abdulkadir@unizik.edu.ng

Abstract

In this study, activated carbons were produced from *Terminalia avicennioides* pods by chemical activation using 50% ortho-phosphoric acid and 1M NaOH labelled as Acid treated *T. avicennioides* activated carbon ATAC/H_3PO_4 and Base treated *T. avicennioides* activated carbon BTAC/NaOH, respectively. Physicochemical properties such as pH, bulk density, moisture content, ash content, volatile matter and fixed carbon were determined. The analysis results show optimum removal efficiency of the selected metals mostly observed at the pH 7, 1hr: 30mins, 0.9 g, and at a temperature of 45°C. The optimum percentage removal on varying the pH (3, 5, 7, 9) were 83%, 80%, 95%, and 35% with ATAC/H_3PO_4 and 80%, 80%, 93%, 70% with BTAC/NaOH for Fe, Ni, Zn and Cd respectively. On varying the contact time (30 mins, 60 mins, 90 mins, 120 mins), optimum percentage removal were 87.2%, 83.6%, 78%, 57.7% with ATAC/H_3PO_4 and 85.7%, 79%, 79%, 59.6% with BTAC/NaOH for Fe, Ni, Zn and Cd respectively. For dosage, 91.8%, 91.0%, 79.0%, 50.8% optimum were obtained with ATAC/H_3PO_4 and 90.7%, 79.2%, 90.9%, 68.8% with BTAC/NaOH for Fe, Ni, Zn, and Cd respectively. The temperature shows an optimum removal of 87%, 80%, 91%, 48% using ATAC/H_3PO_4 and 71%, 76%, 76%, 42% with BTAC/NaOH for Fe, Ni, Zn, and Cd ions, respectively. Generally, the results revealed that ATAC/H_3PO_4 activated carbon works better due to its higher surface of 380.076 m^2/g than BTAC/NaOH activated carbon with a value of 339.852 m^2/g. Cracks showed by Higher Resolution Scanning Electron Microscope further confirmed a better porosity of the ATAC/H_3PO_4 activated carbon. The kinetic plot of the linear form of pseudo-first and second-order for Ni, Cd, Zn and Fe ions adsorption indicated a better correlation between the experimental kinetic data and pseudo-second-order model, which was the best-fit model.

Keywords: *Terminalia avicennioides* pods, Optimum, Physicochemical properties

1.0   INTRODUCTION

The primary source of water pollution is via industrial and domestic activities that generate effluent containing organic, inorganic, and microbial constituents directly discharged into the water bodies without proper treatments (Nargawe and Sharma, 2016). Quite an appreciable number of industries used heavy metals in their operations, thereby leaving behind effluents containing a large amount of non-biodegradable matter such as copper, chromium, nickel, zinc and lead, among others in the mixture (Gangadhar *et al.,* 2012*).* These heavy metals are transported from the industrial sites by run-off water to contaminate water sources downstream and become contaminants of marine, ground, and even surface water (Neeta and Gupta, 2016).

Only about one-quarter of the world's population have access to hygienic drinking water, especially in developing countries like Nigeria **(**Zaharaddeen, 2015). The United Nation's average projections estimated that by 2050, the world population would increase by about 2.9 billion people (WHO and UNICEF, 2013). This rapid increase in population would be accompanied by an increase in demand for water and depletion of water resources, making water a competitive resource in many parts of the world (Amin *et al.*, 2014). The quality of human life is threatened by various environmental problems resulting from rapid urbanisation, industrialisation and other anthropogenic activities (Heejin *et al.,* 2016). Studies revealed that anthropogenic sources and natural geological processes are responsible for contaminating the natural surface water and groundwater with heavy metals (Ai and Ahmad, 2013).

Many industries, including mining, pharmaceutical, plating, battery manufacturing industries, and those involved in producing paints and pigments, ceramic and glass discharge effluents and other industrial wastes into the environment (Nargawe and Sharma, 2016; Ojedokun and Olugbenga, 2015). Industrial and agriculture activities are high, resulting in effluent discharging heavy metals without proper treatment, directly affecting water quality (Ai and Ahmad, 2013). Water industries are interested in providing freshwater adequately by developing cost-effective, stable materials and methods to produce portable and quality drinking water. Various conventional effluent treatment methods are used, such as filtration, evaporation, solvent extraction, bio-sorption, ion-exchange, reverse osmosis, electro-dialysis; these processes are not generally efficient and with few ends up generating waste at the end (Amin *et al.*, 2014).

Chemical modification of the activated carbon surface using acid or base changes the surface functional groups of the carbon and makes it an active point in specific adsorption. This modification improves the adsorbent's hydrophilic/hydrophobic properties and further enhances its binding capacity with metal (Abdulqadir, 2014). The study aimed to prepare, characterise and apply activated carbon from *T. avicennioides* pods to remove selected heavy metals from an electroplating effluent.

2.0   MATERIALS AND METHODS

Sample Collection and Pre-Treatment
T. avicennioides pods were collected in polyethene bags under the tree from Tswachiko village, in Agaie Local Government Area of Niger state. Pods were washed thoroughly with tap water to remove dirt and dust. The sample was further sun-dried for 2 weeks, squashed with hand slightly to remove excess leaves attached and later ground using wooden mortar and pestle to reduce the particle size and obtain powder form.

Metal plating effluent sample was collected from the effluent storage points of the electroplating section at the Scientific Equipment Development Institute (SEDI), Minna Niger State. The sample was manually collected in a 5-litre plastic container using the grab sampling method (collected in two points). The sampler (5-litre plastic container) was dipped into the effluent so that the container faces up while the effluent gets into it. The effluent was well mixed after collection. The plastic container was then carefully corked in and stored in the laboratory for analysis.
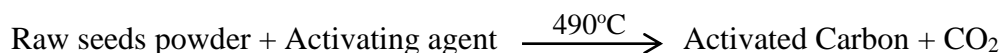
Methods
Effluent digestion
The modified method (Hesham *et al.,* 2012) was used for sample preparation and determination of elements.

Acid, base modification and carbonisation
Standard methods with modification were used for acid and base modification and carbonisation (Zalilah *et al.*, 2015; Madu and Lajide, 2013). Acid (H_3PO_4) modified activated labelled ATAC/H_3PO_4 while the base (NaOH) modified activated labelled BTAC/NaOH. The generalised equation for the process of carbonation is as follows;

$$\text{Raw seeds powder} + \text{Activating agent} \xrightarrow{490^{o}C} \text{Activated Carbon} + CO_2$$

Percentage yield
The percentage yield of the activated carbon produced is the ratio of the weight of the resultant activated carbon to the original precursor weight on a dry basis which was determined according to the method of Ambursa *et al*. (2011).

Burn off
Burn off is determined by finding the weight difference between the precursor and activated carbon divided by the weight of the original samples (Ambursa *et al*., 2011).

Physico-Chemical Test to Determine the Characteristics of Activated Carbon Produced
The activated carbon produced were subjected to physicochemical tests to determine the pH, bulk density and proximate analysis (moisture content, ash content, volatile matter and fixed carbon) using standard procedures (Ekpete and Horsfall, 2011; Smrutirekha, 2014)

Characterisation of the Prepared Activated Carbon

Nova 4200e BET analyser was used to determine the specific surface area of the activated carbons produced (Roozbeh *et al*., 2013) while, a Scanning Electron Microscope (HRSEM) was used to check the surface morphology of the activated carbons (ATAC/H_3PO_4 and BTAC/NaOH) produced (Smrutirekha, 2014).

Batch Adsorption Study

The batch adsorption method was used to study the effects of pH, contact time, adsorbent dosage and temperature on the efficiency and capacity of the activated carbons to adsorb Ni, Cd, Zn and Fe from wastewater (Chigondo, 2013; Nazar *et al.,* 2013).

Data Analysis

The effect of the adsorption parameters such as the pH, contact time, adsorbent dosage and the temperature on the removal efficiency was determined using equation 1 (Said *et al*., 2014).

$$\text{Removal efficiency}(\%) = \frac{C_{o-}\ C_e}{C_o} \times 100$$

Where,

C_o = Heavy metal concentration (mg/L) at initial time,
C_e = Heavy metal concentration (mg/L) at the equilibrium condition.

Kinetics of adsorption was determined as described by Bernard and Jimoh (2013),

EDX

The chemical analysis using the EDX technique detects those protons using a solid detector Si–Li (detection by energy dispersion). The energy of these photons, X, is characteristic of its atoms. A line spectrum (peak) is obtained, corresponding to the photons X of a given energy, representing a given element. The intensity of the characteristic lines is proportional to the concentration of the element in the analytical volume. However, there is a factor of correction depending on the experimental parameters (energy of the incidental beam, its angle) and the sample composition. Thus, only a semi-quantitative analysis is considered. The detection limit is situated at the concentrations of 0.1–1 % (for elements having average or light atomic weight except for unfavourable superposition of characteristic peaks) (Solomon *et al*., 2017).

3.0   RESULTS AND DISCUSSIONS

The initial concentration of metal ions in the effluent before interaction with adsorbent is presented in Table 1.

Table 1: Initial Metal Ion Concentration of the Selected Metals

Metal	Concentration (mg/L)	WHO/UNICEF (2010) Permissible Limit (mg/L)
Cadmium	0.260	0.003
Iron	4421.111	0.300
Nickel	288.176	0.020
Zinc	27.289	3.000

Source: WHO/UNICEF, 2010

This result indicates higher concentrations of Cd, Fe, Ni and Zn metals as compared to the WHO/UNICEF permissible limit. Iron had the highest value of 4421.111 mg/L, which could be attributed to the pickling process before the electroplating or the nature of the metals used (Bernard *et al.,* 2013). During this process, the metal to be plated is washed with sulphuric or hydrochloric acid to remove stains, inorganic contaminants or rust; the pickle liquor forms part of the effluent. However, cadmium indicated a lower concentration of 0.260 mg/L, which might account for its slow dissolution in the pickling process of electroplating or the nature of the metals used in the plating industry. The concentrations of these heavy metals in the electroplating effluent were above the permissible limits and, therefore, need to be treated before discarding or re-using.

Physico-chemical analysis
Results physicochemical characteristics such as pH, bulk density, moisture content, ash content, volatile matter and fixed carbon of $ATAC/H_3PO_4$ and BTAC/NaOH adsorbents are presented in Table 2.

Table 2: Characteristics of $ATAC/H_3PO_4$ and BTAC/NaOH Activated Carbons

Parameters	$ATAC/H_3PO_4$	BTAC/NaOH
Percentage Yield (%)	62.50	43.20
Percentage Burn off (%)	56.90	37.66
pH	7.18	7.64
Bulk density (cm^3/g)	0.83	0.59
Moisture Content (%)	4.20	4.60
Ash Content (%)	9.20	13.47
Volatile Matter (%)	17.28	12.42
Fixed Carbon (%)	69.32	69.51

$ATAC/H_3PO_4$ sample yield (62.50%) was higher than the 43.20% obtained for BTAC/NaOH. In addition, the percentage burn off of $ATAC/H_3PO_4$ and BTAC/NaOH was 37.66% and 56.90%, respectively. This could be the reason $ATAC/H_3PO_4$ yield better due to its lower percentage burn off as the higher the number of materials burned off, the lower the amount of fixed carbon that would be obtained.

The surface of ATAC/H_3PO_4 and BTAC/NaOH were maintained at a slightly alkaline pH of 7.18 and 7.64, respectively, indicating that the washing process was completed. Too high or too low pH is an indication of incomplete acid/base wash. Hence, the activated carbon's 7.18 and 7.64 pH values indicate that moderately activated carbon acid-base complete washing effectively removed the selected heavy metals.

ATAC/H_3PO_4 and BTAC/NaOH bulk densities were 0.83 cm^3/g and 0.59 cm^3/g, respectively. From the results, ATAC/H_3PO_4 and BTAC/NaOH were expected to have good efficiency in removing selected heavy metals. Ash content of ATAC/H_3PO_4 and BTAC/NaOH were revealed to be 9.20% and 13.47%, respectively. ATAC/H_3PO_4 and BTAC/NaOH were expected to be suitable adsorbents because of their low ash content, as shown in Table 2. This agreed with the findings of Smrutirekha (2014). Moisture contents of ATAC/H_3PO_4 and BTAC/NaOH were 4.20 and 4.60%, respectively. However, according to Atef (2016), the general recommended activated carbon storage for its moisture content is expected to be less than 3%; if the percentage moisture content of activated carbon becomes high, micro-organisms especially fungi, would degrade the carbon during their metabolic processes (Atef, 2016).

Volatile matters are those products except moisture, given off by a material as gas or vapour during the carbonisation process. Physico-chemical analysis data in Table 2 showed that the samples treated with ATAC/H_3PO_4 and BTAC/NaOH contained 17.28% and 12.42% volatile matter and yielded 69.32% and 69.51% fixed carbon, respectively.

Results of the Characterisation

Value of surface area and pore volume of ATAC/H_3PO_4 and BTAC/NaOH activated carbons are presented in Table 3.

Table 3: BET for ATAC/H_3PO_4 and BTAC/NaOH

Samples/Parameter	Surface Area (m^2/g)	Pore Volume (cm^3/g)
ATAC/H_3PO_4	380.076	0.1941
BTAC/NaOH	339.852	0.1852

The BET surface area of ATAC/H_3PO_4 was 380.076 m^2/g and was more significant than 339.852 m^2/g obtained for BTAC/NaOH. Pore volume values indicated that both ATAC/H_3PO_4 and BTAC/NaOH were porous with a value of 0.1941 cm^3/g and 0.1852 cm^3/g, respectively. There is, therefore, an increase in the pore volume when the activating agent was changed from base to acid, showing the development of porosity as H_3PO_4 was employed. The pores were thought to be formed partly due to the evolution of gaseous carbonisation products (such as CH_4, CO_2, H_2, H_2O) through the carbonaceous masses and partly due to the metallic salts produced as a result of reactions during carbonisation (Hakan and Ilknur, 2008).

The increase in surface area and pore volume upon activation with H_3PO_4 and NaOH indicated that the metallic salts formed upon activation with H_3PO_4 were removed more during the washing step and created higher porosity in the structure of the adsorbent as compared to that of NaOH.

The higher surface area of ATAC/H_3PO_4 is an indication that the surface would be more suitable for the sorption process.
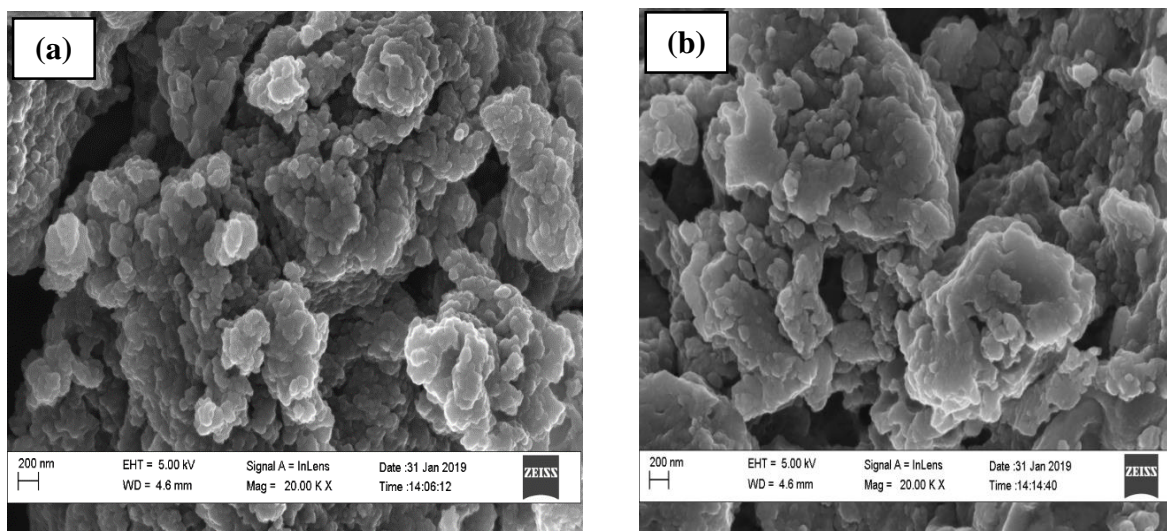
Plate 1: **(a). HRSEM micrographs for ATAC/H_3PO_4**　　**(b). HRSEM micrographs for BTAC/NaOH**

As presented in plate 1, the HRSEM micrographs of ATAC/H_3PO_4 and BTAC/NaOH indicated that the surfaces of both activated carbons were irregular, rough and highly porous, indicating the possibility of good adsorptive properties of ATAC/H_3PO_4 and BTAC/NaOH activated carbons. This showed that the activation stage produced extensive external surfaces with irregular cavities and pores. Although they both have good surface morphology, ATAC/H_3PO_4 had more pores. These pores result from the chemical reagent (H3PO4) evaporation during carbonisation, leaving more empty spaces. Similar findings were reported by Hesas *et al.* (2013) and Deng *et al*. (2010). The presence of these pores provides active sites during the adsorption process. It is worth mentioning that during washing activated carbon, some particles trapped into the pores could block the cracks and cavities from being visible removed. Therefore, the adsorptive capacity of the adsorbents could be further increased if the washing procedure was improved (Mohanty *et al*., 2005).

Elemental Composition
Tables 4, 5 and 6 present the per cent elemental composition of unmodified and chemically (H_3PO_4 and NaOH) modified adsorbents.

Table 4: Elemental composition from EDX of the unmodified adsorbent

S/N	Element	Weight%	Atomic %
1	C	63.55	74.48
2	O	22.50	19.80
3	Si	1.08	0.54
4	P	1.34	0.61
5	K	1.98	0.71
6	Ca	7.35	2.58
7	Mg	2.20	1.27

Table 5: Elemental composition from EDX of ATAC/H$_3$PO$_4$ adsorbent

S/N	Element	Weight%	Atomic %
1	C	74.55	81.29
2	O	20.41	16.71
3	Si	0.65	0.3
4	P	2.59	1.1
5	K	1.8	0.6

Table 6: Elemental composition from EDX of BTAC/NaOH adsorbent

S/N	Element	Weight%	Atomic %
1	C	68.39	80.16
2	O	21.12	18.58
3	Na	1.66	1.02
4	Mg	1.06	0.61
6	Si	0.46	0.23
7	P	1.5	0.68
8	K	1.04	0.37
9	Ca	4.77	1.68

Table 4 shows the carbonised sample's elemental composition, which consisted of C, O, Si, P, K, Ca and Mg with weights (%) of 63.55, 22.50, 1.08, 1.34, 1.98 7.35 and 2.20, respectively. It was observed in Table 5 (for ATAC/H$_3$PO$_4$) that the percentage weight (%) of P increased from 1.34% in unmodified to 2.59% in ATAC/H$_3$PO$_4$. The weight (%) increase of phosphorus in ATAC/H$_3$PO$_4$ was attributed to the use of phosphoric acid during the chemical activation process. After activation, the activated carbon was washed repeatedly using distilled water to remove the excess phosphoric acid. However, the presence of phosphorus explains the presence of a residual phosphoric acid, which was not washed completely (Anyika *et al*., 2017). Table 6 is worthy of mentioning the presence of sodium atoms, which is justified by the presence of hydroxyl (OH)

functional groups as sodium remains electrostatically attached to the hydroxyl group in the material (Islam *et al*., 2017).

Overall, the sample with the highest amount of carbon and the least amount of oxygen was observed to be the most effective. This implies that the higher the carbon content in the sample, the lower is the amount of oxygen and the higher the adsorption capacity. It was observed from Tables 4, 5 and 6 that the acid (H_3PO_4) activated adsorbent had the highest carbon content by weight (74.55 %) and (81.29%) by atom and the lowest amount of oxygen followed by the base (NaOH) activated sample with carbon composition (68.39%) by weight and (80.6%) by atom. On the other hand, the unmodified adsorbent has the least percentage by weight (63.55%) and atomic (74.48%) carbon, respectively. This suggests that samples rich in carbon content can be efficient adsorbents for removing dyes, heavy metals and other organic pollutants from aqueous solution (Xiong *et al*., 2014). EDX studies also showed evidence that an increase in carbon content denotes that activation has occurred successfully.

Effects of Process Parameters on the Percentage Removal
Figures 1 and 2 present the percentage removal of Fe, Ni, Zn and Cd from the effluent after interaction with adsorbent. The experimental condition pH was varied (3, 5, 7, 9) while contact time and adsorbent dosage were kept constant at 120 mins and 0.5 g, respectively.
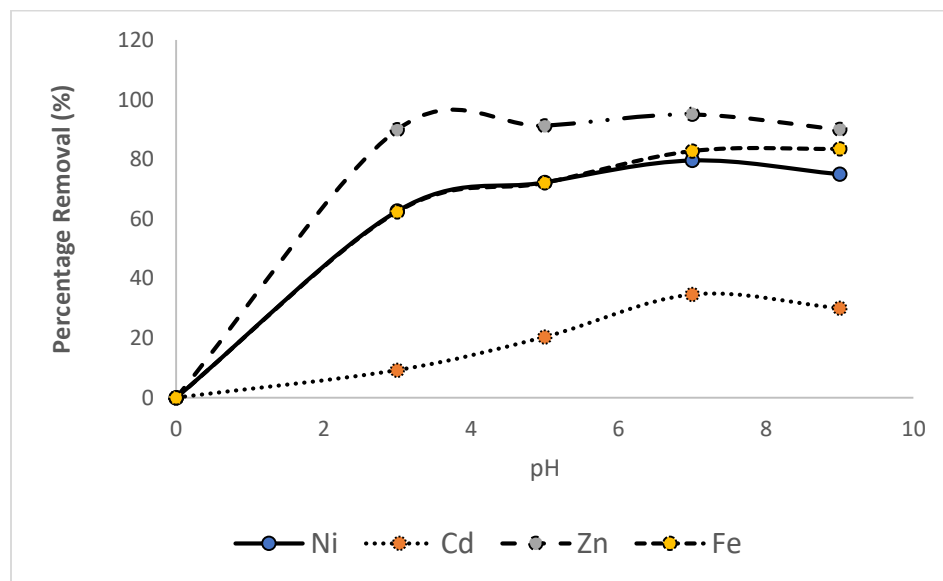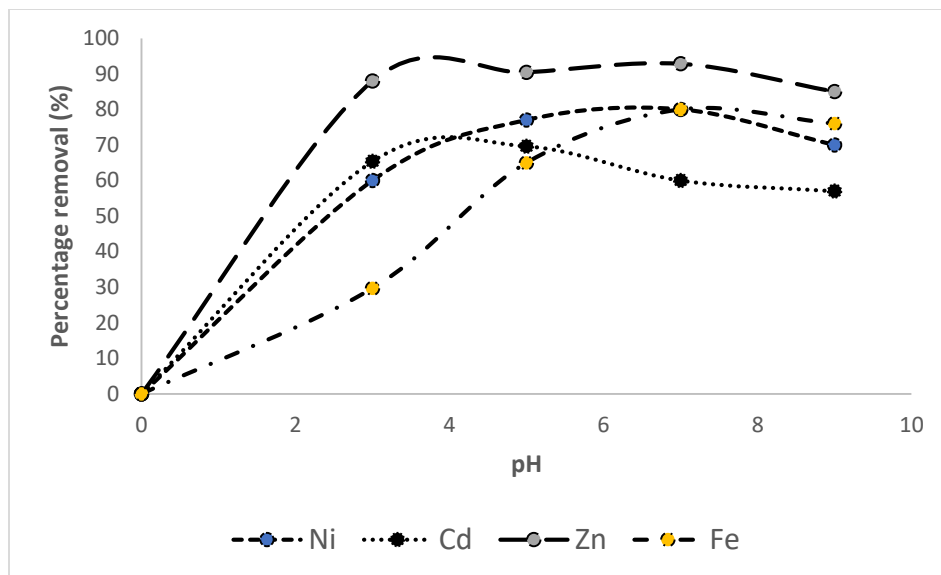

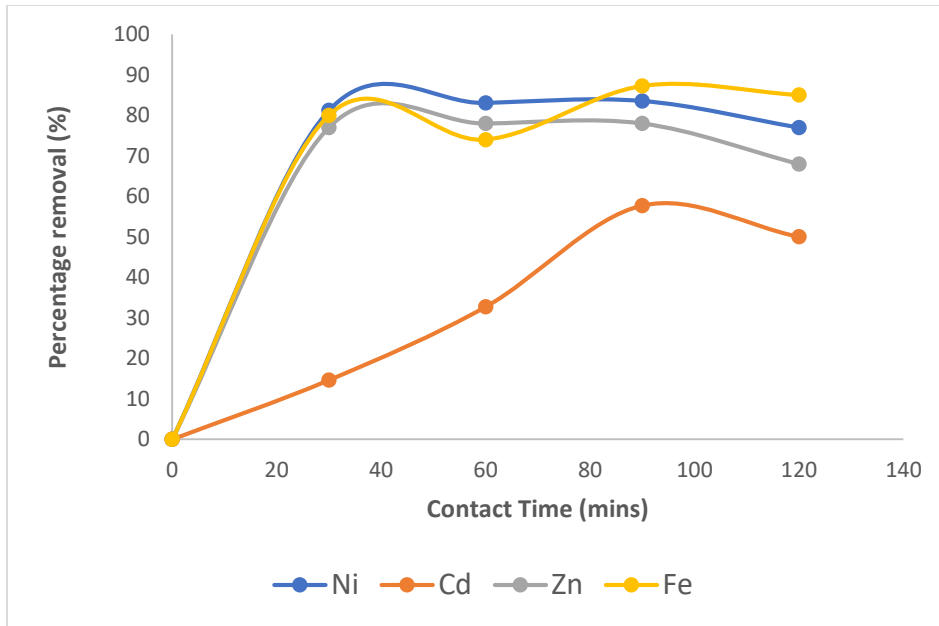**Figure 1: Effect of pH on heavy metal removal by ATAC/H₃PO₄**

Figure 2: Effect of pH on heavy metal removal by BTAC/NaOH

Figures 1 and 2 showed that percentage removal was highest at neutral pH 7.0, reaching the optimum value of 95% and 93% removal of Zn for ATAC/H3PO4 and BTAC/NaOH, respectively. The higher per cent removal of the Zn could be attributed to its smaller atomic radius compared to Ni, Fe and Cd. However, it was observed that the percentage removal decreased gradually with the increase in pH. The order of removal was Zn > Ni > Fe > Cd. Optimum adsorptions were attained at pH 7.0; beyond the pH of 7.0, precipitation occurred. The results obtained are in close agreement with those reported by Mutasim *et al.* (2017). These results could be explained as, in acidic media, i.e. when the pH of the solution was less than 4, the elevated hydrogen ions (H+) complete with the metal ions from reaching the free available sites on the adsorbent surface and prevent the ions from bounding with activated carbon surface due to repulsive forces. Besides that, it is also noted that when the pH values reach 5 and above, the adsorption process was enhanced, and removal percentage get maximum quantities due to lower hydrogen ions (H+) that exist; hence these ions got better chance to occupy the free sites of the active surface.

Subsequently, when the pH proceeds towards the basic region, the values of adsorbed ions increase significantly, specifically at a pH of 7. However, pH 9 mostly recorded lower values and showed a decline in the percentage removal. This can be attributed to ions precipitated by the formation of hydroxide anions (Mutasim *et al.*, 2017; Barkat *et al.*, 2009).

Figures 3 and 4 showed the percentage removal of Fe, Ni, Zn and Cd from the effluent after treatment. Contact time was varied (30 mins, 60 mins, 90 mins, 120 mins), while pH (7) and adsorbent dosage (0.5 g) other parameters were kept constant at room temperature.

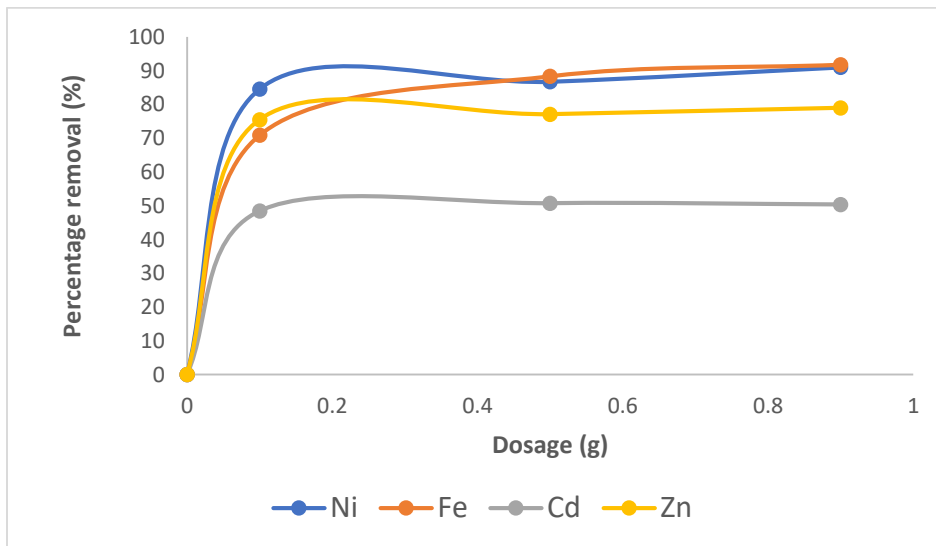**Figure 3: Effect of Contact time on heavy metal removal by ATAC/H₃PO₄**
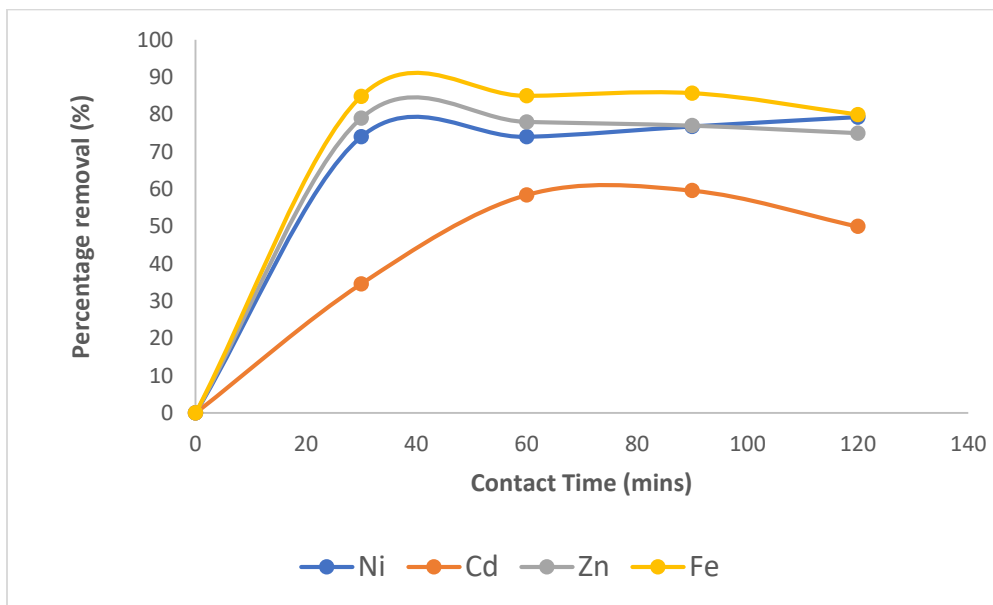
**Figure 4: Effect of Contact time on heavy metal removal by BTAC/NaOH**

The effect of contact time on removing Ni, Cd, Zn and Fe onto ATAC/H₃PO₄ and BTAC/NaOH is shown in Figures 3 and 4. The amount of the adsorbed metal ions increased with increasing time reaching optimum adsorption at 90 mins before decreasing after 120 mins. A decrease in the adsorption capacity is indicative of equilibrium due to saturation of adsorption sites. Rapid adsorption of metal ions during the initial stages of the process was due to the large initial concentration gradient between the adsorbate in solution and the number of available vacant

adsorption sites on the adsorbent surface (Mutasim and Yusuf, 2015). The per cent removal of Ni, Cd, Zn and Fe using ATACH/H_3PO_4 was 83.6%, 57.8%, 78.0%, and 87.2%, respectively and were greater than 76.8%, 59.6%, 77.0% and 85.7% obtained when BTAC/NaOH was used as adsorbent The removal percentage here are closely related; however, the ATAC/H_3PO_4 activated carbon still performs better in removing most of the selected metals Zn and Fe.

Figures 4 and 5 showed the percentage removal of Fe, Ni, Zn and Cd from the effluent after treatment. The experimental conditions were; adsorbent dosage (0.1 g, 0.5 g, 0.9 g), while other parameters were kept constant; contact time (120 mins), pH (7) and at room temperature.

Figure 5: Effect of dosage on heavy metal removal by ATAC/H_3PO_4
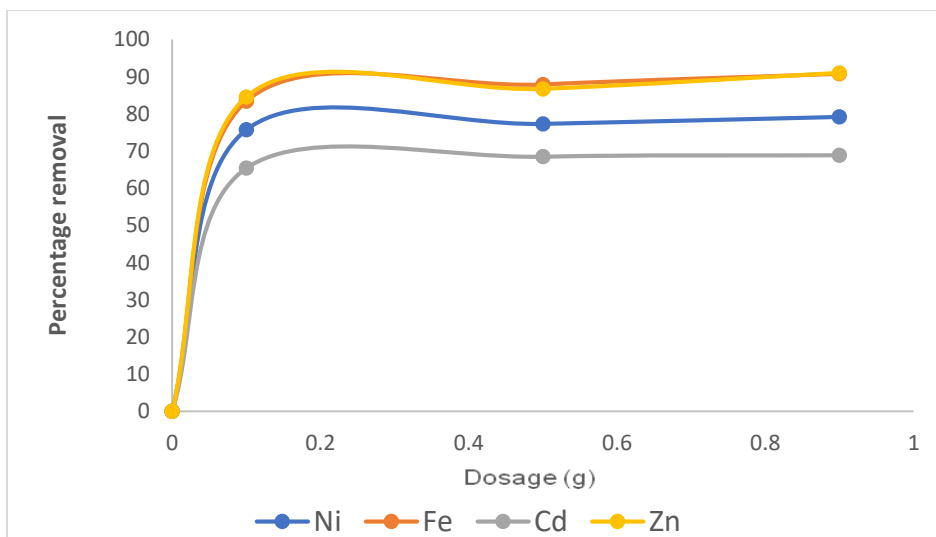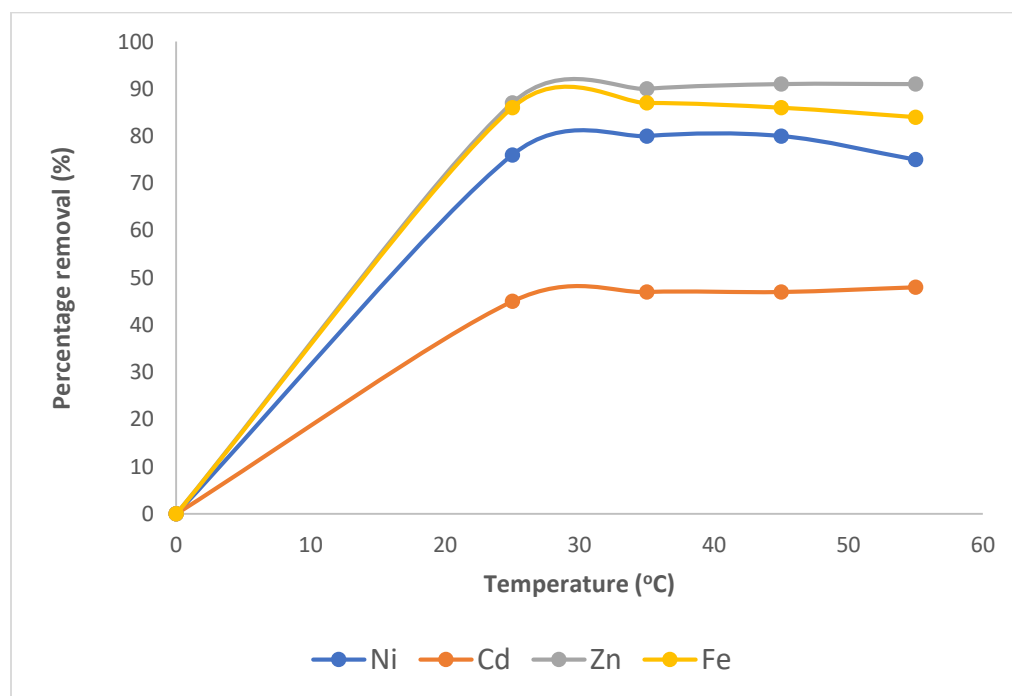

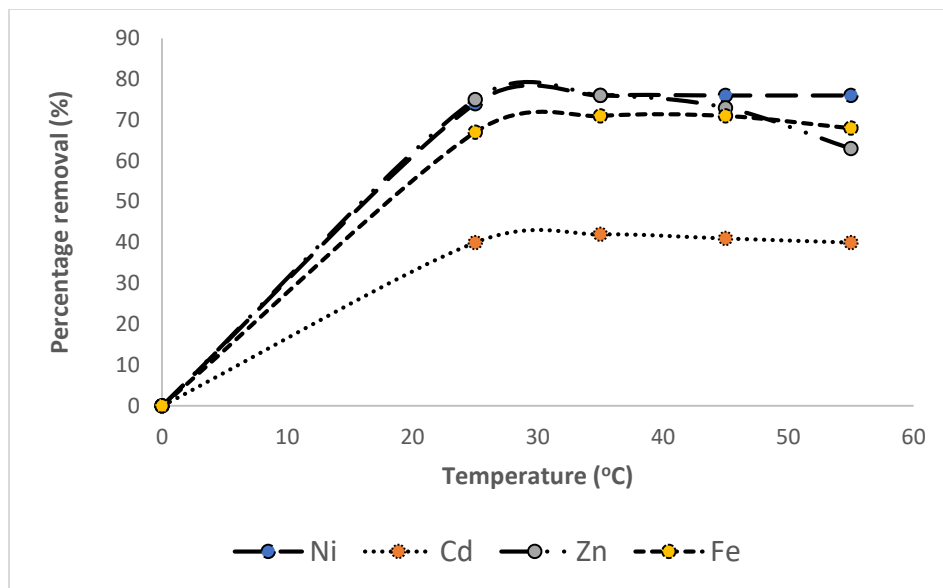**Figure 6: Effect of dosage on heavy metal removal by BTAC/NaOH**

The effects of adsorbent dose on the per cent removal of Ni, Cd, Fe and Zn ions using ATAC/H₃PO₄ and BTAC/NaOH were illustrated in figures 5 and 6. Different doses of adsorbents such as (0.01, 0.5 and 0.9 g) were used, and other adsorption parameters pH, contact time and agitation were 7.0, 120 mins and 200 rpm, respectively. An increase in adsorption capacity with increasing adsorbent dose up to 0.9 g giving the corresponding optimum percentage removal of Ni (91%), Cd (50%), Zn (79%) and Fe (92%) on ATAC/H₃PO₄ and Ni (79%), Cd (68%), Zn (91%) and Fe (91%) on BTAC/NaOH. The acid-treated adsorbent's better performance in removing Ni and Fe could be attributed to the higher surface area of ATAC/H₃PO₄ revealed by the BET analysis as 380.076 m^2/g. However, the BTAC/NaOH proved efficient in removing the metals having a higher percentage in the removal of Cd and Zn; these metals might have more access to the available pore spaces than other selected metals and therefore tend to be more adsorbed.

On the other hand, it was found that further addition over 0.9 g made little or no enhancement in the adsorption process because there was an almost negligible increase in the removal efficiency. The initial increase in adsorption capacity as adsorbent mass increased may be due to an increase in the number of exchangeable or binding sites for metal ion adsorption, after which equilibrium was reached (Mutasim *et al.*, 2017).

Figures 7 and 8 showed the percentage removal of Fe, Ni, Zn and Cd from effluent after treatment. The experimental conditions was; temperature were varied (25 ºC, 35 ºC, 45 ºC, 55 ºC), while other parameters were kept constant; contact time (120 mins), pH (7) and (0.5 g).

Figure 7: Effect of Temperature on heavy metal removal by ATAC/H₃PO₄

Figure 8: Effect of temperature on heavy metal removal by BTAC/NaOH

The effect of temperature variation on the percentage removal of Ni, Cd, Fe and Zn ions onto ATAC/H₃PO₄ and BTAC/NaOH is shown in Figures 7 and 8. A temperature range of 25-55°C was used for the experiments, adsorbent dose of 0.5 g, contact time of 120 mins and pH 7.0. Adsorption of these metals by the adsorbent increased in percentage removal and adsorption capacity at 35°C, while at temperatures between 45 and 55°C, no significant adsorption was observed. Higher rates of adsorption were observed mostly at 35°C with Ni (80%), Cd (48%), Fe (87%) and Zn (91%) for ATAC/H₃PO₄ whereas Ni (76%), Cd (42%), Fe (71%) and Zn (76%) were observed for BTAC/NaOH. However, a low adsorption rate was generally observed at 55°C within the studied range of temperatures. This indicates that the removal of these metal ions is exothermic (Mutasim and Yusuf, 2015). The high removal percentage may be due to the high diffusion rate of metal ions into the pores as the adsorbent's surface area and pore volume were large. However, at high temperatures, the kinetic energy of the species is low, and hence contact between the metal ions and the active sites of activated carbon is not sufficient, resulting in reduced removal efficiency (Mutasim *et al.,* 2015).

Adsorption Kinetics

Adsorption kinetic parameters for pseudo-first and second-order were carefully calculated and recorded in Table 7. Examination of the pseudo-first-order values revealed that the (R^2) values for the ATAC/H₃PO₄ and BTAC/NaOH were within the range of 0.8299 – 0.9770 for Ni, Cd, Zn, and Fe metal ions. At the same time, the (R^2) value for the pseudo-second-order model had a higher value between 0.9913-1 for the same set of metal ions. This indicated a better correlation between the experimental kinetic data and the pseudo-second-order model, the best-fit model. Furthermore, the values of the quantity of the adsorbed metal ions at equilibrium (q_e) obtained experimentally for this study were found to be closer and more consistent with those calculated for the pseudo-second-order kinetics.

(Arshad *et al.,* 2008; Taha *et al.,* 2011; Kujundziski *et al.,* 2015; Boulaiche *et al.,* 2019) who worked independently had reported that the pseudo-second-order kinetic model was more appropriate in describing adsorption of metal ions by absorbents from agricultural materials

Table 7: Kinetic parameters for the adsorption of heavy metals by ATAC/H₃PO₄ and BTAC/NaOH

Adsorbent	Heavy metal	Pseudo-first-order $\ln(q_e - q_t) = \ln q_e - K_1 t$			Pseudo-second-order $\dfrac{t}{q_t} = \dfrac{1}{q_{e^2} K_2} + \dfrac{1}{q_e} t$		
		q_e	K_1	R^2	q_e	K_2	R^2
(ATAC/H₃PO₄)	Ni	40.85	4.08×10^{-2}	0.9158	49.51	5.04×10^{-4}	0.9922
	Cd	10.85	2.30×10^{-2}	0.9469	26.32	1.74×10^{-3}	0.9960
	Zn	62.82	4.19×10^{-2}	0.9712	76.92	8.18×10^{-4}	1.0000
	Fe	95.49	5.27×10^{-2}	0.9410	116.28	6.40×10^{-4}	0.9922
(BTAC/NaOH)	Ni	32.30	4.03×10^{-2}	0.9770	41.15	6.70×10^{-4}	0.9986
	Cd	8.06	2.42×10^{-2}	0.9657	22.03	2.69×10^{-3}	0.9952
	Zn	55.15	4.58×10^{-2}	0.9417	64.10	2.00×10^{-3}	0.9913
	Fe	82.68	3.96×10^{-2}	0.8299	108.69	9.98×10^{-4}	0.9997

4.0   CONCLUSIONS

The prepared activated carbon, ATAC/H₃PO₄ and BTAC/NaOH used in this study was found to have a high capability for removing Ni, Cd, Fe and Zn ions from aqueous solution with ATAC/H₃PO₄ being more effective in the process. This could be attributed to its higher surface area and pore volume. The removal efficiency of the ions was found to depend largely on parameters such as pH of the solution, contact time, adsorbent dosage and temperature. The pH of the solution played a crucial role in enhancing the ability of adsorbents towards the metal ion. An increase in the pH of the solution from 3 to 7 led to an increase in the removal efficiency and subsequently decreased at pH above 7. BET and HRSEM results confirm the preliminary physicochemical tests, which revealed that ATAC/H₃PO₄ and BTAC/NaOH are suitable adsorbents for removing Ni, Cd, Zn and Fe ions from electroplating effluent.

From the results of kinetic plots, it can be proposed that the adsorption of Ni, Cd, Zn and Fe ions onto acid/base activated carbon produced from *Terminalia avicennioides* was adequately defined by the pseudo-second-order adsorption mechanism. Results showed that *Terminalia avicennioides* pods wastes could be used as a precursor for producing low-cost adsorbents.

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