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# Adsorption of Heavy Metals from Wastewaters Using *Adonosia digitata* Fruit Shells and *Theobroma cacao* Pods as Adsorbents: A Comparative Study

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## *Abstract*

*In this study, adsorption of heavy metal ions using activated carbon from* Adonsonia digitata *fruit shells and* Theobroma cacao *pods was carried out to comparatively evaluate their effectiveness as adsorbents for the purpose of removing* $Pb^{2+}$ *and* $Cd^{2+}$ *from synthetic wastewaters.* Adosonia digitata *fruit shells (ADFS) were collected within Yola and its environs, Adamawa State, Nigeria, whereas* Theobroma cacao *pods (TCP) were collected from the divisional office of the Cocoa Research Institute of Nigeria (CRIN) in Ikom, Cross River State, Nigeria. Both samples were crushed resulting in particle sizes of about 300-450 µm and the physicochemical as well as the adsorption properties of the activated carbon produced from both adsorbents were studied. Effects of some process parameters have been investigated in this study as well by following a batch adsorption technique at* $32 \pm 2^oC$*. The percentage removal of* $Pb^{2+}$ *and* $Cd^{2+}$ *was found to increase with the decrease of the initial concentration of metal ions and to increase with the increase of the contact time and the adsorbent dose. The monolayer adsorption capacity,* $Q_o$ *for Pb(II) was found to be 41.20 mg/g and 29.89 mg/g for ADFS and TCP, respectively, whereas the monolayer adsorption capacity* $Q_o$ *for Cd(II) was found to be 34.39 mg/g and 25.10 mg/g for ADFS and TCP, respectively. In conclusion, it was observed that activated ADFS had a higher monolayer adsorption capacity for* $Pb^{2+}$ *and* $Cd^{2+}$ *than activated TCP.*

**Keywords**: *Activated carbon, physicochemical property, monolayer adsorption capacity.*

## 1. Introduction

Pollution due to the presence of heavy metal ions in water and wastewaters has been a major cause of concern for environmental engineers.

Several episodes of heavy metal contamination in aquatic environment have increased the awareness about heavy metal toxicity (Kumar 2006). Among these, for instance in Nigeria, lead poisoning was reported in the Northwestern state of Zamfara (2010) which led to the death of several people and animals as a result of lead contamination of water bodies (streams and rivers) and the environment (Sadeeq 2010; Isah 2010). The presence of heavy metals in the environment is thus of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentration (Malakul *et al*. 1998; Mohan and Singh 2002). Over the years, efforts have been made to find cheaper pollution control methods and materials (Ali and El-Bishtawi 1997;

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Acemioglu and Alma 2001). Adsorption, as an environmental pollution control strategy, has been well highlighted in the literature. Ho (2007) reported that about 9,058 studies have been published on adsorption materials. Among these are Izanloo and Nasseri (2005), Otun *et al*. (2006), Oke *et al*. (2008), Ismail *et al*. (2009), Jagaba (2010), Omeiza (2011) and Adie *et al*. (2012).

In recent years, a number of adsorptive materials such as aquatic plants, agricultural by-products and residues, industrial by-products, saw dust, clay, zeolite, and micro-organisms have been used for the removal of heavy metals from wastewater. Residues from agricultural materials being economical and eco-friendly due to their unique chemical composition, availability, renewability, and low cost seem to be a viable option for heavy metal removal from wastewaters. Thus, the basic thrust of this study was to evaluate the removal of the metal ions of Pb(II) and Cd(II) from synthetic wastewaters by using activated carbon sourced from ADFS and TCP, both being agricultural residues and hence bio-resource materials.

As far as the authors' present knowledge extends, the removal of metal ions from wastewater using activated carbon from ADFS is rare. However, the removal using activated carbon from TCP is documented in a few cases in the literature. This, therefore, points to the need for documentation of heavy metal removal using activated carbon from ADFS and a comparative analysis with activated carbon from TCP. Furthermore, being agricultural residues, they could both serve as adsorbents which is a viable, eco-friendly and economic option for heavy metal remediation.

## 2. Materials and Methods

### 2.1 Materials

In carrying out this study, the following materials and equipment were used: mortar, pestle, sieves (British standard, 300-450 µm), muffle furnace (S302AU), pH meter (CRISON micro pH 2000), orbital shaker (Scigenics Biotech Orbitech), weighing balance (Mettler H31), electric oven, atomic absorption spectrophotometer (Shimadzu AA6800) and desiccators. Other apparatus used were test tubes, crucible, measuring cylinders, spatula, conical flask, volumetric flask and plastic containers. Reagents were prepared using standard methods (APHA 1998).

### 2.2 Methods

**2.2.1 Sample collection**: Samples of ADFS shell (obtained after the edible inner content and seeds have been removed) were collected from Girei and other areas within Yola and its environs, Adamawa State, Nigeria, whereas samples of TCP (obtained after the bean seeds inside the pods have been removed) where collected from the divisional office of the Cocoa Research Institute of Nigeria (CRIN) in Ikom, Cross River State, Nigeria.

**2.2.2 Sample analysis**: Tests and analysis of the samples (ADFS and TCP) were carried out at: National Research Institute for Chemical Technology (NARICT), Zaria, Kaduna State, Nigeria; Crop Science Departmental Laboratory, Modibbo Adama University of Technology, Yola, Adamawa State, Nigeria; and Postgraduate Analytical Laboratory, Department of Chemistry, Ahmadu Bello University (ABU), Zaria, Kaduna State, Nigeria.

**2.2.3 Processing of samples:** The dried ADFS samples were crushed to remove their inner content and seeds, after which the crushed fruit shells were washed clean with water and air-dried to obtain fiber-free and soil-free shell samples. Similarly, the obtained TCP samples were crushed to remove the bean seeds inside the pods, washed clean and air-dried. The air-dried shell samples were ground separately with a mortar and pestle to obtain small particle sizes. The ground samples were then sieved into sizes in the particle range of 300-450 µm.

**2.2.4 Activation and carbonization of samples:** The ADFS and TCP samples were activated and carbonized so that 2.0 g each of ground fiber-free ADFS and TCP were weighed into a crucible and mixed thoroughly with 2 $cm^3$ of 0.1M phosphoric acid ($H_3PO_4$) at an impregnation ratio of 1.0. The impregnation ratio here is defined as the ratio of the weight of $H_3PO_4$ to the weight of the ADFS/TCP samples. The soaking time was set at 12 hours after which the crucible and its content was heated at a temperature of about 500ºC for an activation time period of 15 minutes in a muffle furnace. This procedure was repeated in batches for the two samples until the required mass of each sample was achieved.

The activated samples were washed separately with 0.5M $NaHCO_3$. The acidity of the washed liquor was repeatedly monitored until the pH reading was within the range of about 6-7. Finally, the activated carbon of each sample was dried in an oven with the temperature set at 105ºC.

**2.2.5 Preparation of stock solutions:** Activating solutions of $H_3PO_4$, in addition to the heavy metal solutions of $Pb^{2+}$ and $Cd^{2+}$, for the adsorption tests were prepared in stock solutions of up to 1,000 mg/L.

**2.2.6 Preparation of standard solutions of $Pb^{2+}$ and $Cd^{2+}$ (synthetic wastewaters):** In the preparation of a stock solution of lead ions, procedures specified in APHA (1998) were followed. Specifically, a known mass (1.599 g) of lead nitrate $Pb(NO_3)_2$ was dissolved in 200 mL of distilled water, then 10 mL of concentrated $HNO_3$ was added and the resulting solution was diluted to the 1,000-mL mark using de-ionized water. A working solution was prepared from the stock solution by diluting 20 mL of the stock solution to 1,000 mL with de-ionized water. Similarly, a synthetic cadmium ion solution was prepared by dissolving a known mass of cadmium salt ($Cd(NO_3)_2.4H_2O$) in distilled water (APHA 1998). Thus, 1.599 g of cadmium nitrate was dissolved in distilled water, then 10 mL of concentrated $HNO_3$ was added and the solution diluted to the 1,000-mL mark using de-ionized water. A working solution was then prepared as described in the procedure for lead.

**2.2.7 Physicochemical parameters of ADFS/TCP:** This was achieved by determining the moisture content, volatile solid and ash content, water and acid solubility, pH and bulk density.

**2.2.8 Investigation of adsorption potentials of activated carbon from ADFS/TCP:** In investigating the adsorption potentials of activated carbon from ADFS/TCP, the effects of adsorbent dose, contact time, and initial metal ion concentration on the percentage removal of Pb(II) and Cd(II) were examined.

**a. Effect of the adsorbent dose on the adsorption of Pb(II) and Cd(II) onto the adsorbents:** The effect of the adsorbent dose on the percentage removal of metal ions was investigated by varying the adsorbent dose in the range of 0.5 to 2.5 g for 150 minutes at a fixed pH value. The final concentration of solutions was determined using atomic absorption spectrophotometer and the percentage removal of $Pb^{2+}/Cd^{2+}$ was then obtained.

**b. Effect of the contact time on the adsorption of Pb(II) and Cd(II) onto the adsorbents:** The effect of the contact time on the adsorption of Pb(II) and Cd(II) was also investigated. Thus, 1.0 g each of the adsorbents (activated ADFS/TCP) were taken (separately) into five beakers containing 50 mL of metal solution at an initial concentration of 20 mg/L. The solutions were agitated at a fixed stirring speed of 180 rpm for varying time periods ranging from 30 to 150 minutes at a fixed pH value. The final concentration of each solution was determined using atomic absorption spectrophotometer and the percentage of $Pb^{2+}/Cd^{2+}$ was then obtained.

**c. Effect of the initial metal ion concentration on the adsorption of Pb(II) and Cd(II) onto the adsorbents:** The effect of the initial metal ion concentration on the percentage removal of metal ions (adsorption) was investigated by varying the concentration of the metal ions ($Pb^{2+}/Cd^{2+}$) in the range of 2.5 to 20 mg/L. Thus, 50 mL each of 5 separate concentrations of metal ions (ranging from 2.5 to 20 mg/L) were taken into 5 beakers containing a fixed mass (1.0 g) of the adsorbent. The solutions were agitated at a fixed stirring speed of 180 rpm for a predetermined contact time of 150 minutes at a fixed pH value. The final concentration of each solution was determined using atomic absorption spectrophotometer.

**2.2.9 Adsorption capacity test**: For the determination of the adsorption capacity of the adsorbent for $Cd^{2+}$, five 50-mL portions of the working solution of lead ions containing 20 mg/L of $Pb^{2+}$ were taken into five different beakers and distinct known masses (0.5, 1.0, 1.5, 2.0, and 2.5 g) of the adsorbent were added to each portion (specifically at the same controlled initial pH of the solution). The mixture was stirred at 180 rpm for a predetermined time for which equilibrium was attained. The supernatant of the mixture was then filtered through Whatman® filter paper (Grade 40). The determination of the lead ion concentration was done with the use of Atomic Absorption Spectrophotometer (AAS). The same procedure was followed in the determination of the adsorption capacity of the adsorbent for $Cd^{2+}$. The amount of solute ($Pb^{2+}$ and $Cd^{2+}$) removed (adsorbed) at equilibrium, $q_e$, was computed as follows:

$$q_e = (C_o - C_e)\, V / M. \qquad (1)$$

The amount of metal ions ($Pb^{2+}$ and $Cd^{2+}$) removed at a given time, $q_t$, and the percentage of $Pb^{2+}$ and $Cd^{2+}$ removed from the solution, $R$(%), were calculated as follows:

$$q_t = (C_o - C_t)\, V / M, \text{ and} \qquad (2)$$

$$R = 100\, (C_o - C_t) / C_o. \qquad (3)$$

In Eqs. (1)-(3), $C_o$, $C_t$, and $C_e$ are the initial liquid-phase concentration of sorbate, the experimental concentration (mg/L) at time $t$, and the equilibrium liquid-phase of sorbate, respectively, while $M$, $V$ and $R$ are the adsorbent mass, the volume of the solution (50 mL), and the percentage of metal ions adsorbed, respectively.

## 3. Results and Discussion

### 3.1 Physicochemical Characteristics of ADFS and TCP

The moisture content, the volatile solids ash content, the bulk density, and the pH of raw and carbonized samples were determined. In addition, raw samples (of ADFS and TCP) were digested (by wet digestion) to determine the concentration of some specific metals in the samples. The summary of the results is shown in Table 1.

**3.1.1 Moisture content (%):** The moisture content of ADFS and TCP was found to be 7.29% and 10.05%, respectively. Generally, the yield and quality of produced activated carbon can be improved by the removal of moisture. The lower the moisture percentage, the better the yield and quality of the activated carbon. These values (for ADFS and TCP) were both found to be generally lower than values obtained from activated carbon from papaya seeds (Omeiza 2011). Furthermore, the obtained result was found to be comparable with that of activated carbon from *Borassus aethiopum* (also known as African palmyra, black rhun palm or toddy palm) and *Cocos nucifera* (coconut) (Adie *et al*. 2012).

**3.1.2 Ash content (%):** According to Allen (1974), the ash content is a measure of the mineral content of the samples. The ash content in this study was found to be 2.81% and 4.48% for ADFS and TCP, respectively. This is favorable because the ash serves as interference during the adsorption process. The lower the ash content, the better the material. Both values (for ADFS and TCP) are slightly higher compared with the value obtained for powdered corn cobs (Adie *et al*. 2010).

**3.1.3 Volatile solids:** Volatile solids were found to constitute about 89.27% of the mass of ADFS, while these of TCP were found to be about 85.47%. These values are comparable with values obtained for powdered corn cobs (Adie *et al*. 2010).

Table 1. Physicochemical properties of raw and carbonized (ADFS/TCP) samples.

| Parameter | ADFS | TCP |
|---|---|---|
| Physical | | |
| Moisture(%) | 7.29 | 10.05 |
| Volatile Solids | 89.27 | 85.47 |
| Ash content (%) | 2.81 | 4.48 |
| pH | | |
| (i) Raw | 6.42 | 6.31 |
| (ii) Carbonized | 6.11 | 6.24 |
| Bulk density, g/cm$^3$ | | |
| (i) Raw | 0.44 | 0.41 |
| (ii) Carbonized | 0.51 | 0.49 |
| Chemical | | |
| Solubility in water (%) | 1.22 | 0.99 |
| Solubility in 0.25M HCl (%) | 7.32 | 5.41 |
| Calcium (mg/g) | 0.14 | 0.17 |
| Iron (mg/g) | 1.11 | 2.03 |
| Aluminium (mg/g) | 0.04 | 0.02 |
| Cadmium (mg/g) | nil | nil |
| Lead (mg/g) | nil | nil |

The high percentage of volatile solids in ADFS and TCP is indicative of the fact that both adsorbents can be destroyed easily and metal recovery can be effectively employed for the recovery of metal ions from adsorbents after they have been used for adsorption of such metals.

**3.1.4 Water and acid solubility:** The solubility of ADFS and TCP in water was 1.22% and 0.99%, respectively, while the acid solubility of ADFS and TCP was found to be 7.34 and 5.41%, respectively. This shows that TCP will be more stable than ADFS in a neutral aqueous medium as well as in an acidic medium. The water and acid solubility values obtained for both adsorbents were observed to be higher when compared to values obtained from carbonized apricot stones (Kobya 2004). This is basically attributable to the nature of the adsorbents as well as the nature of chemical activation and carbonization process carried out in producing the activated carbon adsorbents. In addition, it was observed that the obtained result was comparable with findings of Adie *et al*. (2012) for activated carbon from African palmyra or toddy palm (*Borassus aethiopum*) and coconut *(Cocos nucifera)*.

**3.1.5 pH:** The pH values for raw ADFS and TCP were 6.42 and 6.31, respectively, whereas these of carbonized ADFS/ TCP were 6.11 and 6.24, respectively, after several washings. The pH of activated carbon depends on the nature of the activating process and the activating agent used. The pH can be modified by washing (Abram 1973), and that of carbon in suspension can vary in the range of 4 to 12.

**3.1.6 Metal concentrations:** The results of wet digestion of the samples (ADFS and TCP), show that 1 g of ADFS contains 0.14 mg of calcium ($Ca^{2+}$), 1.11 mg of iron ($Fe^{2+}$), and 0.04 mg of aluminum ($Al^{3+}$), whereas 1 g of TCP contains 0.17 mg of calcium ($Ca^{2+}$), 2.03 mg of iron ($Fe^{2+}$), and 0.02 mg of aluminum ($Al^{3+}$). Basically, it has been postulated that calcium salts undergo a displacement reaction in the presence of water (Oke *et al*. 2008). This shows that both ADFS and TCP underwent reactions with lead/cadmium ions, which reduced the pH to a region that supports the removal of these metal ions by the adsorbents. Furthermore, the end product reacted with the lead/cadmium ions to precipitate the metal ions. This indicates that, apart from the volatile portions of the adsorbents which can absorb these ions (lead/cadmium), the presence of the important coagulants ($Ca^{2+}$), ($Fe^{2+}$) and ($Al^{3+}$) in the adsorbents helped forming flocks between the adsorbents and the metal ions leading to the precipitation of said metal ions (lead/cadmium).

## 3.2 Batch Adsorption Studies

**3.2.1 Effect of contact time:** The experimental runs measuring the effect of contact time on the batch adsorption of $Pb^{2+}$ and $Cd^{2+}$ (initial metal ion concentration of 20 mg/L, temperature of 32 ± 2ºC, agitation speed of 180 rpm, and fixed pH) is as shown in Figs. 1 and 2.

By comparing the two plots, it can be observed that the increase in contact time from 30 to 120 minutes significantly enhanced the removal of $Pb^{2+}/Cd^{2+}$ from the synthetic wastewaters using the adsorbents (ADFS and TCP). Furthermore, the initially rapid adsorption gradually gave way to adsorption at a slow rate, indicative of the fact that the process tended to approach an equilibrium state between 140 and 150 minutes (for both adsorbents). The maximum percentage removal of $Pb^{2+}$ using activated carbon from ADFS was found to be about 98.50%, whereas for TCP it was about 95.15%. Furthermore, the maximum percentage removal of $Cd^{2+}$ using activated carbon was 98.15% for ADFS and 97.10% for TCP. In both cases, the activated carbon from ADFS was found to have a higher percentage removal for both metal ions from the synthetic wastewaters. Thus, as observed in this study, the removal of $Pb^{2+}/Cd^{2+}$ by adsorption onto both adsorbents increased rapidly in the beginning and then slowly until the equilibrium time (150 minutes) was reached. This is in agreement with findings of Ho and Mckay (1998).

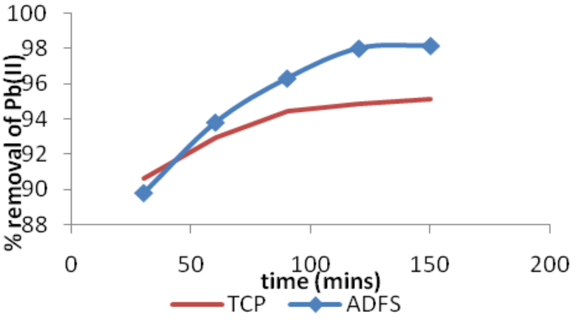

Fig. 1. Effect of contact time on the removal of Pb(II) using activated carbon from ADFS and TCP.

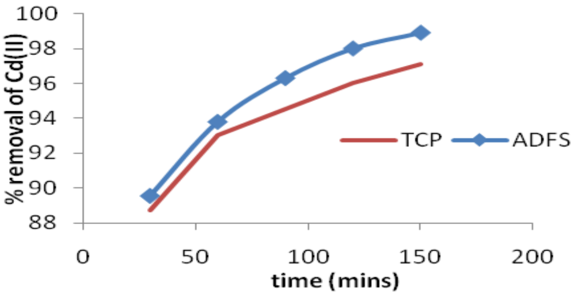

Fig. 2. Effect of contact time on the removal of Cd(II) using activated carbon from ADFS and TCP.

**3.2.2 Effect of ion concentration:** Figures 3 and 4 show the effect of initial metal ion ($Pb^{2+}/Cd^{2+}$) concentration on its removal. For $Pb^{2+}$ using ADFS as adsorbent, the percentage removal decreased from 99.8% to 99%, while for TCP, the percentage removal decreased from 99.6% to 99.15% with an increase in metal concentration from 2.5 to 20 mg/L. For $Cd^{2+}$ using ADFS as adsorbent, the percentage removal decreased from 99.64% to 99.05%, while for TCP, it deceased from 99.61% to 98.92% with an increase in metal concentration from 2.5 to 20 mg/L. This is generally in agreement with findings of Gupta and Mohapatra (2003) and Zouboulis *et al*. (2002).

The trend in this finding can be explained as follows: at higher concentration, most of $Pb^{2+}/Cd^{2+}$ are left unabsorbed due to saturation of the adsorption sites. The ratio of sorptive surface-to-ion concentration, however, decreases with increasing the metal ion concentration and the ion removal is reduced.

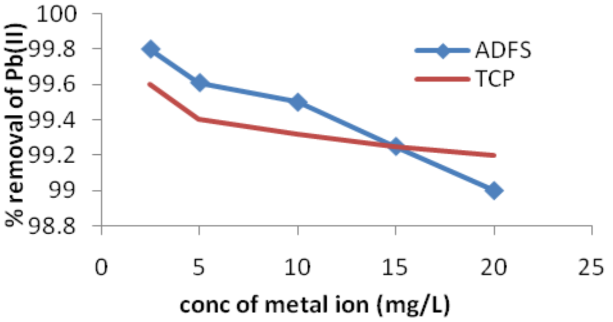

Fig. 3. Effect of initial concentration of Pb(II) on its removal from synthetic wastewater of Pb(II) using activated carbon from ADFS/TCP.

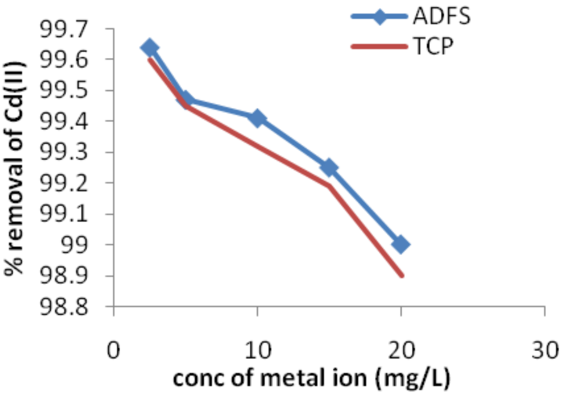

Fig. 4. Effect of initial concentration of Cd(II) on its removal from synthetic wastewater of Cd(II) using activated carbon from ADFS/TCP.

**3.2.3 Effect of adsorbent dose:** The effect of adsorbent dosage is depicted in Figs. 5 and 6. Both adsorbents where used at doses ranging from 0.5 g (10 g/L) to 2.5 g (50 g/L) in a batch adsorption technique.

The dose for each adsorbent was varied between 0.5 g and 2.5 g in 50 mL of aqueous solution of the metal ion (equivalent to dosage of 10 g/L to 50 g/L) in a batch adsorption technique. In each case, the increase in adsorbent dose resulted in an increase in the percentage removal of $Pb^{2+}/Cd^{2+}$ for both adsorbents. However, it was observed that after a certain adsorbent dose between 1.5 and 2.0 g, the removal efficiency (%) did not increase so significantly.

The maximum percentage removal of $Pb^{2+}$ using activated carbon from ADFS was found to be 99.85% at the maximum adsorbent dose of 2.5 g (50 g/L), while that of activated carbon from TCP was 99.81%.

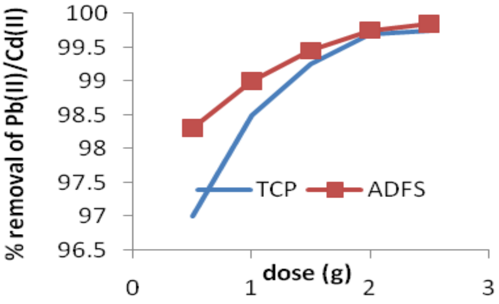

Fig. 5. Effect of adsorbent dose on $Pb^{2+}$ removal using activated carbon from ADFS and TCP.

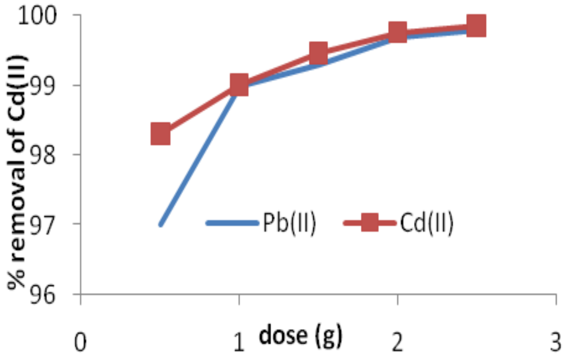

Fig. 6. Effect of adsorbent dose on $Cd^{2+}$ removal using activated carbon from ADFS/ TCP.

For $Cd^{2+}$, however, the maximum percentage removal for ADFS was found to be 99.79%, while that for TCP was 99.72% at the maximum adsorbent dose of 2.5 g (50 g/L).

It is evident that activated carbon from ADFS had a higher removal percentage of both metal ions than activated carbon from TCP.

The increase in percentage removal of $Pb^{2+}/Cd^{2+}$ with the increase in adsorbent dosage may be explained as follows: with the increase in the adsorbent dosage, more surface area is available for adsorption due to its increase in active sites on the adsorbents or due to conglomeration of carbon at higher doses. Furthermore, the difference in sorption capacities between the adsorbents is related to the type and concentration of the surface group responsible for the adsorption of metal ions from its solution (Dakiky *et al*. 2002).

## 4. Conclusion

From experiments, observations and results obtained from this study, the suitability of using activated ADFS/TCP for the removal of Pb(II) and Cd(II) from synthetic wastewaters through batch adsorption studies has been highlighted. The obtained experimental results showed that process parameters such as adsorbent dose, initial metal concentration, and contact time affected the uptake of both adsorbents (for the uptake of Pb(II) and Cd(II)). The effect of various process parameters showed that the percentage adsorption/removal decreased with the increase in initial metal ion concentration, whereas with the increase in contact time and adsorbent dose, there was an increase in percentage adsorption or removal of metal ions. Conclusively, this works shows that locally available agricultural residual materials such as *Adosonia digitata* fruit shells (ADFS) and *Theobroma cacao* pods (TCP) could easily be sourced to produce activated carbon which can be used as efficient adsorbent for lead and cadmium ion removal from wastewater, representing an environmentally effective means of utilizing these agricultural residues. However, it was established that activated ADFS carbon had a higher monolayer adsorption capacity for $Pb^{2+}/Cd^{2+}$ than activated carbon produced from TCP.

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