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# COMPARATIVE STUDIES ON THE USE OF ACTIVATED SNAIL (*Achanita fulica*) AND PERIWINKLE SHELLS (*Typanotonus fuscatu*) IN THE REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS

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## ABSTRACT

This study seeks to compare the application of activated snail and periwinkle shells in the removal of heavy metal ions from aqueous solution. Snail and periwinkle shells obtained from local markets in Warri, Nigeria, were carbonized, activated and characterized. Batch adsorption experiment was carried out to determine the effect of pH, concentration, adsorbent dose and contact time on the adsorption process. Data obtained were examined using adsorption isotherms. Characterization result showed that activated carbon obtained from periwinkle shells had higher values of pH, pore volume, moisture content and porosity than the values obtained for activated snail shells. The maximum pH obtained for the adsorption of $Pb^{2+}$ and $Cd^{2+}$ ions using activated periwinkle shell carbon (APSC) and activated snail shell carbon (ASSC) were 7 for $Pb^{2+}$ and 4 – 10 for $Cd^{2+}$. The percentage adsorption of these ions onto APSC were 96.70% $Pb^{2+}$ and 100% $Cd^{2+}$ while that of ASSC were 95.00% $Pb^{2+}$ and 68.80% $Cd^{2+}$. The optimum adsorbent dose and contact time for the removal of these ions, using both adsorbents, were 3 g and 90 min, respectively. Results revealed that APSC had better adsorption capacity than ASSC for most parameters studied. Of the four adsorption isotherms models used for this study, Langmuir had the highest regression coefficient ($R^2$ = 0.9852 for APSC and 0.8950 for ASSC). Data for adsorption kinetics exhibited a good compliance with pseudo-second order kinetic model.

**Keywords**: Heavy metals, Activated carbon, Adsorption isotherms, Periwinkle shell, Snail shell.

## INTRODUCTION

The environmental pollution due to globalization and rapid industrialization are becoming more alarming and poses a threat to humans. Industrial activities and used metallic materials gives rise to large quantities of metallic wastes, that are ejected into water bodies and land dump sites. Heavy metal present in wastewater and industrial effluents is a major worry to environmental scientists. In the recent years, the threat pose by annual metallic discharge into the environment is far greater than the combined total threat posed by radioactive and organic wastes (Gunatilake, 2015).

Research on heavy metals has therefore become a prominent topic for environmental researchers because "heavy metals have no known biological use and they are toxic to most living things" (Abdul-Salam and Adekola, 2005).

Pollution caused by the availability of heavy metal ions in water and solutions has become a major issue for Environmental Scientists. Many incidents of metal contamination in aquatic ecosystem have expanded the consciousness of heavy metal threat (Kumar, 2006). This include lead poisoning that was recorded in Zamfara, a North-Western state of Nigeria in the year 2010, which resulted to the death of many residents of the area (Sadeeq, 2010). The availability of heavy metals in our surrounding is a vital threat because of their utmost toxicity and proneness of bio-accumulation in the food chain even in a minute quantity (Mohan and Singh, 2002). Attempts have been made over the years to find more economical materials and control methods for the removal of heavy metal from wastewaters and environment (Ali and El-Bishtawi, 1997).

Adsorption process being the most common and the primary method for the removal of metal ions from aqueous solution, has gained more acceptance than other methods, because it is cheaper to operate. Other methods are chemical precipitation, ion exchange resin, electrochemical treatment etc. These processes are however found to be too costly when heavy metals are present in low concentration (Okuo and Okolo, 2006).

There is an existing growing concern in the making of activated carbon from agricultural by-products and industrial wastes (Rahman *et al.,* 2006) such as periwinkle shell (Badmus *et al.*, 2007), cocoa pod, husk (Sricharoenchaikal *et al.,*2007), walnut shells, physic nut waste, peach stone, coconut shells, bamboo stem waste, palm kernel shells (El-wheikh, *et al.,* 2003; Razada *et al.,* 2005).

Snail and periwinkle shells are environmentally unfriendly and regarded as waste by the consumers. These shells which are readily available in South-South geopolitical zone of Nigeria has sharp edges when broken and can cause physical injuries to human. There is need to convert these wastes to useful purposes which as well can help to clean up our environment.

This study therefore seeks to prepare and evaluate activated carbon from periwinkle and snail shells for the removal of $Cd^{2+}$ and $Pb^{2+}$ from aqueous solution.

## MATERIALS AND METHODS

### Collection and Preparation of Sample

Snail shells were collected from snail sellers in Jugbale Market in Orhuwhorun town, Warri while Periwinkle shells were collected from Aladja town in Ovwian -Aladja town, both in Delta State, Nigeria. They were thoroughly cleaned by washing with warm water, rinsed with distilled water, sun-dried for five days, dried for 3 h at 105 °C in an electric oven and allowed to cool in a desiccator for 1 h. The snail shells and periwinkle shells were carbonized separately in a muffle furnace at 600 °C for 3 h, and allowed to cool to a room temperature.

### Sample Treatment before Activation

Prior to grinding, the grinding machine was thoroughly washed with deionized water and allowed to dry. Some quantities of samples were used to flush the machine thrice and discarded before the grinding. The charred ground samples were sieved with 180 μm standard Tyler sieve No. 80 to obtain uniform particle size. The carbonized snail and periwinkle shells were activated using 0.5 M $ZnCl_2$ solution.

### Method of Activation

To initiate the activation process of the carbonized snail shell, 50 g of the material were dissolved in 150 mL of a 0.5 M $ZnCl_2$ solution. The resulting mixture was heated until it formed a slurry. Subsequently, the slurry was transferred into a crucible and subjected to a heating process at 800 °C for a duration of 3 h within a muffle furnace, followed by cooling to room temperature. Afterward, the material underwent a washing procedure with distilled water and was then dried in an oven at 110 °C for 2 h. Once dried, the sample was cooled to room temperature and stored in an air-tight container, making it ready for utilization. This procedure was repeated with 50 g of carbonized periwinkle shell (Gumus and Okpeku, 2015).

### Determination of pH, Pore Volume, Porosity, Ash Content, Moisture Content and Bulk Density

The pH, pore volume, porosity, ash content, moisture content and bulk density were determined using the methods described by Gumus and Okpeku (2015).

### Determination of Functional Groups Present in Carbonized Periwinkle and Snail Shells

The infrared (IR) analysis of activated periwinkle and snail shells carbon were done using a Perkin-Elmer model RX1 Fourier transform infrared (FT-IR) spectrophotometer. A 100 mg KBr disks containing one percent of the ground powder of each samples were prepared less than 24 h before reading was taken (Hossain and Aditya, 2015).

### Adsorption Experiments

This involves the addition of the prepared adsorbent into freshly prepared dilute solutions of lead and cadmium metal ions. The experiments were conducted in multiple batches, each exposed to distinct conditions, including pH, initial metal ion concentration, contact time, and adsorbent dose. Subsequently, the filtration of the adsorbent biomass from the solution was performed. The quantification of remaining heavy metal concentrations in the different solutions was accomplished using an atomic absorption spectrophotometer (AAS), specifically the Buck Scientific Model 210VGP, located in the Department of Chemistry at the University of

Benin, Benin City.

The effect of pH on the percentage removal of $Pb^{2+}$ and $Cd^{2+}$ onto adsorbent was investigated by varying the pH (2 to 10) of aqueous solution of $Pb^{2+}$ and $Cd^{2+}$. Thus, 50 mL of each aqueous solution was taken into beakers 1 - 6 having a pH range of 2 - 10 containing a fixed mass of 3 g of adsorbent and fixed concentration of 6 mg/L. The solution was agitated at a speed of 180 rpm for 3 h and filtered. The optimum pH was obtained by determining the concentration of the filtrates using AAS. The experiments on the effect of metal concentrations, contact time and adsorbent dose at the optimum pH were determined according to the methods described by Okuo *et al.* (2008).

The results obtained from these batch adsorptions analyses were fitted into Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms (Charles *et al.*, 2014).

## RESULTS AND DISCUSSION

Characterization of ASSC and APSC revealed that their ash content were relatively high (Table 1), indicating the presence of inactive matter. This could be due to the fact that these activated carbons are of animal origin, which are known to have high carbon contents. Result of the moisture contents for activated periwinkle shell carbon (8.20%) was approximately twice that of the activated snail shell carbon (4.80%). This difference may be due to the composition of the two adsorbents (Table 1).

**Table 1:** Physical properties of activated snail shell carbon (ASSC) and periwinkle shell carbon (APSC).

| Parameters | Activated Periwinkle shell Carbon (APSC) | Activated snail shell carbon (ASSC) |
|---|---|---|
| Moisture content (%) | 8.20±0.33 | 4.80±0.33 |
| Ash Content (%) | 50.10±0.08 | 52.00±0.08 |
| Pore Volume ($cm^3/g$) | 2.60±0.20 | 1.50±0.20 |
| Bulk density ($g/cm^3$) | 1.67±0.00 | 1.67±0.00 |
| pH of raw sample | 7.10±0.00 | 7.90±0.00 |
| pH of activated carbon before washing | 10.30±0.01 | 10.20±0.01 |
| pH of activated carbon after washing | 7.24±0.24 | 7.23±0.24 |

It has been shown that lower moisture content leads to increase in the rate of adsorption. The relatively high value of moisture content may also be due to the doping agent used for activation as compared to Ugwuoha *et al.* (2017) where 0.6 and 0.01% were obtained when KOH and $H_3PO_4$ were used as doping agents respectively.

The pore volume/porosity of the activated periwinkle and activated snail shell carbons (Table 1) indicated that both adsorbents have well established large internal surface areas (Mui *et al.*, 2004). The porosity value obtained may be due to the application of doping agent ($ZnCl_2$) which assisted in the breakdown of organic matter to release volatile matter and hence the evolution of micro structure (Mui *et al.,* 2004).

The two adsorbents had the same bulk densities (1.6 $g/cm^3$). The high bulk density values also indicate that the adsorbents will not be easily regenerated, due to their ability to hold more adsorbate per unit weight (Viswanathan *et al.,* 2009) and a carbon unit of bulk density of about 0.5 $g/cm^3$ is adequate for adsorption (Okiemen *et al.,* 2007). Higher density leads to more volume activity and normally represents better quality activated carbon (Laine *et al.,* 1989).

The pH measurements of the raw samples of periwinkle and snail shell before activation indicated that both were fairly neutral. The pH of the activated periwinkle and snail shell carbons were very alkaline which revealed that the increase in pH was caused by the activating agent ($ZnCl_2$). This is in agreement with findings of Gumus and

Okpeku, (2015). The values of the pH of the two adsorbents after washing were 7.24 and 7.23, respectively. These values fall within the acceptable pH range (pH 6 - 8) for most applications (Akash and O'Brien, 1996).

### Fourier Transformed Infrared (FTIR) Analysis

In order to identify functional groups present in the carbonized periwinkle and snail shells, FTIR analysis was carried out and the results are presented in Table 2.

**Table 2:** Functional groups identified in ASSC and APSC.

| APSC | | ASSC | |
|---|---|---|---|
| **Wave No. ($cm^{-1}$)** | **Assigned Functional Groups** | **Wave No. ($cm^{-1}$)** | **Assigned Functional Groups** |
| 1761.00 | Carboxylic acids | 1794.70 | Acyl group |
| 1410.80 | Alkyl group | 1698.10 | Unsaturated ketones |
| 1082.8 | Ethers | 872.00 | *meta*-Disubstituted aromatics |
| 861.00 | *meta*-Disubstituted aromatics | 711.90 | *ortho*-Disubstituted aromatics |
| 711.90 | *Ortho*-Disubstituted aromatics | | |

According to Okuo and Okolo (2006), "the functional groups known to be effective in the removal of heavy metal ions from solution are the amine, amide, phenolic, carboxylic and hydroxyl groups". From the FT-IR results, APSC possessed more of such functional groups than ASSC.

### Effect of pH, Concentration, Adsorbent Dose and Contact Time on $Pb^{2+}$ and $Cd^{2+}$ Ions Removal by APSC and ASSC

Table 3 presents the concentrations of removed $Pb^{2+}$ and $Cd^{2+}$ ions by APSC and ASSC across various pH levels. The optimal pH range for $Cd^{2+}$ ion removal using APSC was observed to be 4-10. The adsorption of $Pb^{2+}$ exhibited a gradual increase with rising pH, reaching its peak at 93.30% for APSC at pH 7. However, beyond pH 7, there was a decline in adsorption, potentially attributed to the formation of soluble hydroxyl complexes. The increase in solution pH led to the initiation of metal hydrolysis and precipitation at pH > 7, with adsorption commencing before hydrolysis. The pH range of 2-7 showed a proportional increase in deprotonation of the adsorbent surface, resulting in a reduction of $H^+$ on the adsorbent surface. This generates more negative charges on the adsorbent surface, that favour adsorption of the positively charged groups and the positive site on the adsorbent surface (Abdusalem and Adekola, 2005).

In the same vein, the maximum pH range for cadmium ion removal for ASSC was 6-10. Adsorption of $Pb^{2+}$ on ASSC also increased steadily as the pH increased up to 7, reaching the highest value of 93.30%, and after pH 7 there was a reduction in the adsorption.

**Table 3:** Effect of pH on $Pb^{2+}$ and $Cd^{2+}$ removal by APSC and ASSC.

| APSC | | | | | | | | ASSC | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH Range | Initial Concentration (mg/L) | Equilibrium Concentration (mg/L) | | $C_i – C_e$ (mg/L) | | Percentage Removal (%) | | pH Range | Initial Concentration ($C_i$) (mg /L) | | Equilibrium Concentration ($C_e$) (mg /L) | | $C_i – C_e$ (mg /L) | | Percentage Removal (%) | |
| **pH** | **$Pb^{2+}$/$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** | **pH** | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** |
| 2 | 6.00 | 1.10 | 3.10 | 4.90 | 2.90 | 81.70 | 48.33 | 2 | 6.00 | 8.00 | 0.54 | 3.10 | 5.46 | 4.90 | 91.00 | 61.30 |
| 4 | 6.00 | 1.00 | 0.00 | 5.00 | 6.00 | 83.33 | 100.00 | 4 | 6.00 | 8.00 | 0.56 | 1.50 | 5.60 | 6.50 | 93.00 | 81.30 |
| 6 | 6.00 | 0.98 | 0.00 | 5.02 | 6.00 | 83.70 | 100.00 | 6 | 6.00 | 8.00 | 0.58 | 0.00 | 5.15 | 8.00 | 85.80 | 100.00 |
| 7 | 6.00 | 0.40 | 0.00 | 5.60 | 6.00 | 93.30 | 100.00 | 7 | 6.00 | 8.00 | 0.40 | 0.00 | 5.60 | 8.00 | 93.30 | 100.00 |
| 8 | 6.00 | 1.00 | 0.00 | 5.00 | 6.00 | 83.33 | 100.00 | 8 | 6.00 | 8.00 | 1.29 | 0.00 | 4.71 | 8.00 | 78.50 | 100.00 |
| 10 | 6.00 | 0.77 | 0.00 | 5.23 | 6.00 | 87.20 | 100.00 | 10 | 6.00 | 8.00 | 1.08 | 0.00 | 4.92 | 8.00 | 82.00 | 100.00 |

Table 4 represents the maximum concentration of lead removal. This was achieved at a concentration of 6 $mgL^{-1}$ (96.7%) with ASSC and 6 $mgL^{-1}$ (95.8%) with APSC.

The highest removal of cadmium was gotten at the concentration of 8 $mgL^{-1}$ for ASSC while that of APSC was achieved at a concentration range of 2-6 $mgL^{-1}$. APSC showed a wider range and a better adsorption capacity (100%) for cadmium.

The difference in percentage removal might be due to the difference in organic content of the different adsorbents (Ekop *et al.,* 2005) and variations in chemical properties of the adsorbates, especially the hydration energies and ionic sizes of the two ions.

**Table 4:** Effect of initial solution concentration on $Pb^{2+}$ and $Cd^{2+}$ ions removal by APSC and ASSC at pH 7.

| **APSC** | | | | | | | **ASSC** | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Initial Concentration (Mg/L)** | **Equilibrium Concentration(mg/L)** | | **$C_i - C_e$ (mg/L)** | | **Percentage Removal** | | **Initial Concentration (mg/L)** | **Equilibrium Concentration(mg/L)** | | **$C_i - C_e$ (mg/L)** | | **Percentage Removal** | |
| | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **Concentration (Mg/L)** | **$Pb^{2+}$** | **$Cd^{2+}$** | | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** |
| 2.00 | 0.10 | 0.00 | 1.90 | 2.00 | 95.00 | 100.00 | 2.00 | 0.20 | 0.80 | 1.80 | 1.20 | 90.00 | 64.00 |
| 4.00 | 0.40 | 0.00 | 3.60 | 4.00 | 90.00 | 100.00 | 4.00 | 0.40 | 1.50 | 3.60 | 2.50 | 90.00 | 62.50 |
| 6.00 | 0.20 | 0.00 | 5.80 | 6.00 | 96.70 | 100.00 | 6.00 | 0.30 | 2.10 | 5.70 | 3.90 | 95.00 | 65.00 |
| 8.00 | 0.40 | 0.00 | 7.60 | 8.00 | 95.00 | 95.00 | 8.00 | 0.50 | 2.50 | 7.50 | 5.50 | 93.80 | 68.80 |
| 10.00 | 1.60 | 1.40 | 8.40 | 8.60 | 84.00 | 86.00 | 10.00 | 1.60 | 6.70 | 8.40 | 3.30 | 84.00 | 33.00 |

The optimum adsorbent dose for $Pb^{2+}$ using both ASSC and APSC was 3 g. The percentage removal of $Pb^{2+}$ using ASSC was found to be 87.30% while that of APSC was 93.30%. It was also observed that the two adsorbents had the same percentage removal of cadmium ion for the adsorbent dosages investigated. This further confirmed that both adsorbents might be better for the removal of cadmium ion (Table 5). However, APSC adsorbed more lead ion (93.30%) than ASSC (87.30%).

With an escalation in adsorbent dosage, a greater surface area becomes accessible for adsorption, either due to the augmentation of active sites on the adsorbent or the aggregation of carbon at elevated doses. Also, the difference in sorption capacities between the adsorbents for lead ion removal may be linked to the type and concentration of the surface group that is causing the adsorption of initial ions from its solution (Dakiky *et al.,* 2002).

**Table 5:** Effect of adsorbent dose on $Pb^{2+}$ and $Cd^{2+}$ removal by APSC and ASSC at optimum pH 7.

| APSC | | | | | | | | | ASSC | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Adsorbent dose (g) | Initial Concentration (mg /L) | | Equilibrium Concentration (mg /L) | | $C_i - C_e$ (mg/L) | | Percentage Removal (%) | | Adsorbent dose (g) | Initial Concentration (mg /L) | | Equilibrium Concentration (mg /L) | | $C_i - C_e$ (mg/L) | | Percentage Removal (%) | |
| **Dose** | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** | **Dose** | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** | **$Pb^{2+}$** | **$Cd^{2+}$** |
| 2 | 6.00 | 6.00 | 0.71 | 0.00 | 5.30 | 6.00 | 88.30 | 100.00 | 2 | 6.00 | 8.00 | 1.00 | 0.00 | 5.00 | 8.00 | 83.30 | 100.00 |
| 3 | 6.00 | 6.00 | 0.40 | 0.00 | 5.60 | 6.00 | 93.30 | 100.00 | 3 | 6.00 | 8.00 | 0.76 | 0.00 | 5.24 | 8.00 | 87.30 | 100.00 |
| 4 | 6.00 | 6.00 | 0.68 | 0.00 | 5.32 | 6.00 | 88.70 | 100.00 | 4 | 6.00 | 8.00 | 1.51 | 0.00 | 4.49 | 8.00 | 74.80 | 100.00 |
| 6 | 6.00 | 6.00 | 1.11 | 0.00 | 4.89 | 6.00 | 81.50 | 100.00 | 6 | 6.00 | 8.00 | 1.54 | 0.00 | 4.46 | 8.00 | 74.30 | 100.00 |
| 8 | 6.00 | 6.00 | 1.40 | 0.00 | 4.60 | 6.00 | 76.70 | 100.00 | 8 | 6.00 | 8.00 | 1.58 | 0.00 | 4.42 | 8.00 | 73.70 | 100.00 |
| 10 | 6.00 | 6.00 | 1.50 | 0.00 | 4.50 | 6.00 | 75.00 | 100.00 | 10 | 6.00 | 8.00 | 1.78 | 0.00 | 4.22 | 8.00 | 70.30 | 100.00 |

The findings presented in Table 6 demonstrate that an increase in contact time (from 30 to 90 min) has a significant impact on enhancing the removal of $Pb^{2+}/Cd^{2+}$ from the aqueous solution, utilizing both adsorbents. Additionally, the initial rapid adsorption undergoes a gradual shift towards desorption for $Pb^{2+}$, suggesting that the process tends to reach an equilibrium state between 60 and 90 min. The maximum percentage removal of $Pb^{2+}$ for ASSC and APSC was observed to be 85.30% at 90 min.

Consequently, the adsorption-driven removal of $Pb^{2+}$ exhibits a rapid increase initially, followed by a slower progression until equilibrium is achieved (at 90 min). This pattern aligns with the observations made by Ho and McKay (1998).

**Table 6:** Effect of contact time on $Pb^{2+}$ and $Cd^{2+}$ ions removal by APSC and ASSC at optimum pH, concentration and adsorbent dose.

| APSC |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| Contact Time(min) | Initial Concentration (mg /L) |  | Equilibrium Concentration (mg /L) |  | $C_i – C_e$ (mg/L) |  | Percentage Removal (%) |  |
|  | $Pb^{2+}$ | $Cd^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ |
| 30 | 6.00 | 6.00 | 1.10 | 0.00 | 4.90 | 6.00 | 81.70 | 100.00 |
| 60 | 6.00 | 6.00 | 0.98 | 0.00 | 5.02 | 6.00 | 83.70 | 100.00 |
| 90 | 6.00 | 6.00 | 0.89 | 0.00 | 5.11 | 6.00 | 85.30 | 100.00 |
| 120 | 6.00 | 6.00 | 1.08 | 0.00 | 4.92 | 6.00 | 82.00 | 100.00 |
| 150 | 6.00 | 6.00 | 1.38 | 0.00 | 4.62 | 6.00 | 77.00 | 100.00 |

| ASSC |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| Contact Time (min) | Initial Concentration (mg /L) |  | Equilibrium Concentration (mg /L) |  | $C_i – C_e$ (mg/L) |  | Percentage Removal (%) |  |
|  | $Pb^{2+}$ | $Cd^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ |
| 30 | 6.00 | 8.00 | 1.96 | 0.00 | 4.04 | 8.00 | 63.30 | 100.00 |
| 60 | 6.00 | 8.00 | 0.95 | 0.00 | 5.05 | 8.00 | 84.20 | 100.00 |
| 90 | 6.00 | 8.00 | 0.88 | 0.00 | 5.12 | 8.00 | 85.30 | 100.00 |
| 120 | 6.00 | 8.00 | 1.27 | 0.00 | 4.73 | 8.00 | 78.80 | 100.00 |
| 150 | 6.00 | 8.00 | 1.38 | 0.00 | 4.62 | 8.00 | 77.00 | 100.00 |

### Percentage Reduction vs. Contact Time for $Pb^{2+}$ Adsorption onto ASSC and APSC

A graphical representation in Figure 1 depicts a positive slope when plotting the logarithm of % reduction against the logarithm of contact time. The % reduction increases with extended contact time, reaching its peak at 90 minutes (85.30%) for both adsorbents before showing a decline. The deviation of the line from the origin in Figure 1 suggests that intra-particle movement may not solely be the rate-limiting step, as indicated by Badmus *et al.* (2007). It is plausible that the movement of the water sample through the particle sample interface into the pore of the particles, along with adsorption on the available surface of the adsorbent, contributes to the adsorption process.

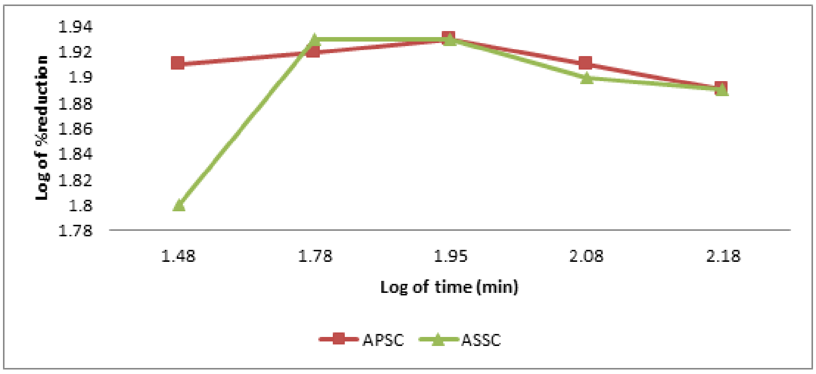

**Figure 1:** Changes in Adsorption with Contact Time (adsorption kinetics).

### Pseudo-second order Parameters and Coefficient of Determination for Different Adsorbents

The pseudo-second-order model posits that the rate-limiting step is the surface adsorption process, necessitating chemisorption. Here, the removal from a solution is due to physicochemical interactions between two phases (Wang *et al.*, 2007).

The pseudo-second order equation is given in Equation 1 (Ho and McKay 1999).

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \qquad (1)$$

Where $h = kq_e^2$ ($mg\,g^{-1}min^{-1}$) can be regarded as the initial adsorption rate when t → 0 and k is the pseudo-second-order rate constant of adsorption ($g\,mg^{-1}min^{-1}$).

A straight line plot of $t/q_t$ vs. t was obtained and this is in good agreement with second order kinetics. The pseudo-second order parameters and coefficient of determination obtained for the two adsorbents are given in Table 7. The regression coefficients were respectively 0.994 and 0.786 for APSC and ASSC.

**Table 7:** Pseudo-second order parameters and coefficient of determination for different adsorbents

| **Adsorbent** | **Pseudo-second order equation** | | | |
|---|---|---|---|---|
| | Qe | H | K | $r^2$ |
| APSC | 78.52 | -16.13 | -0.0027 | 0.994 |
| ASSC | 76.92 | 66.67 | 0.0113 | 0.786 |

### Elovich Equation Parameters and Coefficient of Determination for the Different Adsorbents

Elovich equation (Eqn. 2) is one of the best models describing activated chemical adsorption (Juang and Chen, 1997).

$$\left(\frac{dqt}{dt}\right) = aexp(-bqt) \qquad (2)$$

Where a and b are constants. The constant "a" is taken as the initial rate because (dqt/dt) approaches 0. The linear form of eqn. 2 is eqn. 3.

$$qt = \left(\frac{1}{b}\right) In(ab) + \left(\frac{1}{b}\right) Int \qquad (3)$$

The regression coefficient $r^2$ for the adsorption of lead by both adsorbents for the Elovich equation were 0.139 and 0.347 for plot of $q_t$ against $Int$. This shows that the result cannot be represented by the Elovich equation because of the lower $r^2$ values (Table 8).

**Table 8:** Elovich equation parameters and coefficient of determination for the different adsorbents

| | **Elovich Equation** | | |
|---|---|---|---|
| | B | a | $r^2$ |
| APSC | -0.5464 | - | 0.139 |
| ASSC | 0.1229 | 7.282 | 0.347 |

### Langmuir Adsorption Isotherm Constants and Coefficients for $Cd^{2+}$ and $Pb^{2+}$ ions onto ASSC and APSC

Langmuir isotherm is represented by equation 4 (Langmuir, 1918).

$$qe = \frac{Q_o K_L C_e}{1 + K_L C_e} \qquad (4)$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation into linear form;

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o K_L C_e} \qquad (5)$$

Where $q_e$ represent the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), $C_e$ is equilibrium concentration of adsorbate ($mg/L^{-1}$), $Q_o$ = the maximum monolayer coverage capacity (mg/g) and $K_L$ is Langmuir isotherm constant (L/mg).

The values of $Q_o$ and $K_L$ were calculated from the intercept and slope of the Langmuir plot of ${}^{1}/_{q_e}$ against ${}^{1}/_{C_e}$ . The essential features of the Langmuir isotherm can be represented in terms of equilibrium parameter $R_L$, a dimensionless constant known as separation factor (Langmuir, 1918).

$$R_L = \frac{1}{1 + (1 + K_L C_o)} \qquad (6)$$

Where $C_o$ represent the initial concentration.
The adsorption nature is unfavourable if $R_L>1$, favourable if $0<R_L<1$, linear if $R_L = 1$ and irreversible if $R_L = 0$.

Here, the values of $Q_o$. $K_L$, $R_L$ and $R^2$ obtained showed $R_L$ values is $0<R_L<1$. It implies that Langmuir isotherm is best fitted for both ASSC and APSC.

The isotherm was linear with a good linear correlation coefficient ($R^2$) ranging from 0.8950 to 0.9852 and fitted well with the Langmuir model. The high value of $K_L$ (74.53 L/mg) for ASSC implies that strong interaction does exist between adsorbate ($Cd^{2+}$) and adsorbent.

### Freudlich Adsorption Isotherm Constants and Coefficients for $Cd^{2+}$ and $Pb^{2+}$ ions onto ASSC and APSC

Freundlich isotherm is based on sorption on heterogeneous surface and is represented in equation 7.

$$Q_e = K_f C_e^{1/n} \quad (7)$$

Where $K_f$ = Freundlich isotherm constant (mg/g), $C_e$ is equilibrium concentration of adsorbate (mg/L), $Q_e$ = amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), and n = adsorption intensity (Freundlich, 1906).

The well-known logarithm (linear) form of Freundlich model is given by equation 8.

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (8)$$

The constant $^1/_n$ signifies the strength of adsorption in the adsorption process, while $K_f$ serves as an approximate indicator of adsorption capacity. A value of n equal to 1 implies independence of partition between the two phases from concentration. If the value of $^1/_n$ is below one, it indicates normal adsorption and provides insight into the favorability of the adsorption process (Mohan and Karthikeyan, 1997).

When plotting $\log Q_e$ against $C_e$, a linear graph is obtained, with $\log K_f$ and $^1/_n$ corresponding to the intercept and slope, respectively. The obtained values for $^1/_n$ (ranging from 0.2951 to 0.5441) suggest that the adsorption of $Cd^{2+}$ and $Pb^{2+}$ onto ASSC and APSC was favorable. However, the $R^2$ values (ranging from 0.1360 to 0.4366) for both adsorbents are comparatively low when compared to the Langmuir model, indicating that the Langmuir model provides a better fit than the Freundlich model.

### Temkin Adsorption Isotherm Constants for $Cd^{2+}$ and $Pb^{2+}$ ions onto ASSC and APSC

This model operates on the assumption that the heat of adsorption (which is a function of temperature) for all molecules within the layer decreases linearly, as opposed to logarithmically, by excluding extremely low and high concentration values. Additionally, the model incorporates a factor that precisely considers the interactions between the adsorbent and adsorbate. Temkin equation is given in eqn. 9 (Temkin and Pyzhev, 1940).

$$qe = \frac{RT}{b} In(A_T C_e) \quad (9)$$

Which transforms to eqn. 10

$$\text{Thus, } q_e = BInA_T + BInC_e \quad (10)$$

$$\text{Where } B = \frac{RT}{b_T}$$

Where; $A_T$ represent Temkin isotherm equilibrium binding constant (L/g), $b_T$ represent Temkin isotherm constant, R represent universal gas constant (8.314J/mol/K), T represents Temperature at 298K and B represent constant related to heat of sorption (J/mol).

The values of $b_T$, $R^2$, B and $A_T$ obtained from the Temkin plot ranged from 5.778-6.043, 0.6216-0.7142, 0.4090-0.4290 and 0.4580-0.8570, respectively, for both adsorbents and adsorbates. The values for B (0.4090 – 0.4290 KJ/mol) for the various adsorbents showed that the heat of sorption might be the physical adsorption type. The $R^2$ values are 0.6216 ($Cd^{2+}$) and 0.6770 ($Pb^{2+}$) for ASSC, while that of APSC are 0.7142 and 0.677 for $Cd^{2+}$ and $Pb^{2+}$ respectively. The model fitted best for APSC ($Cd^{2+}$).

### Dubinin-Radushkevich (DRK) Adsorption Isotherm Constants and Coefficient for $Cd^{2+}$ and $Pb^{2+}$ ions onto ASSC and APSC

This isotherm is used to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The DRK equation is given as;

$$q_e = (q_s)\exp(-K_{ad}{}^2) \quad (11)$$

Which transforms to;

$$Inq_e = In(q_s) - K_{ad}\varepsilon^2) \quad (12)$$

Where $q_e$ is the amount of adsorbate in the adsorbent at equilibrium (mg/g), $q_e$ is the theoretical isotherm saturation capacity (mg/g), $K_{ad}$ represent Dubinin-Radushkevich isotherm constant ($mol^2/kJ^2$) and is the Dubinin-Radushkevich constant (Dubinin, 1960).

This model was used to differentiate the chemical from physical adsorption of $Cd^{2+}$ and $Pb^{2+}$ with its mean free energy, E per molecule of adsorbate. This was calculated using equation 13.

$$E = \left[\frac{1}{\sqrt{2K_{ad}}}\right] \qquad (13)$$

To find ε, equation 14 was used.

$$\varepsilon = RTIn\left[1 + \frac{1}{C_e}\right] \qquad (14)$$

Where R is the gas constant ($8.314\ Jmol^{-1}K^{-1}$), Ce represent adsorbate equilibrium concentration in mg/L and T represent the absolute temperature Kelvin.

Temperature dependency is one of the unique features of DRK model. The constants $q_s$ and $K_{ad}$ were gotten from the plot of $Inq_e$ against $^2$

The $R^2$ values obtained are 0.9164 ($Cd^{2+}$) and 0.7860 ($Pb^{2+}$) for ASSC, while that of APSC are 0.7892 and 0.7860 for $Cd^{2+}$ and $Pb^{2+}$, respectively. The model fitted best for ASSC ($Cd^{2+}$) over Langmuir, Freundlich and Temkin model.

## CONCLUSION

This study has shown that ASSC and APSC are effective adsorbents for the removal of heavy metal ions from aqueous solutions. The uptakes of both adsorbates ($Pb^{2+}$ and $Cd^{2+}$ ions) were affected by the process parameters. Of the four adsorption isotherms used for the equilibrium studies; Langmuir was best fitted for the two adsorbent (APSC and ASSC). The adsorption mechanism for this study follows pseudo-second order kinetic model. Therefore, activated snail and periwinkle shells carbons are active biosorbents for the removal of $Cd^{2+}$ and $Pb^{2+}$ from aqueous solutions.

## CONFLICT OF INTEREST

There is no conflict of interest

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