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SORPTION STUDY OF H_2SO_4 ACTIVATED PERIWINKLE SHELL USING SEM AND XRD ANALYSIS

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ABSTRACT

The study focuses on the potential of periwinkle shells as an effective adsorbent for removing heavy metals, particularly copper ions, from industrial wastewater. The Scanning Electron Microscopy (SEM) analysis suggests that the activated carbon had a favourable porosity, with sharp adsorbent surfaces coated with Cu^{2+} to create smooth surfaces. The results indicate that the activated carbon had a high surface area, which could enhance its adsorption capacity. The X-ray Diffraction (XRD) spectrometry suggests that the peaks in the range 2θ equal to 23.61, 24.1, and 27.5 correspond to the existence of carbon in the structure. The results indicate that the activated carbon had a high degree of crystallinity, which could enhance its adsorption capacity. The effect of temperature on the adsorption capacity of the activated carbon was analyzed, and the results showed that the adsorption capacity increased with an increase in temperature. The effect of adsorbent dosage on the adsorption capacity of the activated carbon was analyzed, and the results showed that the adsorption capacity increased with an increase in adsorbent dosage.

Keywords: Activated carbon, Adsorption, SEM Analysis, Periwinkle shell, XRD Analysis.

INTRODUCTION

The issue of water pollution due to heavy metal contamination has gained significant attention in recent years. Metals such as arsenic and copper, which are commonly found in industrial wastewater, pose a serious threat to the environment and human health when they enter aquatic ecosystems (Smith, 2018). Various heavy metal removal methods have been explored to mitigate this problem, with adsorption emerging as an efficient and eco-friendly technique (Jones & Brown, 2019). The periwinkle shell is one intriguing adsorbent that has gained attention for its potential in heavy metal removal.

Periwinkles (*genus Littorina*) are marine gastropod molluscs that inhabit intertidal

zones and coastal areas. Their shells are composed primarily of calcium carbonate ($CaCO_3$) and exhibit a porous structure with a substantial surface area (Johnson *et al.,* 2020). This unique structure makes periwinkle shells a promising candidate for adsorption studies. Utilizing waste materials such as periwinkle shells provides an eco-friendly approach to waste disposal and contributes to the sustainable management of natural resources (Adams, 2017).

Numerous studies have investigated the adsorption capabilities of periwinkle shells in the removal of various heavy metals, including copper. Research by Johnson (2018) demonstrated the high adsorption capacity of periwinkle shells for arsenic, especially at neutral pH conditions. Additionally, a study by Adams & Davis (2020) investigated the competitive adsorption of copper on periwinkle shells, highlighting the complex nature of adsorption in real-world scenarios.

Using periwinkle shells as an adsorbent to remove copper from contaminated water sources is a promising and sustainable approach. With their unique structure and high surface area, periwinkle shells have demonstrated significant potential for heavy metal adsorption. Further research is needed to optimise adsorption conditions and understand the underlying mechanisms to develop efficient and cost-effective treatment methods (Jones & Brown, 2019).

In response to this challenge, researchers have turned to alternative, sustainable solutions, such as the utilization of natural adsorbents like periwinkle shells. Despite the promising potential of periwinkle shells for heavy metal adsorption, there exists a critical gap in understanding the intricate details of the adsorption process, optimal conditions, and the overall efficacy of periwinkle shells as a practical solution for copper removal.

MATERIALS AND METHODS

SAMPLE COLLECTION

A mass of 500 g of periwinkle (Tympanotonus fuscatus) empty shells were purchased from a local seller in the relief market in Owerri (Imo State, Nigeria) and stored in a plastic container. The empty shells were hammered into pieces and soaked in tap water for 5 days to dissolve the impurities of the dust, sand, and soluble particles. The shells were removed and washed several times under continuous agitation in flowing tap water to remove any loose particles. The periwinkle shells were dried at 120 °C for 48 h in preparation for milling. The shells were pulverized to powder by a locally fabricated ball mill at

workshop 3 of Eke Awka market in Anambra state, Nigeria.

Carbonization Process

The periwinkle shell powder (PSP) powder was calcined at 800 °C in a muffle furnace for 3 hours at 100 °C/10 min to improve the surface properties and uniform size to obtain PSA. PSA was sieved through a 75 µm mesh sieve to remove large particles and then stored in a plastic container. (Gimba and Bahago, 2004; Omeiza *et al*., 2011). The equation for the process is shown below:

$$\text{Perwinkle shell} \xrightarrow{500°C\ 5\ minutes} C + CO^2$$

Periwinkle Carbon Activation

Activation of the charred periwinkle was carried out as follows: 200 g of the charred sample was mixed with 250 ml of 5.5 M H_2SO_4 and heated until a paste was formed. It was then subjected to a temperature of 700ºC for 3 hours and then cooled to room temperature. The samples were washed with de-ionized water several times until pH 6-7, filtered with Whatman No. 1 filter paper and then dried in the oven at 110ºC for 8 hours. The equation for the process is shown below.

$$Carbonized\ plantain\ peel \xrightarrow{700°C, AA\ 3\ Hours} AC + CO^2\ (Activation)$$

AA is the activating agent, and AC is the activated charcoal.

Characterization Studies

Moisture and Dry Mater Content Determination

Clean crucibles were dried, and 2.00 g of the raw periwinkle shell was placed in the crucible and weighed. This was dried in an oven at 105ºC for 3 hours, after which they were cooled in a desiccator and then weighed (Allen *et al.*, 1997)

$$\text{Moisture}[\%] = \frac{\text{Loss in weight on drying(g)}}{\text{Initial sample weight(g)}} \text{x}$$

$$100$$

$$\text{Dry matter}[\%] = \frac{\text{Oven dry weight(g)}}{\text{Initial sample weight}} \text{x}\ 100$$

Ash Content Determination

Crucibles were heated in a furnace at about 500ºC, cooled in a desiccator, and then 2.00g of periwinkle shell sample were weighed in them. The crucibles containing the dry sample were placed in a furnace, then the temperature was raised to 700ºC. After 3 hours, the crucibles were removed and allowed to cool in desiccators, after which they were weighed, and the content

of the periwinkle shell was evaluated (Ocholi, 2006; Pattabhi *et al.,* 2008; Shetty and Rajkumar, 2009)

$$\text{Ash}[\%] = \frac{\text{Ash weight(g)}}{\text{Oven dry weight(g)}} \text{x } 100$$

Bulk density

A 100 cm^3 calibrated measuring cylinder was washed and dried. 50 cm^3 of the water was added to the measuring cylinder. It was noted. 2 grams of the sample was transferred into the measuring cylinder, and the volume of the increased water level was recorded. Care was taken to ensure there were no air bubbles before taking volume measurements (Bhatia, 2006)

Calculation

Volume of water displaced (cm^3) = Final volume – Initial volume

$$\text{Bulk density}(g/cm^3) = \frac{\text{Mass of samples}}{\text{Volume of water displaced}}$$

Density of Carbonized Material

Procedure

A 100 cm^3 calibrated measuring cylinder was washed and dried. 20 cm^3 of the water was added to the measuring cylinder and was noted. 4.0 grams of the carbonized was transferred into the measuring cylinder, and the volume of the increased water level was recorded. Measurement was taken to ensure there were no air bubbles before taking volume measurements.

Calculation

Volume of water displaced (cm^3) = Final volume – Initial volume (Vb-Va)

$$\text{Bulk density}(g/cm^3) = \frac{\text{Mass of carbonized}}{\text{Volume of water displaced}}$$

Determination of surface area

The surface area of various particle sizes was determined using the iodine adsorption method. The amount of aqueous solution was estimated by titrating a blank with standard thiosulphate solutions and comparing the titrated values against an iodine-containing sample.

$$\text{Iodine value} = \frac{(B - S)\text{x M x } 126.91)}{B \text{ x } W}$$

B and S are the volumes of thiosulphate solution required for blank and sample titrations, respectively. W, the mass of the activated plantain husk sample and M, the concentration of (mol/l) of iodine solute and 126.91, the atomic mass of iodine. The iodine number is used to determine the

surface area of different particle sizes of the activated carbon by measuring the activated carbon's micropore content on iodine adsorption from the solution. This is equivalent to the surface area of activated carbon (Drake *et al*., 1996).

Preparation of Standard solutions of Cu^{2+}solution (1000 mg/dm^3)

Copper nitrate $Cu(NO_3)_2.3H_2O$ of 1.8990 g was dissolved in 100 cm3 deionized water. This was then transferred into a 500 cm3 volumetric and made up to mark with deionized water. The working solution concentrations of 50, 100, 200, 250, 300, 400, and 500 mg/dm3 were prepared from 1000 mg/dm^3 of stock by serial dilution (Al-Asheh *et al*., 2000).

Adsorption Experiments

The experiments were carried out using the method of Argun *et al.,* (2007). Exactly 50.0cm^3 of the working solution was measured into polythene bottles, and 0.5g adsorbent was transferred into these bottles. The mixtures in polythene bottles were agitated simultaneously with an essential reciprocating shaker at 200rpm for 3 hours and left undisturbed on the desk for 24 hours to allow the system to equilibrate. After 24 hours, the mixture was filtered through a Whatman filter paper into another 100cm^3 polyethene bottle. (Okiemen and Okiemen, 2001). The concentration of the residual or remaining metal ion in the filtrate after the adsorption process was determined using AAS. The amount of the metal adsorbed was calculated using the equation.

Where q_e is the amount of adsorbate ion adsorbed in milligrams per gram of the adsorbent, Co is the initial concentration of the metal ion before the adsorption process. At the same time, C_e is the equilibrium concentration of the metal ion in the filtrate after the adsorption process, m is the mass of the adsorbent, and V is the volume of the solution in cm^3.

The equation that gives percentage of metal ion removal by the periwinkle shell adsorbent is given by:

$$\% \text{ Removed} = \frac{(\text{Co} - \text{Ce})}{\text{Co}} \text{x } 100$$

C_o is the initial concentration of the metal ion before the adsorption process. While C_e is the equilibrium concentration of the metal ion in the filtrate after the adsorption process

Effect of Adsorbent Dosage on the Removal of Cu^{2+}

Adsorbent dosages of 0.5, 1.0, 1.5, 2.2, 2.5, and 3.0 g were used to determine the adsorption efficiency of activated carbon of periwinkle shell on Cu^{2+}. Each pre-

weighed adsorbent was mixed with 100 mg/dm^3 of selected heavy metals and agitated for 60 minutes in a Griffin shaker at 27±2°C. The adsorbent and adsorbate solution were separated by filtration using Whatman filter paper. The concentrations of un-adsorbed heavy metals were determined using the **Atomic Absorption Spectrometry (**AAS) technique (Ahalya *et al*., 2005; Krishnakumar *et al.,* 2007).

Effect of temperature on the Adsorption of Cu^{2+}

The adsorption capacities of various selected metals were determined using variable temperatures. The setup is exposed to 45, 60, 75, 90, 100 and 120oC temperatures, respectively. Data determined from here helps estimate the thermodynamic behaviour of the adsorption process, whereby a decrease in the adsorption rate as the temperature increases would denote an exothermic system and vice versa. The setup was left to stand on a magnetic stirrer and agitated at 100 rpm at optimum conditions (0.5 g dose of adsorbent, 60 mins). (Lakherwal, 2014).

Atomic Absorption Spectrometry

The concentration of the residual metal ion in the filtrates after the adsorption process was determined using the Shimadzu Scientific Absorption Spectroscopy machine, model number VGP 240. An air-acetylene flame was used for all the determinations.

Adsorption Modeling of Heavy Metal ions

Equilibrium adsorption experiments have been carried out to evaluate the adsorption capacity of the adsorbent. The batch equilibrium for the adsorption was performed in a set of Erlenmeyer flasks (250 ml) where solutions of metal ions (50 ml) with different initial concentrations (20-120 mg/dm^3) were placed in these flasks. An equal mass (0.5 g) of particle size 325µm activated carbon was added to each metal solution. The pH was adjusted to 7 by adding either a few drops of diluted hydrochloric acid or sodium hydroxide; the operation temperature was the ambient temperature (27±2°C). Thereafter, the different supernatants were filtered, and the concentration remaining in the filtrates was determined using a spectrophotometer. The adsorption rates of the various samples were determined from the uptake level of the selected heavy metals in their aqueous

solution. The degree of adsorption was determined using the Langmuir and Freundlich models.

RESULTS AND DISCUSSION

The results of the periwinkle shell H_2SO_4 activated carbon analysis, as shown in Table 1 below, show that the yield of the activated carbon was 66.10%, with a moisture content of 1.27%, ash content of 8.00%, and a dry matter of 97.00%. The surface area of the activated carbon was found to be 41.00% m2/g, with a pH of 6.10, a bulk density of 0.49, and a density of carbonized material of 1.68 g/cm3. The results suggest that periwinkle shell H_2SO_4 activated carbon has favourable physiochemical properties for use as an adsorbent.

Table 1: Periwinkle shell H_2SO_4 Activated Carbon

Parameters	Results
Yield	66.10
Moisture content	1.27%
Ash Content	8.00%
Dry Matter	97.00%
Surface area (m2 g -1)	41.00%
pH	6.10
Bulk Density	0.49
Density of Carbonized Material (g/cm3)	1.68

Table 2: Physiochemical properties of water sample

Parameters	SAMPLE
Odour	Objectionable
Appearance	Not clear
Colour	Milkfish
pH	8.14
Temp. (^oC)	30
TDS (mg/l)	14000
EC (µS/cm)	35.28
Turbidity (NTU)	44.70
TSS (mg/l)	63.40
Hardness (mg/l as $CaCO_3$)	13.78
Copper (mg/L)	44.70

The physicochemical properties of the water sample were also analyzed, and the results, as shown in Table 2 above, indicate that the water had an objectionable odour, was not clear, and was milkfish-coloured. The pH of the water was 8.14, with a

temperature of 30°C, TDS of 14000 mg/l, EC of 35.28 μS/cm, turbidity of 44.70 NTU, TSS of 63.40 mg/l, and hardness of 13.78 mg/l as $CaCO_3$. The results suggest the water sample was contaminated with copper ions, which could be removed using the periwinkle shell H2SO4 activated carbon.

Scanning Electron Microscopy (SEM) Analysis

SEM images for studied AC before and after the adsorption process are represented in Figures 1 and 2, respectively. According to our observations, there was a consistency between surface microparticles on the H2SO4-activated periwinkle shell. This result agrees with the established literature (Mohammed *et al.,* 2012). SEM images were indicative of favourable porosity of the surface of the evaluated H2SO4-activated periwinkle shell. As can be seen, the sharp adsorbent surfaces are coated with Cu^{2+} to create smooth surfaces.

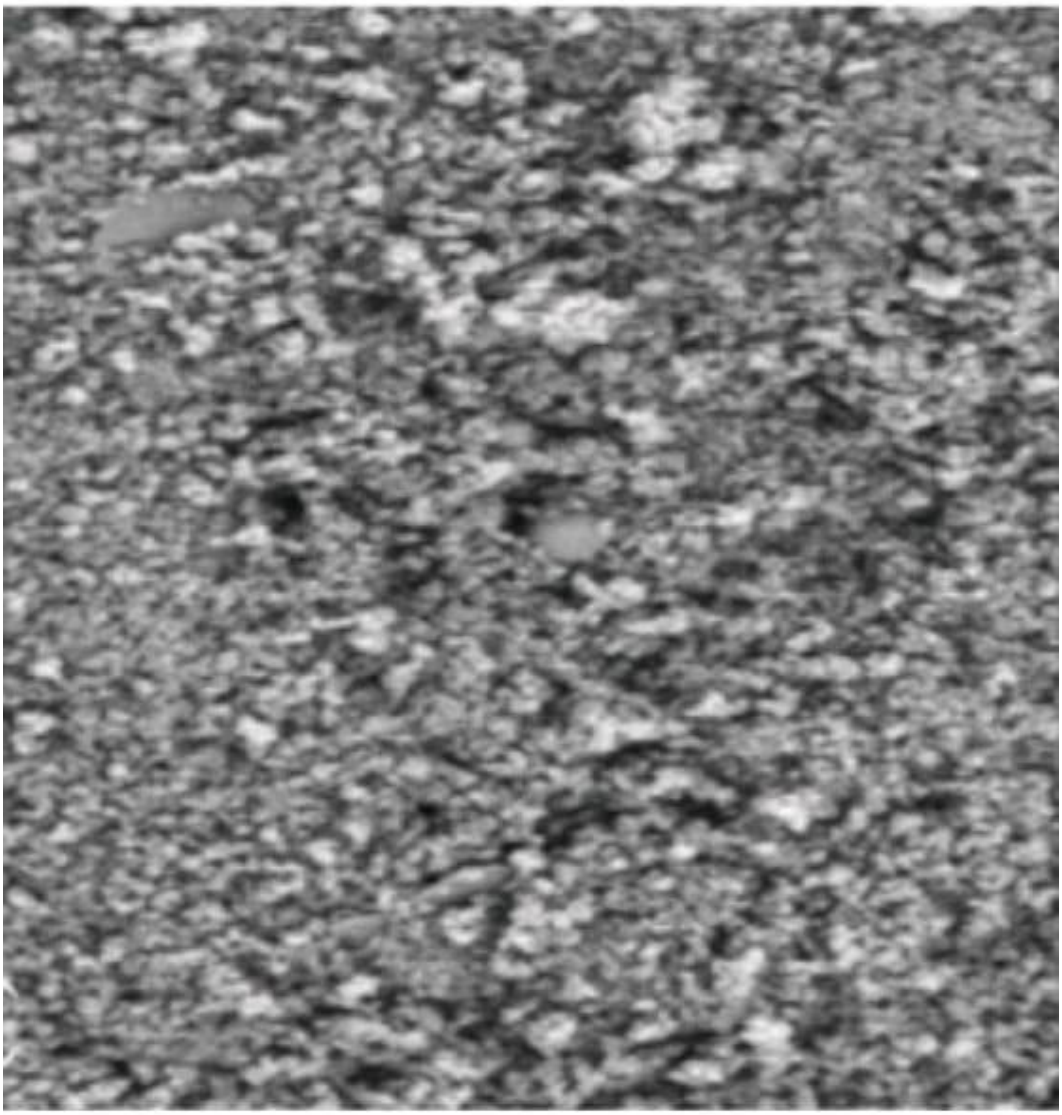

Figure 1: SEM images of H_2SO_4 Activated Periwinkle shell before adsorption process(x500)

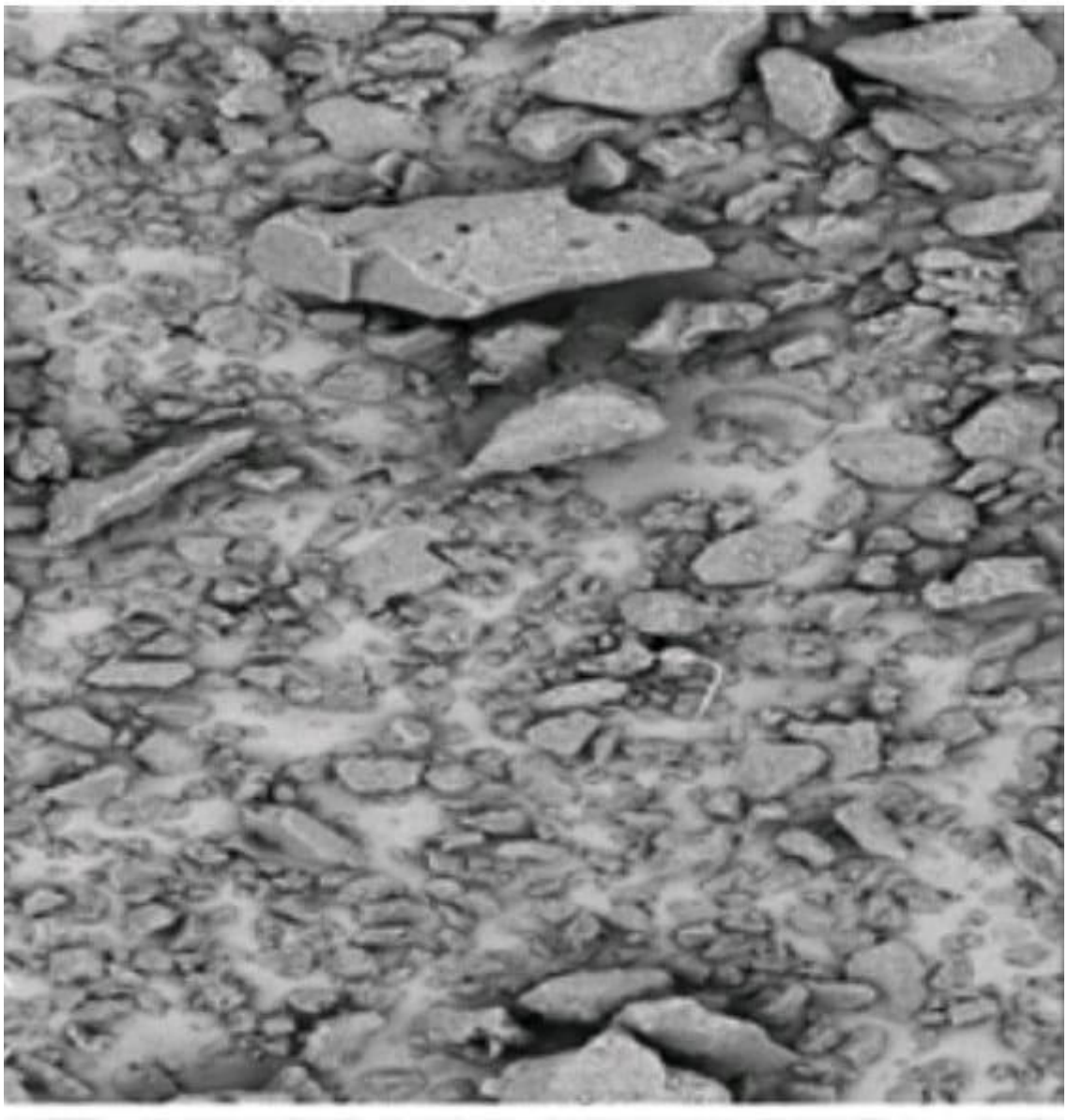

Figure 2: SEM images of H_2SO_4 Activated Periwinkle shell after adsorption process(x500)

X-ray Diffraction analysis

X-ray Diffraction (XRD) spectrometry of H_2SO_4 Activated Periwinkle shell before and after the adsorption process are represented in Figures 3 and 4, respectively. According to this analysis, the peaks in the range 2θ equal to 23.61, 24.1, and 27.5 correspond to the existence of carbon in the structure. This result agrees with many reports on mollusc shells-cockle shells (Mohamad *et al.,*2016) and mussel shells (Roy and Marie,2012)

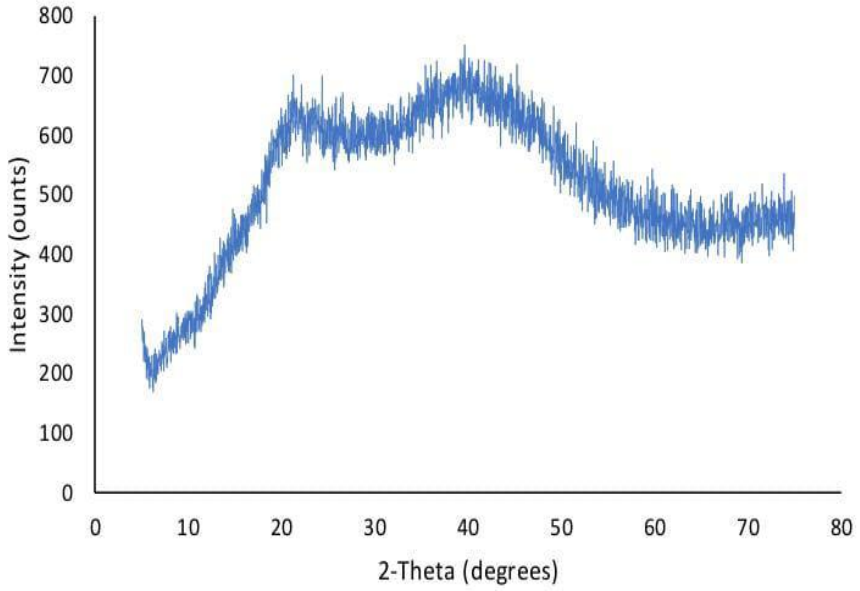

Figure 3: X-ray Diffraction (XRD) spectrometry of H_2SO_4 Activated Periwinkle shell before the adsorption process

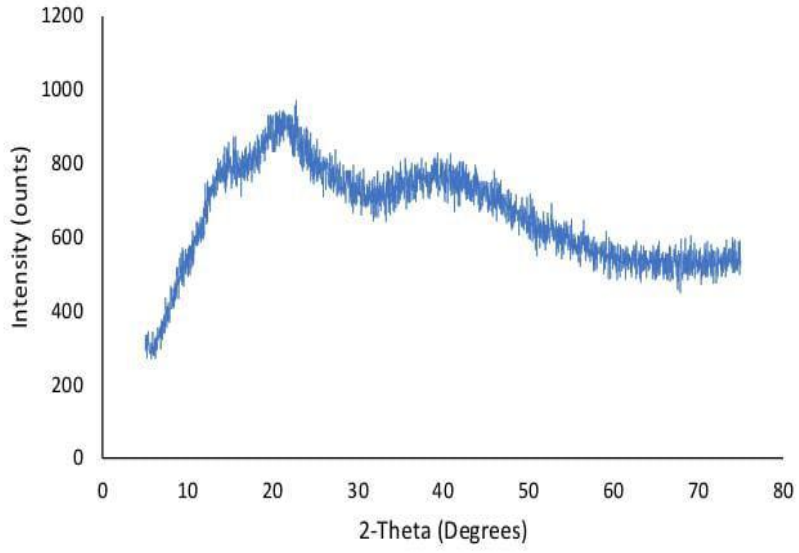

Figure 4: X-ray Diffraction (XRD) spectrometry of H_2SO_4 Activated Periwinkle shell after adsorption process.

Effect of temperature

From Table 3, it was observed that as the temperature increased, there was an increase in the Removal efficiency for $Cu^{2+,}$ from 73 -89% respectively. However, at a reaction temperature of 60°C, there was a decrease in the Removal efficiency of Cu^{2+} ions and a further temperature increase to 100°C equilibrium was attained. The reduction in adsorption with an increase in temperature suggests weak adsorption interaction between periwinkle H_2SO_4 activated carbon surface and metal ions because the boundary layer decreases due to the increased tendency of the Copper ion to escape from the periwinkle H_2SO_4 activated carbon surface to the solution phase. Elevated temperatures can accelerate the adsorption process, allowing for quicker attainment of equilibrium between the adsorbate and adsorbent (Sathya & Martha, 2017).

The setup was left to stand on a magnetic stirrer and agitated at 100 rpm, at optimum conditions at 0.5g dose of absorbent, Time = 60mins, Particle size = < 75(µm), P^{H} = 2.00, Volume of CU^{2+} polluted water used = 50ml, C_o = 44.70mg/L

Table 3: Effect of Temperature

Temperature (^{O}C)	C_e (CU^{2+} conc. (mg/l)	q_e (Amount of CU^{2+} adsorbed)(mg/g)	% Removal efficiency
20	5.21	3.95	88.34
40	5.14	3.96	88.50
60	5.06	3.96	88.68
80	4.97	3.97	88.88
100	4.53	4.02	89.87
120	4.91	3.98	89.00

Effect of Adsorbent dosage

The effect of the adsorbent dosage on the removal efficiency of Cu^{2+} was studied at adsorbent dosages of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 g. From Table 4, it was observed that the removal efficiency of the adsorbent dosage increased for Cu^{2+} heavy metals as the adsorbent dosage increased as was observed when the adsorbent dosage was increased from 0.5g to 1.0g where further increment in the adsorbent dosage resulted in a decline in the removal efficiency rapidly due to the growing number of adsorbent process of diffusion and binding

of the better adsorbate molecules on the available sites beyond this the adsorbent becomes saturated. (Ahalya *et al.*, 2005; Krishnakumar *et al.,* 2007).

The setup was left to stand on a magnetic stirrer and agitated at 100 rpm, Temperature =100^{0}C, Particle size = < 75(µm), P^H = 2.00, Time =60mins, Volume of CU^{2+} polluted water used = 50ml, C_o = 44.70mg/L.

Table 4: Effect of Adsorbent Dosage

adsorbent dosage (g)	C_e (CU^{2+} conc. (mg/l)	q_e (Amount of CU^{2+} adsorbed)(mg/g)	% Removal efficiency
0.5	3.82	4.09	91.45
1.0	3.91	4.07	91.25
1.5	5.27	3.94	88.21
2.0	8.82	3.59	80.26
2.5	10.30	3.44	76.96
3.0	13.71	3.10	69.33

CONCLUSION

In conclusion, the study on the adsorption capabilities of periwinkle shells for removing copper from water sources presents a promising and sustainable solution for addressing heavy metal contamination in industrial wastewater. The investigation comprehensively analyses the adsorption mechanisms, optimal conditions, and the overall efficacy of periwinkle shells as a natural adsorbent. The study's objectives have been successfully addressed through the materials and methodology outlined, including determining the effect of temperature and adsorbent dose on the adsorption characterization of periwinkle shells. The study holds promise for improving public health by exploring the possibility of utilizing periwinkle shells to ensure safer drinking water, particularly in regions facing challenges related to heavy metal contamination.

RECOMMENDATIONS

The findings of this study recommend further exploration of the practical application of periwinkle shells as an

adsorbent for removing Cu^{2+} in industrial wastewater treatment processes. They emphasise the potential for large-scale industrial applications and collaboration with industry partners and environmental agencies.

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