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# Immobilization of Polyoxometalate-Ionic Liquid on Coconut Shell Nanoporous Carbon Support: An Improved Material for Water Purification

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Access to clean water by all is one of the UN Sustainable Development Goals. To achieve this, there is need to prepare sustainable materials for efficient water purification. This research aims to immobilize the Polyoxomatelate-Ionic Liquid (POM-IL), {[CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>]<sub>4</sub>N}<sub>7</sub>[α-PW<sub>11</sub>O<sub>39</sub>] on nanoporous carbon (NC) prepared from coconut shell to form an advanced material (POM-IL@NC) for effective removal of multiple contaminants from polluted water. The POM-IL@NC material was characterized by Fourier Transform-Infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) Analysis and Brunauer-Emmett-Teller (BET) method. The material was then tested respectively for the removal of copper and lead using Atomic Absorption Spectroscopy (AAS) and methylene blue using Ultraviolet-Visible (UV-Vis) Spectroscopy from simulated polluted waters via adsorption. The material was further subjected to antimicrobial analysis. The results showed that the POM-IL@NC material performed better than the pristine NC in the removal of copper. lead and methylene blue from the contaminated water. The POM-IL@NC also exhibited significant improvement in antimicrobial activity than NC against Escherichia coli and Staphylococcus aureus. This shows that the new material could effectively be applied for multiple contaminants treatment of polluted water.

**Keywords:** Polyoxometalates; Ionic Liquid; Coconut shell; Nanoporous carbon; Contaminated Water.

#### 1. Introduction

The provision of portable water, especially, to the teeming populace in developing African countries like Nigeria remains one of the Sustainable Development Goals.1 Across the world, water sources are contaminated by human activities resulting from increasing urbanization and industrialization. activities include poor disposal of domestic wastes, sewages, run-offs from baths, showers, sinks and toilets, and sludge from small- and large-scale industries. They usually result in water pollution due to the deposition of various contaminants including heavy metals, organic and microbial wastes in these water sources,2 which are directly available to the populace for drinking and other domestic applications.

Heavy metals refer to any metallic element with atomic density greater than 4000 kg/m<sup>3</sup> and are toxic or poisonous even at low concentration. They include Pb, Cu, Cd, Ni, Co, Fe, Zn, and Cr and are non-biodegradable.<sup>3, 4</sup> Heavy metals

contamination in water is a major concern because of their toxicity and threat to human life and the environment.<sup>4</sup> Other contaminants in water such as suspended solids can lead to anaerobic condition whereas organic contaminants such as pesticides can cause depletion of natural oxygen. Also, the presence of phosphates and nitrogen can improve the growth of microbes, which can cause diseases and even deaths.<sup>5</sup> It is therefore important that water from these sources are treated from several contaminants before use.

Several methods have been used in the treatment of contaminated water including adsorption, chemical precipitation, reverse osmosis, filtration, ion-exchange, distillation, photo-oxidation and electrolysis. Among these however, the adsorption process has become one of the most common method of water purification, possibly due to the simplicity of the process, cost implication and the range of

adsorbent materials available for use as water filters. Adsorbent materials that have been applied in the treatment of contaminated water include chitosan, zeolites, activated carbons, clay minerals etc.<sup>8,9</sup>

Activated carbon is the oldest known and most widely used of these adsorbents. It is an amorphous form of carbon with a high degree of porosity and associated large surface area, which makes it an excellent adsorbent for a wide variety of pollutants including heavy metals and organics in both liquid and gaseous phases. 10-12 Due to availability and cost, among others, it has been prepared from a wide variety of agricultural by-products and wastes including pine bark, rice husks, saw dust, cotton, fiber, biomass of fungi and yeast, Carica papaya seed, coconut shells etc. 13-16

Coconut shell is an abundant waste resources obtained from coconut, which is widely produced in Nigeria. The shell is effective in making activated carbon for heavy metal removal from waste water.<sup>14</sup>

A major limitation of activated carbon and other adsorbents is that they are mostly applied in the removal of a single pollutant such as heavy metals or organics in contaminated water. So the water purification process will involve several purification steps, which can lead to high cost among others.<sup>17</sup> It is in a bid to tackle this challenge, and provide more sustainable water treatment options that will utilize adsorbents which are able to tackle several contaminants at once that Herman et al. first reported the removal of multiple contaminants from water using a Polyoxometalate-Supported Ionic Liquid Phase (POM-SILP) material. The material consisted of a water-insoluble POM-IL supported on a porous silica support. The POM-IL was made of an antimicrobial alkylammonium cations  $(n-C_7H_{15})_4N^+$ and the lacunary polyoxometalate anion ( $[\alpha-SiW_{11}O_{39}]^{8-}$ ). POMs are anionic molecular metal oxide clusters formed by high oxidation states early transition metals. The lacunary POMs usually have sites for binding with metals. 18, 19

In contributing to tackling this challenge, this work aims to immobilize a POM-IL on coconut shell-based nanoporous carbon support and test the effectiveness of the new material for multicontaminants removal from polluted water. The POM to be explored here is ( $[\alpha\text{-PW}_{11}O_{39}]^{7\text{-}}$ ) and the prepared adsorbent material will be tested respectively for the removal of copper, lead and methylene blue via adsorption.

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#### 2. Materials and Methods

#### 2.1 Materials

Coconut shells were collected from Gwadabawa Central Market, Sokoto State, Nigeria and used as precursor for nanoporous carbon. The samples were washed thoroughly with distilled water, oven-dried overnight at 100°C, pulverized and sieved with 150 µm-sieve to obtain the raw coconut shell sample (RC). Potassium hydroxide (KOH, Merck) was used as the activating agent for the nanoporous carbon (NC). Double distilled water was used for the experiments. Other chemicals used were hydrochloric acid (HCI, Fisher Scientific, 37%), sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>.2H<sub>2</sub>O, Merck, 99%), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, Merck, 99.9%, ), glacial acetic acid (CH<sub>3</sub>COOH, Fisher Scientific, 99.7%), potassium chloride (KCI, Sigma-Aldrich, 99%), tetraheptylammonium bromide, **THPAB** Sigma-Aldrich,  $([CH_3(CH_2)_6]_4N(Br),$ 99%). chloroform (CHCl<sub>3</sub>, Sigma-Aldrich, acetone (CH<sub>3</sub>COCH<sub>3</sub>, Fischer Scientific, 99.6%). toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, Fischer Scientific, 99.5%), copper (II) sulfate pentahydrate (CuSO<sub>4</sub>.5H<sub>2</sub>O, Sigma-Aldrich, 99.99%), lead (II)nitrate  $(Pb(NO_3)_2,$ Sigma-Aldrich, 99.99%) methylene blue (Sigma-Aldrich). All reagents used were AR grade chemicals.

# 2.2 Synthesis of $K_7[\alpha\text{-PW}_{11}O_{39}]\cdot 14H_2O$ (POM)

 $K_7[\alpha\text{-PW}_{11}O_{39}]\cdot 14$   $H_2O$  was prepared using standard literature procedure. A solution of 181.5 g of  $Na_2WO_4\cdot 2H_2O$  (0.55 mol) in 300 mL water was mixed with 50 mL of 1 M  $H_3PO_4$  (0.05 mol) and 88 mL of glacial acetic acid (1.53 mol). The resulting mixture was refluxed for 1 h and allowed to cool to room temperature. 60 g of KCl (0.8 mol) was then added into the solution and a large amount of white precipitate was formed immediately. The solution was filtered. The white solid was air-dried, weighed and characterized.

# 2.3 Synthesis of {[CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>]<sub>4</sub>N}<sub>7</sub>[ $\alpha$ -PW<sub>11</sub>O<sub>39</sub>] (POM-IL)

 $\{[CH_3(CH_2)_6]_4N\}_7[\alpha-PW_{11}O_{39}]$  was prepared using a similar method as described in literature for  $\{[CH_3(CH_2)_6]_4N\}_8[\alpha-SiW_{11}O_{39}].^{17}$  In a round-bottom flask, a solution of  $K_7[\alpha-PW_{11}O_{39}].^{14}$  H<sub>2</sub>O (2.50 g, 0.781 mmol, 1.00 eq.) was dissolved in 50 mL of water, heated to 50 °C and a solution of  $[CH_3(CH_2)_6]_4N(Br)$  (2.68 g, 5.467 mmol, 7.00 eq) in toluene (80 mL) was added. The mixture was vigorously stirred for 5 minutes and the organic layer was separated. After removal of the solvent under reduced pressure, the off-white highly viscous liquid was solvent-stripped once with 50 mL toluene and three times with 50 mL chloroform and characterized.

# 2.4 Preparation of Nanoporous Carbon (NC) from coconut shells

Nanoporous carbon support was prepared with modifications to the method described elsewhere<sup>21</sup> using only one thermal treatment. Raw coconut shell powder (10 g) in a beaker was thoroughly mixed with KOH (30 g) as chemical activator in a 1:3 ratio before adding double distilled water (20 mL). The slurry was stirred for an hour and allowed to stand for 24 h for activation. It was then dried in an oven at 110 °C before carbonation. Carbonation was done using a tube furnace in an atmosphere of Ar. The furnace was heated to 500°C at a rate of 10°C/min and the temperature was maintained at 500°C for 3 h. After cooling to room temperature, the carbonized material was washed thoroughly with 0.1 M HCl and double distilled water until the pH was about 7. The material was then dried at 105 °C for 1 h, smoothened and stored in wellfitted airtight container for further studies.

# 2.5 Immobilisation of $\{[CH_3(CH_2)_6]_4N\}_7[\alpha-PW_{11}O_{39}]$ on NC to form $\{[CH_3(CH_2)_6]_4N\}_7[\alpha-PW_{11}O_{39}]@NC (POM-IL@NC)$

The immobilization was achieved via a similar route described for  $\{[CH_3(CH_2)_6]_4N\}_8[\alpha SiW_{11}O_{39}$  @ silica.<sup>17</sup> Briefly, {[CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>]<sub>4</sub>N}<sub>7</sub>[ $\alpha$ -PW<sub>11</sub>O<sub>39</sub>] (0.22 mmol, 1.31 g)) was dissolved in acetone (50 mL) and nanoporous carbon from coconut shells, NC (4.79 g) was added. The dispersion was gently shaken for 5 minutes and the solvent was removed under reduced pressure. Acetone (50 mL) was added, and the shaking/solvent removal procedure was repeated three times. After vacuum-drying, the pure product  $\{[CH_3(CH_2)_6]_4N\}_7[\alpha-PW_{11}O_{39}]@NC$  was obtained as a dark brown free-flowing powder. The POM-IL loading corresponds to 21 wt.-%.

### 2.6 Characterization of Materials

FTIR spectra were recorded on a Bruker Alpha spectrometer fitted with a Platinum ATR module (4000 - 400 cm<sup>-1</sup>). Spectra were recorded for solid samples after drying for at least 1 h. UV-Vis analyses were done on a UV-1800 Shimadzu UV spectrophotometer using 1-cm quartz cells with a resolution of 1 nm between 200 and 800 nm. 32 mM of the original solution was used for the Surface morphology was analysed analysis. using Scanning electron microscopy (SEM, Phonem Prox, Malysia), operated at an accelerated voltage of 10 kV, XRD analysis was conducted using XRD, Philips X' Pert Pro with Cu K $\alpha$  radiation of wavelength of 0.15416 nm at the range of 5 - 80°. The specific surface area of the sample was measured by the Brunauer-Emmett-Teller (BET) method with an automated chemisorption/physisorption surface

analyzer (QuadraSorb Station 5.04) at 77 K and analyse using Quantachrome QuadraWin Data Acquisition and Reduction software. Thermal delay was 360 s, outgas time was 12 h, outgas temperature was 120 °C. Simulated polluted and filtered waters were analysed directly for copper and lead using AAS machine (GB Scientific Equipment Pty Ltd).

## 2.7 Water Filtration Experiment

In the water filtration experiment, the adsorbent phase was made using a Pasteur pipette, glass wool and the prepared adsorbent materials (NC and POM-IL@NC respectively). Small quantity of the wool was used to plug the pipette and the adsorbent material (0.6 g) was filled on top of the wool and tapped gently to optimize the packing of the adsorbent. Batches of simulated aqueous solution (10 mL) containing Pb (2.2 mM) or Cu (1.4 M), which is 45, 000 times the WHO permissible limit of the respective metals (Pb = 0.01 mg/L or 0.048  $\mu$ M and Cu = 2 mg/L or 32 μM)<sup>22</sup> or methylene blue (32 mM) were passed over separate adsorbent phases of NC and POM-IL@NC at a flow rate of ca. 4 mL min<sup>-1</sup>.17 Adsorption of the respective pollutant was determined by measuring the concentration of the pollutant remaining in the filtered solution for Cu and Pb and UV-Visible using AAS spectroscopy for methylene blue.

# 2.8 Standardization of the Test organisms and Antibacterial Analysis

The antimicrobial activity of NC and POM-IL@NC were determined against *Escherichia coli* (gram negative) and] *Staphylococcus aureus* (gram positive) using agar well diffusion method.<sup>23</sup>

The isolates of E. coli and S. aureus were obtained from the Department of Microbiology, Faculty of Science, Sokoto State University, Sokoto. Their purity were confirmed and the colonies from the subculture plates were suspended in 10 mL of Luria Bertani (LB) broth (Tryptone 10.0 g, Yeast extract 5.0 g, NaCl 10.0 g in 1000 mL distilled water) and incubated at 37 °C for 18-24 h in an orbital shaker at 150 rpm to attain logarithmic phase culture. The turbidity of the test suspension was then standardized to the 0.5 McFarland standard of approximately 1.5×108 CFU/mL. The adjusted suspension was used as inoculum for lawn culture preparation within 15 min. Sterile Muller-Hinton Agar (MHA) (g/L) (Beef infusion: 300; Casein hydrolysate 17.5; Starch: 1.5; Agar: 15; pH 7.2±0.2) was prepared. The media was sterilized at 121 °C at 15 lbs for 15 min. The diluted bacterial cultures adjusted to a 0.5 McFarland turbidity (1×108 CFU mL<sup>-1</sup>) was spread evenly over the entire surface of the agar plates using sterile cotton swab. The plates were incubated for 15 min at room temperature. Using

a well puncture 6–8 wells of 6 mm diameter were made for drug loading. Mueller–Hinton agar plates were used for the determination. Disks with different sample (NC or POM-IL@NC) concentrations were sonicated in distilled water and pipetted and placed on the surface of agar using forceps. After a period of pre-incubation (for 15 min), the inoculated plates were incubated at appropriate temperature for 24 h. The zone of inhibition was measured by Vernier caliper as a parameter of antibacterial property of the samples. A control was run using the antibiotic (Amoxicillin).

#### 2.9 Statistical Analysis

Analyses were performed in triplicates and results were expressed as mean ± SD. SPSS 19 was used to determine statistical significant difference (P>0.05) in parameters among groups using one-way ANOVA.

#### 3. Results and Discussion

#### 3.1 Products Yield

The yield of the starting materials and adsorbent materials are shown in Table 1. The yields were in the range observed for similar materials in literature. 17, 20, 21

Table 1: Yields of materials

Sample	Weight (g)	Yield (%)
K <sub>7</sub> [α-PW <sub>11</sub> O <sub>39</sub> ]·14 H <sub>2</sub> O	150	90
$\{[CH_3(CH_2)_6]_4N\}_7[\alpha-PW_{11}O_{39}]$	1.73	39.9
Nanoporous carbon (NC)	3.1	31
$\{[CH_3(CH_2)_6]_4N\}_7[\alpha$	6.1	100
PW <sub>11</sub> O <sub>39</sub> ]@NC		

## 3.2 Characterization of Adsorbent Materials.

 $K_7[\alpha-PW_{11}O_{39}]\cdot 14$   $H_2O$  and  $\{[CH_3(CH_2)_6]_4N\}_7[\alpha-PW_{11}O_{39}]$  were characterized by FTIR. The IR spectrum of  $K_7[\alpha-PW_{11}O_{39}].14H_2O$  shows vibrational bands at 1085 and 1040 cm<sup>-1</sup> attributed to  $v_{as}(P-O)$ , 949 for  $v_{as}(W-O_t)$ , 883 and 848 cm<sup>-1</sup> for  $v_{as}(W-O_b)$ , 791 and 725 cm<sup>-1</sup> for  $v_{as}(W-O_b)$  within  $W_3$  groups, 595 for δ (O-P-O), and 509 cm<sup>-1</sup> for δ (W-O-W). Peaks at 1606 cm<sup>-1</sup> and the broad peak around 3106 to 3633 cm<sup>-1</sup> were assigned to water. These correspond to values previously reported.<sup>20</sup> The FTIR spectrum of  $\{[CH_3(CH_2)_6]_4N\}_7[\alpha-PW_{11}O_{39}]$  in addition to the expected bands for P-O and W-O vibrations at 516, 658, 753, 790, 869, 889, 949, 1044, 1052,

and 1105 cm<sup>-1</sup>, contains bands associated to the  $\{[CH_3(CH_2)_6]_4N\}$  cations at 1375, 1457, 1468, 2857, 2927, and 2938 cm<sup>-1</sup>. Figure 1 shows the FTIR spectra of (a) Raw coconut shell (b) the nanoporous carbon (NC) and (c) POM-IL@NC material. The spectrum of the raw coconut shell showed bands assigned to several organic functional groups in raw coconut shells including: a broad peak around 3384.21 cm-1 for OH stretch, a peak at 2914.87 cm<sup>-1</sup> for C-H stretch, a peak at 1714.75 cm<sup>-1</sup> for C=O stretch in aldehydes or ketones, a peak at 1595.37 cm<sup>-1</sup> for C=C aromatic and peaks around 1237.17 to 1035.44 cm<sup>-1</sup> for C-O stretch of alcohols, carboxylic acid, ethers, and esters. These peaks disappeared in the spectrum of NC. The FTIR spectrum of NC did not show many peaks possibly due to its black body property. It shows bands similar to those observed Dipterocarpus alatus fruits (DF) activated carbon at 1087 and 1175 assigned to C-O stretching in carboxyl acids, alcohols, phenols and esters and 1554 cm<sup>-1</sup> which was assigned to C=C peaks in aromatic rings.<sup>24</sup> The FTIR spectrum of the POM-IL@NC material, in addition to the bands present in the NC, showed bands at 755, 798, 881, 955, 1042 and 1092 cm<sup>-1</sup> attributed to the POM framework and bands at 2855, 2927, 2931 cm<sup>-1</sup> attributed to the  $\{[CH_3(CH_2)_6]_4N\}$  cations. These demonstrate that the material is a hybrid of the different unit as proposed.

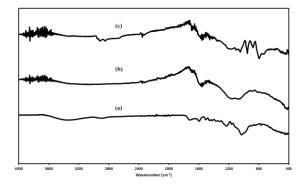
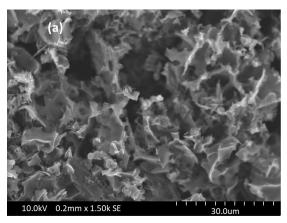


Figure 1: FTIR spectra of (a) Raw Coconut shell (b) NC and (c) POM-IL@NC.

The surface morphology of NC and POM-IL@NC were further examined on a Scanning Electron Microscope. Figure 2 (a) and (b) are micrographs of the NC and POM-IL@NC materials respectively. The figures show particles of irregular shapes and sizes. Also, the material in Figure 2(b) exhibited particles that are more compacted than those in Figure 2(a) indicating that the POM-IL packed into the pores of the NC making the particles more compacted.



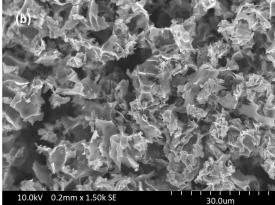
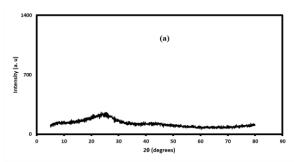


Figure 2: SEM images of (a) NC and (b) POM-IL@NC

XRD analysis of NC and POM-IL@NC materials gave the patterns in Figure 3. Figure 3(a) shows a broad peak around 25.5° for carbon<sup>23</sup> whereas Figure 3 (b) shows peaks at 5.5, 6.17, 7.82, 8.65° which were assigned to the POM framework in addition to peaks for carbon. This correspond to those reported by Hosseinyzade et al.<sup>25</sup> and further proves that the POM-IL@NC is a hybrid material of the POM, IL and NC.



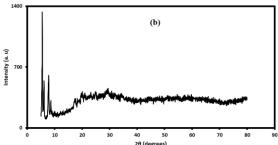


Figure 3: XRD patterns of (a) NC and (b) POM-IL@NC

The porosity properties of the materials were then studied using  $N_2$  adsorption—desorption isotherm and the results are summarized in Table 2. Generally, the materials can be termed nanoporous (pore diameter < 100 nm) and can be specifically termed as mesoporous (pores with diameter of 2 to 50 nm). <sup>26</sup> Although, the BET Surface area of the materials were low, the properties of the POM-IL@NC material was generally less than those of the NC material. This shows that the POM-IL entered inside the pores

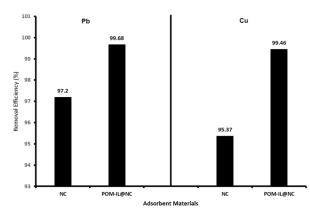
of the NC thus reducing the pore radius and volume.

Sample	BET Surface Area (m²/g)	Pore diameter (nm)	Pore volume (cc/g)
NC	20.005	3.348	0.172
POM-IL@NC	12.470	2.752	0.033

## 3.3 Heavy Metals (Cu and Pb) Adsorption Properties

The general aim of this research was to apply the prepared POM-IL@NC material for sustainable and efficient water purification. In a bid to achieve this, the materials (NC and POM-IL@NC) were tested for their removal efficiency of copper and lead from simulated polluted water. The polluted water had 45, 000 times the WHO permissible limit of these metals (Pb = 2.2 mM, Cu = 1.4 M). The WHO permissible limit of the metals in drinking water are Pb (0.01 mg/L or 0.048  $\mu$ M) and Cu (2 mg/L or 32  $\mu$ M).<sup>22</sup> The results of the heavy metals adsorption study are shown in Figure 4. From the figure, it can be observed that both materials reduced the metals (Pb and Cu) levels to acceptable percentages (over 95%).22 These results are in line with previous reports that had linked the ability of materials like raw coconut shell to absorb lead or other metals from waste water to the nature of the surface area and pores.27-29 It is noteworthy however, that the POM-IL@NC material performed better than the NC material for both lead and copper. This could be due to the presence of lacunary site in the POM, which provides additional avenue for the absorption of metals. Also, it could be noticed that for both materials, the removal efficiency of lead was better than that of copper. This has been attributed to the ionic size of the ions. Both are in the +2 state and have the ionic radius, Cu<sup>2+</sup> (0.73

Å) and Pb<sup>2+</sup> (1.19 Å). So, the bigger lead is removed more than the smaller copper.<sup>30</sup>

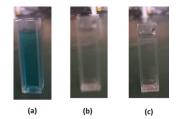


**Figure 4:** Heavy metals removal properties of NC and POM-IL@NC materials. Pollutant concentration: Pb = 2.2 mM, Cu = 1.4 M; WHO limit: Pb = 0.01 mg/L  $(0.048 \ \mu\text{M})$ , Cu = 2 mg/L  $(32 \ \mu\text{M})^{22}$ 

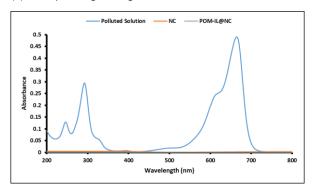
## 3.4 Methylene Blue Adsorbent properties

In this study, methylene blue was used as model for organic pollutants. Aqueous solution of the pollutant (32 mM) was also passed through adsorbent columns of NC and POM-IL@NC materials and the adsorption properties of methylene blue were studied by UV-Visible spectroscopy. Figure 5 is a picture of the polluted water sample and the water after passing through the adsorbents whereas Figure 6 is the UV-Vis spectra of the samples. A pictorial change in colour from blue to colourless is observed in Figure 5 as the polluted water is passed through the filter columns indicating adsorption of the organic pollutant by the adsorbent materials. Also, Figure 6 shows that the absorption bands for methylene blue at 250, 300 and 650 nm all disappeared as the polluted water was passed through the adsorbent materials (NC and POM-IL@NC). These results are in agreement with the reports of Mohan and Sheena who recorded that activated carbon has

more ability to reduced methylene blue than the raw coconut shell.<sup>27</sup> It shows that in addition to removing copper and lead, our POM-IL@NC material is also a good removal of methylene blue from polluted water.



**Figure 5:** Picture of water (a) contaminated with methylene blue (b) after passing through NC filter and (c) after passing through POM-IL@NC filter.



**Figure 6:** Removal of Methylene blue pollutant from polluted water by filtration through NC and POM-IL@NC adsorbent materials. Conditions: [MB]=32 mM; filtration volume=10 mL

## 3.5 Antimicrobial property of Adsorbent Materials

In a bid to ascertain whether the POM-IL@NC could also be used to remove microbial contaminants from contaminated water as the ionic liquid (THPA cation) is known to be antimicrobial and Herman et al had previous report POM-SILP materials to show antimicrobial properties.<sup>17</sup> They were tested for antimicrobial activity and the results are given in Table 3.

Table 3: Zone of Inhibition of Adsorbent materials (NC and POM-IL@NC) on Microorganisms

Concentration (µg/mL)	Zone of inhibition of growth (mm)			
	NC		POM-IL@NC	
	E. coli	S. aureus	E. coli	S. aureus
500	2.0±0.01	1.6±0.02	19.2±0.4	17.6±0.2
250	1.2±0.02	0.8±0.01	17.4±0.6	14.5±0.3
125	0.9±0.13	0.2±0.01	13.2±0.1	11.5±0.42
62.5	-	-	8.7±0.3	7.4±0.1
Amoxicillin \250 μg/mL (+ control)	24±0.82	22±0.51	24±0.82	22±0.51

Values are mean ± standard deviation.

The table shows that POM-IL@NC exhibits significant improvement in antimicrobial activity than NC against the two organisms tested as seen from the zone of inhibition of growth. The POM-IL@NC material inhibited the growth of

Escherichia coli at all the concentrations with highest zone of 19.2±0.4 mm observed at 500 μg/mL whereas the lowest zone of inhibition of 8.2±0.3 mm at 62.5 μg/mL. Similar trend was observed for *Staphylococcus aureus*, although

with a lower activity  $(17.6\pm0.2 \text{ to } 7.4\pm0.1 \text{ mm})$ . No activity was observed for the NC at 62.5 mg/mL. The results also show that the activity demonstrated by the materials was concentration dependent; i.e., as the concentration decreases the activity decreases. The activity demonstrated by the POM-IL@NC material was comparable to that of the standard antibiotic (Amoxicillin). The results also showed the Gram negative (Escherichia coli) organism is more susceptible than the Gram positive (Staphylococcus aureus) organism. This claim is so because at each of the concentrations, the zone of inhibition of growth of the Gram negative is higher than that of the Gram positive organism. This is in line with previous reports.30

## 4. Conclusion

The immobilization of the Polyoxometalate-Ionic Liquid,  $\{[CH_3(CH_2)_6]_4N\}_7[\alpha-PW_{11}O_{39}]$  on a coconut shell-based nanoporous carbon to form a hybrid adsorbent material,  $\{[CH_3(CH_2)_6]_4N\}_7[\alpha-PW_{11}O_{39}]$ @NC was successfully done. The material showed an improved efficiency than the pristine nanoporous carbon (NC) material in the removal of heavy metals (Pb and Cu), methylene blue and microbial contaminants from polluted water. This has great implication in the provision of a range of multi-contaminants removal materials for meeting the need of provision of clean water to the teeming populace in Africa.

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#### **Conflict of Interest**

The authors declare that there is no conflict of interest.

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