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Application of Synthesized Metal Organic Frameworks of Silver Benzene-1, 4-Dicarboxylate on Crude Oil Spill

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Abstract: This research synthesized, characterized, and applied the metal organic framework of silver benzene 1, 4-dicaboxylate for crude oil adsorption on water, which was simulated. Silver-metal organic frameworks (Ag-MOFs) were synthesized by reacting hydrated silver nitrate, $AgNO_3.6H_2O$, with 1, 4-benzenedicarboxylic acid (BDA) in N, N-dimethylformamide as a solvent. Solvothermal method was utilized for the process. The MOFs obtained were studied by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy dispersive x-ray spectroscopy (EDX). The adsorbent surface had large pores, and SEM micrographs revealed a mixture of particles with tetrahedral, flat, or plate-like shapes. Ag, C, and O, had an elemental composition of 50.9%, 29.6%, and 19.5%, according to EDX respectively. An adsorption research was done using 1 mL, 2 mL, 3 mL, and 4 mL of crude oil at adsorbent (Ag-MOF) doses of 0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1 g for the adsorption of the crude oil from 50 mL of distilled water. The data obtained revealed that 0.2 g adsorbed 0.7 mL, 0.4 g adsorbed 0.8 mL, 0.6 g adsorbed 0.9 mL, and 0.8 g and 1.0 g of Ag-MOF adsorbed 1 mL. 1g of Ag-MOF applied to different volumes of the crude oil, showed an adsorption of 100% of the 2 mL, 2.9 mL (96.67%) of 3 mL, and 3.7 mL (92.5%) of 4 mL. The result of the effect of pH, showed an excellent adsorption at the pH used. Composites with clay and charcoal were used for the adsorption of the crude oil. The composite with clay was good, but not as good as charcoal for adsorption of crude oil. These results imply that an optimized quantity of Ag-MOF can be utilized in crude oil spill remediation in our environment.

1. Introduction

Metal Organic Frameworks (MOFs) are crystalline complexes made up of organic multidentate linkers and metal ions. Organic magnets made of crystalline coordination polymers appear to be a potential alternative (Lopez, 2018). By turning their organic ligands into metal centers and inserting functional inorganic molecules in porous MOFs, these materials exhibit magnetic characteristics that may be tailored to the molecular scale (Zhou and Kitagawa, 2014). Hosting guest molecules in MOFs has been discovered to dramatically increase electrical conductivity (Talin, 2014). Degayner, Jeon, Sun, Dinca, and Harris discussed the linking of redox-active ligands (2017). According to Darago, Aubre, Yu, Gonzalez, and Long, pyrrazine can cause long-range charge transfer, intense magnetic conversion, high conductivities, and magnetic arrangement (2015). According to Dong (2018) conjugated MOFs with multilayer formed with electrical conductivities of 105 Sm^{-1} have been created. Kambe, (2013) developed MOFs by linking N, O, S of ligands with transition metal ions, which showed π-d conjugation in 2-dimentional planes. Many metal ions proffer diverse coordination and geometries, (Lingjuan, 2012).

MOFs are the most current compounds that may be used as alternative adsorbents in a variety of industrial and environmental studies, according to Ferey, Draznieks, Serre, and Millange (2005). MOFs may be used to remove pollutants from gas and separate it, (Mueller,2006), and gas storage (Gallo and Glossman 2007). Both Wu, Hu, Zhang, Lin (2005) and Chen, Yang, Zapata, Lin, Qian, and Lobkovsky (2005) reported on drug delivery and catalysis applications of MOFs. According to Rowsell, Spencer, Eckert, Howard, and Yaghi (2005), MOFs contain a number of characteristics that enable them to be precisely prepared, rigid, and flexible. Philip, Christopher, Erling, Alexander, Michael, Jürgen, Bernhard, Warnan, and Fischer (2021) described how they employed a molecular catalyst contained in a metal-organic framework (MOF) to improve the performance of a molecular catalyst. YameiSun, Xue, Liu, Jia, Li, Liu, Lin, Liu, Liu, Li and Su., (2021) prepared NiRu0.13-BDC, which they said exhibited noteworthy hydrogen emission activity at all pH. Hydrogen is used as a fuel and its storing in MOF materials was presented by Yaghi, Eubank, Forster, (2009). Brandon, Parker, Paley, Gonzalez, Biggins, Oktawiec, and Long**,** (2019), found that individually, Co^{2+}(m-dodbc) and Ni^{2+}(m-bobdc) were useful to isolate 1-butene from 2-butene isomers.

In 2020, examined papers on MOFs by Giliopoulos, Zamboulis, Giannakoudakis, Bikiaris, and Triantafyllidis offered a comprehensive overview of all MOF nanocomposites' applications in biomedical devices. Andriotou, Diamantis, Zacharia, Itskos, Panagiotou, Tasiopoulos, and Lazarides (2020) showed that lanthanide MOF materials they developed were effective for temperature sensing. 2D metal-organic framework created by chemical vapour accretion was studied by James Claire, Solomos, Kim, Wang, Siegler, Crommie, and Kempa., (2020). They concluded that the devices might be integrated into detectors and actuators based on their findings. Cameron, Carpenter-Warren, Alexandra, and Slawin (2021) used Methanol/water ($MeOH/H_2O$) reagent to make three coordination polymers with varied dimensionalities, which were analyzed using single-crystal X-ray diffraction. Posidona oceanica (L.) was employed as a biosorbent for crude oil spill cleaning in saltwater by Senda and Amjad (2019). Oil is a key source of energy in contemporary industries, as raw materials for chemicals and synthetic polymers, according to Senda and Amiad (2019). Mircea and Long (2008) utilized MOFs in gas purifications of methane, which they said was fast. Andrea, Sudik, Adrien, Wong-Foy, Keeffe, and Yaghi, (2006) applied MOFs for the detection of hydrophilic gases like ethanol and methanol.

Silver is a group 11 element with atomic number 47, mass number 108, three major oxidation states (0, +1, and +2), and two naturally occurring isotopes, (Egorova and Revina,2000). The manufacture and uses of silver nanoparticles were reviewed by Kholoud, Abou, Ala, Abdulrhman, and Reda. (2010). They claimed that noble metal nanoparticles, like silver, had noticeable physical, chemical, and biological characteristics from their counterparts.

Metal-organic frameworks, according to Adedibu, Tella, and Isaac (2012), are a kind of porous polymeric compounds comprising metal ions connected by organic bridging ligands of metal ions and the organic component, and they perform best at extremely low temperatures. Hussein, Jin, Ha-Ming and Wang (2013) investigated the adsorption of CO_2 and CH_4 on amino-functionalized Zr-MOF nanoparticle.

Hiroyasu, Kyle, Michael, Yaghi (2013) investigated metal-organic framework chemistry and applications. According to their review, reticular synthesis establishes connections, resulting in crystalline metal-organic frameworks (MOFs).

According to JoséMara, Susana, Cherif, Youssef, and Alejandro (2016), their findings showed that using MOF-5 has a lot of potential for use in environmental protection, particularly the removal of lead present in tap water and industrial waste.

Xili Cui, Niu, Shan, Yang, Hu, Wang, Lan, Li, Wojtas, Ma and Xing. (2020), employed ZU-61 and it was used to separate isomers of xylene.,_Antypov, Shkurenko, Bhatt, Belmabkhout, Adil, Cadiau, Suyetin, Eddaoudi, Rosseinsky and Matthew (2020), demonstrated that the progressive activity of two framework-forming components, numerous atomic anions and pyrazines, influence both diffusion and separation. MOFs are most favourable in storing gases, James Mitchell crow, (2012). Cu-MOF was created by Orodu and Dikio in 2021 and utilized for crude oil adsorption. It was established that Cu-MOFs were effective adsorbents. This research aim to synthesis, characterize and apply metal organic framework of silver for crude oil adsorption on water in the Niger Delta Region of Nigeria. The process was simulated in the laboratory.

2. Materials and Methods

2.1 Materials

Reagent used are; N,N-Dimethylformamide [HCON(CH3)2 DMF,99.8%; Silver nitrate, $AgNO_3.6H_2O$,98%,Sigma-Aldrich],Methanol,CH_3OH, 99.9%; Sigma- Aldrich, Magnetic stirrer, Beaker (250 mL), Electronic Heating mantle, Measuring cylinder, Filter paper, Reflux kit, Electronic weighing balance, Centrifuge machine, pipettes, thermometer, separating funnel, shaker. Crude oil was collected from the Etelebou well 11T, Gbarain in Bayelsa State, and clay and charcoal were procured from Warri in Delta State. Nigeria.

2.2 Methods

2.2.1 Synthesis Procedure

Silver metal organic framework (Ag-MOF): Silver MOFs were synthesized by solvothermal method. 50 mL DMF was transferred into a round bottom flask, with 1.6897 g $AgNO_3$ and 1.6613 g benzene 1,4-carboxylic acid and mildly stirred. The solution was transferred into the 250 mL round bottom flask, to reflux for 4 hours at 120^0C while stirring, a silver coloured crystal was formed at 120^0C in about 1 hour 29 minutes. The solution obtained was centrifuged and a solid Ag-BDA was left behind; after decanting. Several methanol washes were performed before the crystals were produced and oven-dried for 30 minutes at 40 ℃.

2.2.2 Characterization.

A Fourier transform infrared (FTIR) spectrometer (Perkin Elmer Instruments, USA) was used to characterize the as-synthesised Ag-MOF for any existing functional groups. The scanning range was 400–4000 cm^{-1}. An energy dispersive x-ray (EDX) detector attached to a scanning electron microscope (SEM) was used to analyze the surface morphology.

2.2.3 Adsorption Study.

Adsorption studies was carried out using the as- synthesized Ag-MOF. The adsorbate was crude oil. For the adsorbent dose investigation, the masses of 0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1.0 g of Ag-MOF were weighed and placed in various conical flasks with 50 mL distilled water. Afterwards, 1 mL of crude oil was added to every sample that had been weighed. After that, the mixture was shaken for 30 minutes. Volume concentration variation was used to determine the adsorbent capacity for crude oil in water with respect to a constant mass of adsorbent. This was done by altering the amount of crude oil utilized, using 1.0, 2.0, 3.0, and 4.0 mL, and utilizing 1 g of Ag-MOF. The composite was prepared by weighing 1:1 ratio of both MOF/clay and MOF/charcoal. MOF and charcoal and MOF were weighed in a 1:1 ratio to create the composite. For the batch adsorptions, 1 g of MOF, clay, and charcoal were utilized in total. The study used pH values of 4.4, 6.85, and 9.0 to examine the impact of pH on adsorption.

3. Result and Discussion

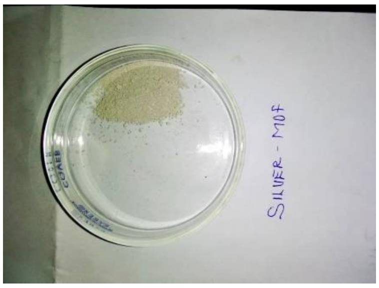


Plate 1. Oven dried silver - MOF sample obtained from synthesis.

Figure 1 below, gives us an idea of how the coordinated-polymer chains looks like on production within the molecule that was obtained during the synthesis.

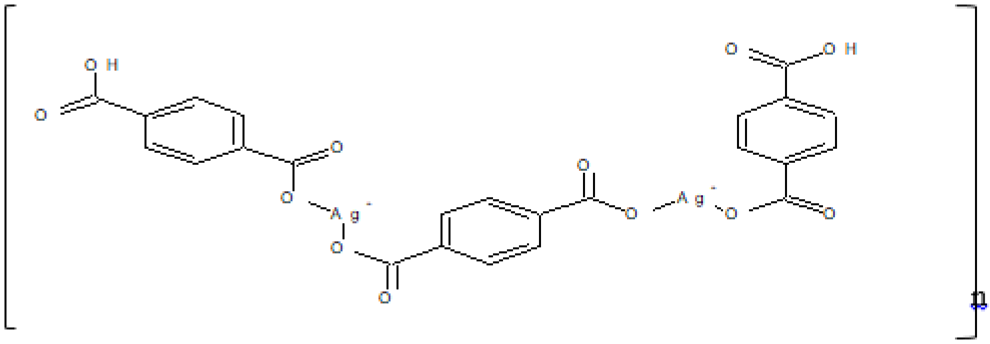


Figure 1: Ag-MOF conceivable bonding and repeating units.

3.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis.

The Fourier transform infrared spectrum of BDA is presented in figure 2. Fourier transform infrared studies provide information in respect of the functional groups and various metal ions present in the as-synthesized material. The expected functional groups are C=O, C-H, C=C, C-C, C-O, and O-H, and their assignments are presented in table 1.

The reaction of the metal with BDA is expected to give a similar spectrum to the functional groups present in the BDA.

An absorbance vs wavenumber plot of the Ag-MOF values in Figure 2's FTIR spectrum is shown (cm^{-1}). A ring in-plane C-H stretch at the 3091 cm^{-1} wavenumber location reveals the presence of alkanes with robust bond strengths. At the 1514 cm^{-1} wavenumber position, a bending is present which has medium to strong bond strength. At 1356 cm^{-1} wavenumber position, C-O stretch is present which has a weak bonding strength. At 1086 cm^{-1} wavenumber position, a ring in- and out-of- plane bending is present which has a variable strength. At the 736 cm^{-1} wavenumber C-H bending aliphatic is present which has a weak strength. At the 528 cm^{-1} wavenumber a C-H bending in C=C-H is present which has a medium to strong strength. Figure 3, below is the original ftir spectrum of the BDA used for the synthesis. When compared with the wavenumber gotten in figure 2 as shown in table 1, it showed variations in the wavenumbers confirming that there a reaction and a new product formed.

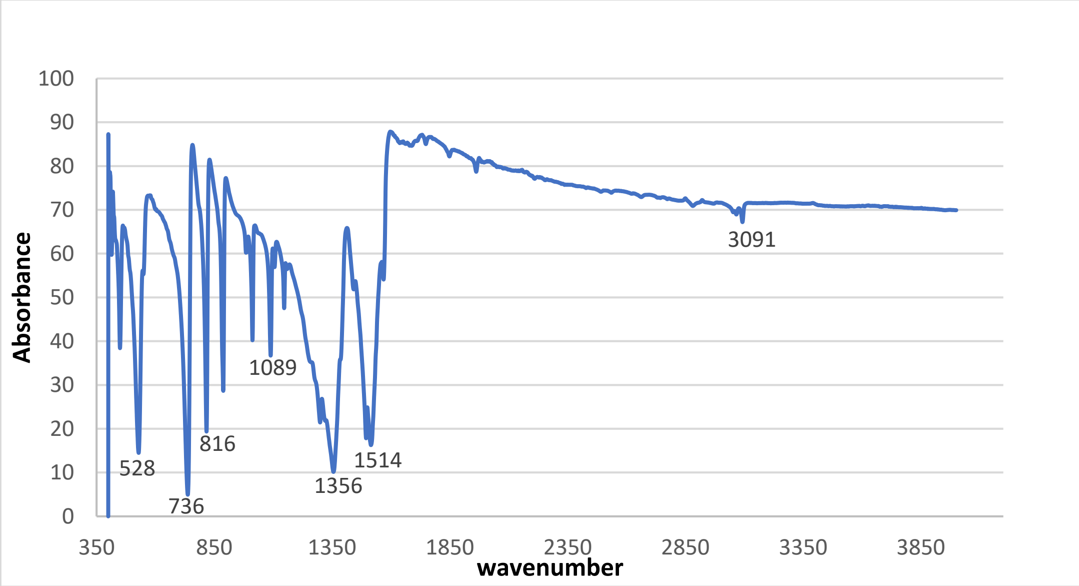


Figure 2: FTIR spectra of as-synthesized of Ag-MOF.

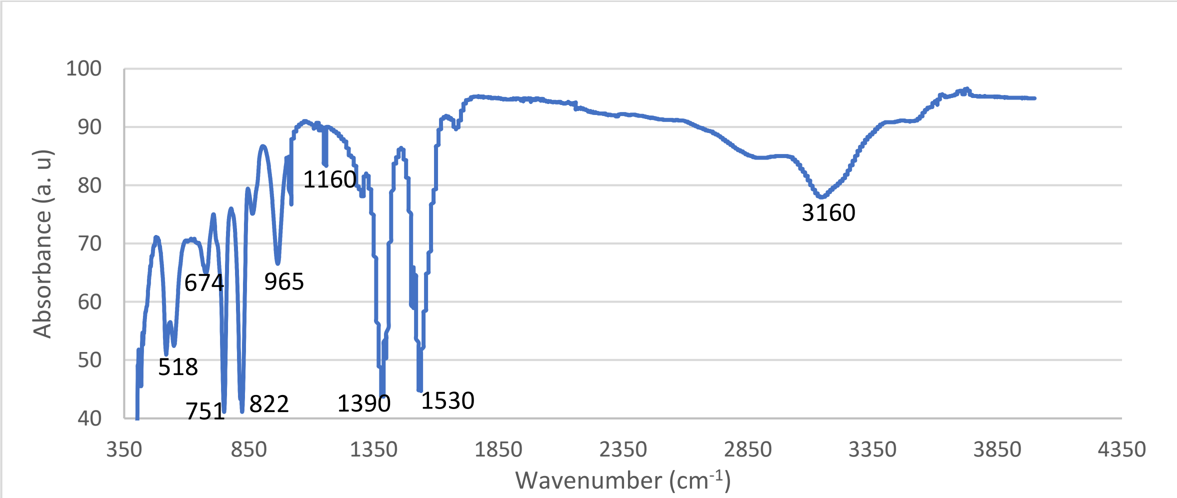


Figure 3: FTIR spectrum for bezene-1,4-dicarboxylic acid.

Table 1: Comparison of FTIR wavenumbers (cm-1) of Ag-MOF and BDA after synthesis.

Sample	**Wave number (cm^{-1})**									
BDA	3160	1530	1390	1160	1020	965	822	751	674	518
Ag-MOF	3091	1514	1356	1145	1089	1011	888	816	736	528

Table 1 shows the wavenumbers for the peaks that appeared for the metal organic framework of silver MOF and 1,4-benzene- dicarboxylic acid. The observed change in wavenumbers from the FTIR spectrum has shown that, there was formation of the Ag-MOF. The absorption band of silver and 1,4-benzenedimethylcarboxylic acid lies in the region of 528 and 518 cm^{-1} in the spectra. The assigned aromatic C-H stretching vibration originates from 1,4-benzenedicarboxylic acid. The weak and strong bands at 736 and 748 cm^{-1} separately are assigned residues of C=C stretching vibration beginning from the C=C bonds of the 1, 4 benzenedicarboxylic acid and C-C skeletal vibration of the ring.

3.2 Scanning Electron Microscopic (Sem) Spectrum.

Using a scanning electron microscope, the surface morphology of the as- synthesized metal organic framework materials was investigated (SEM). Figures 4(A) and 4 (B) show the SEM of the as-synthesised material at two magnifications.

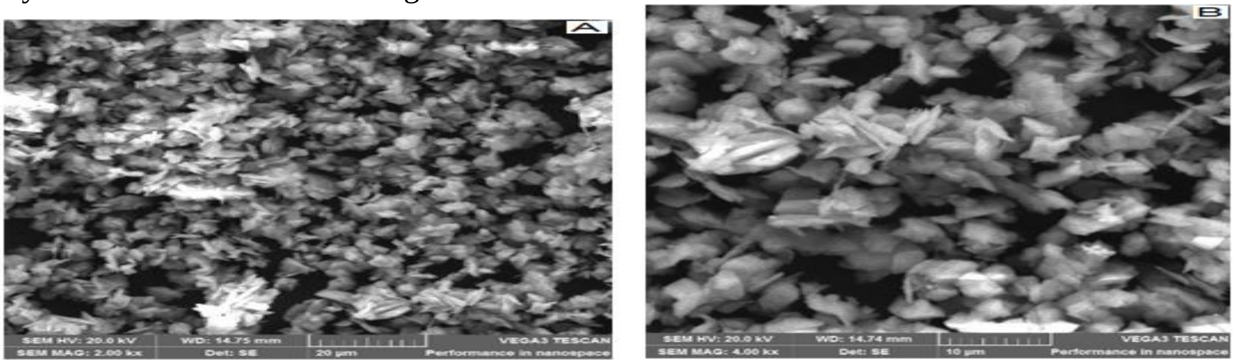


Figure 4(A): SEM image of Ag-MOF (x20 µm). (B): SEM image of Ag-MOF (x10 µm).

The SEM images on all the magnifications show an adsorbent surface with spacious pores and an assemblage of particles having tetrahedral, flat or plate-like structures.

The porous surface morphology revealed by SEM image may be responsible for high adsorption of the crude oil.by the Ag-MOF adsorbent.

3.3 Energy Dispersive X-Ray. (Edx) Spectroscopy

The metal components in the as-produced material are disclosed by EDXS, a powerful characterization technique. This is a perfect indicator of the substance's efficient manufacture and, unmistakably, its purity. In the silver MOF EDXS, just the elements oxygen, carbon, and silver are visible (figure 5). Silver's elemental makeup is 50.9 percent silver, 29.6 percent carbon, and 19.5 percent oxygen. At 3.0 keV, the Ag peak occurred. It is isotope-free and pure. The carbon and oxygen are evidences of the metal - CO linkages in the as-synthesized materials.

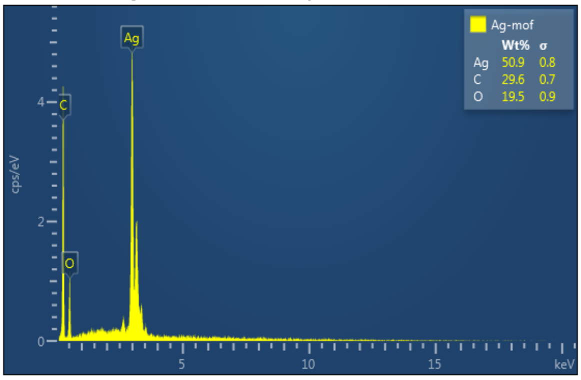


Figure 5: Benzene-1,4-dicarboxylic acid (BDA) (Terephthalic Acid) Linker of Silver Metal Organic Framework (Ag-MOF) using Energy Dispersive X-ray Spectroscopy (EDX).

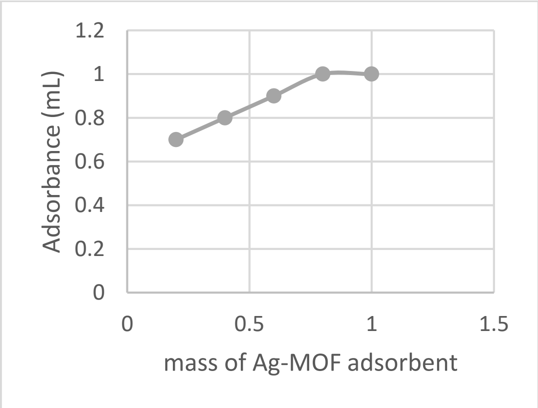
3.4 Adsorption Results

Table 2 and Figure 6 illustrate the impact of adsorbent dosage on the adsorption of crude oil by Ag-MOF.

The result shows that the adsorption of crude oil by Ag-MOF increased with an increase in the dosage of samples until an equilibrium was established at 0.8 g for gold and 1.0 g for silver. The percentage adsorption for silver MOF ranged from 70–100%. The high percent adsorption indicates the as-synthesized Ag-MOF could pass for a good adsorbent for crude oil.

Table 2: Effect of adsorbent dose on crude oil adsorption by Ag-MOF

Mass of Ag-MOF in gram(g)	**Volume of crude oil Adsorbed (mL)**
0.2	0.7
0.4	0.8
0.6	0.9
0.8	1.0
1.0	1.0



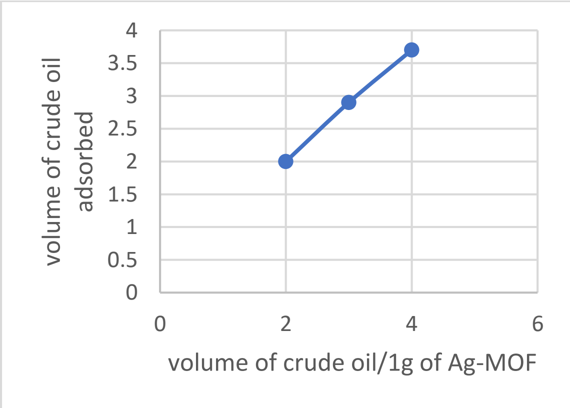


Figure 6: Effect of adsorbent dosage on the Adsorption of crude oil by Ag-MOF. And Figure 7: Volume of Crude oil in (mL)/1g of Ag-MOF respectively given above.

Based on the outcome of the effect of dosage, a variation of volume concentration was performed in order to know the extent to which the crude oil can be adsorbed by a constant mass of Ag-MOF. The volume of the crude oil was increased to 2.0, 3.0, and 4.0 mL, with Ag-MOF remaining constant at 1 gram. The result obtained is given in Table 3 and Figure 7.

Table 3: Volume of Crude oil in (mL)/1g of Ag-MOF.

Volume of Crude oil in (mL)/1g of Ag-MOF	**Volume of crude oil Adsorbed (mL)**
2.0	2.0
3.0	2.9
4.0	3.7

The result from the variation of adsorbate volume to a constant adsorbent mass shows an inclining linear correlation which indicates that adsorption at constant mass of adsorbent increased with increasing adsorbate volume. The capacity for adsorption of crude oil by Ag-MOF increased with increase in volume at constant mass. From the EDX result, the percentage of the silver metal (50.9%) may have increased the amount of charges on the surface of the Ag-MOF, which get bettered its adsorptive property.

Table 4: Result of crude oil adsorption by composite of Ag-MOF/clay

Composite of Ag-MOF/clay in gram(g)	volume of crude oil Adsorbed (mL)
0.2 g	0.9
0.6 g	0.9
0.8 g	1.0

Adsorption with composites: The composites of the Ag-MOF/clay and Ag-MOF/charcoal were also applied for crude oil adsorption. The result for Ag-MOF/clay adsorption is presented in Table 4 and Figure 7. The result of the adsorption with Ag-MOF/charcoal is presented in Table 5 and Figure 8.

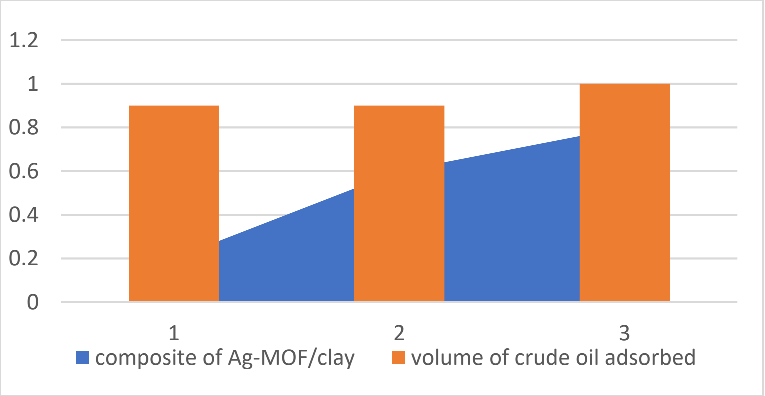


Figure 7: Combination chart for the Ag-MOF/clay composite (blue) and the volume of crude oil adsorbed (orange).

The results indicated that the adsorptive performance of Ag-MOF/clay and Ag-MOF/charcoal composites was very effective, as the quantity of crude oil (1 mL) was completely taken up with increasing composite dosage: the exception being that it was better with the Ag-MOF/charcoal than the Ag-MOF/clay composite. At 90-100% adsorption by the Ag-MOF/clay with a varying mass of the adsorbent, the composite is an effective adsorbent for crude oil. The adsorption result for all is 100%. The charcoal composite had greater influence in the process because of better physical properties such as, large surface area, pores of different sizes which enhances the adsorption.

Table 5: Result of crude oil adsorption by composite of Ag-MOF/charcoal

Composite of Ag-MOF/charcoal in gram(g)	volume of crude oil Adsorbed (mL)
0.2g	1.0
0.6g	1.0
0.8g	1.0

Figure 8, below is a combo chart used to describe the efficacy of the adsorption of crude oil by the composite of the silver MOF and charcoal. The blue colour represent the masses of adsorbent used and the orange colour represent the amount of crude oil adsorbed. The proved that composite of silver MOF/charcoal is an outstanding adsorbent.

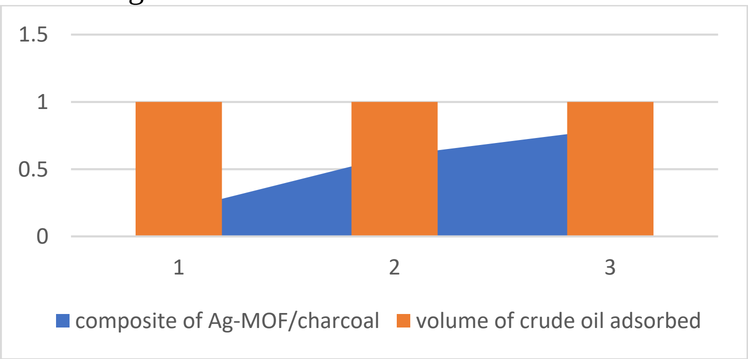


Figure 8: Combined chart of efficiency of the different masses of the composite (Ag-MOF/charcoal) and volume of oil adsorbed

pH effect on the adsorbent (Ag-MOF): The pH effect is given in table 6 below. The pH levels used were 4.4, 6.85, and 9.0.

The effect of pH results for Ag-MOF on its adsorption capacity is presented in Figure 9. For each of the pH used, Ag-MOF showed a very good adsorption by adsorbing 100% of the crude oil. In other words, the pH of the water on which the crude oil was floating did not affect the uptake of the oil by the Ag-MOF adsorbent.

Table 6: Volume of Crude oil 1 mL/1 g of Ag-MOF/pH

Volume of Crude oil 1mL/1g of Ag-MOF/pH	Volume of crude oil Adsorbed (mL)
pH 4.4	1.0
pH 6.85	1.0
pH 9.0	1.0

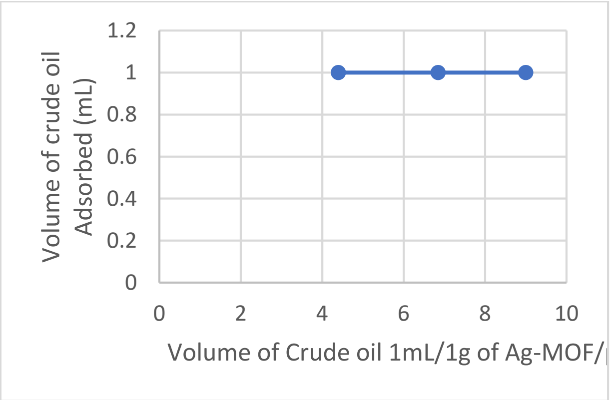


Figure 9: Result of pH effect on the adsorption property of Ag-MOF.

Adsorption Equilibrium and Isotherm Study: The adsorption of crude oil by Ag-MOF was subjected to equilibrium study and some isotherm models to ascertain the prevailing type of adsorption. The results are shown in figures 10 and 11. The result in Figure 10 shows that quantity of oil adsorbed increased with increase in initial volume of crude oil, while percent adsorption increased with initial volume of oil used to a maximum. On isotherm study, the Freundlich and the Redlich-Peterson models were the closest and best correlated with the experimental data, thus it may be suggested that physisorption may have been the prevailing process of the adsorption of the crude oil by Ag-MOF.

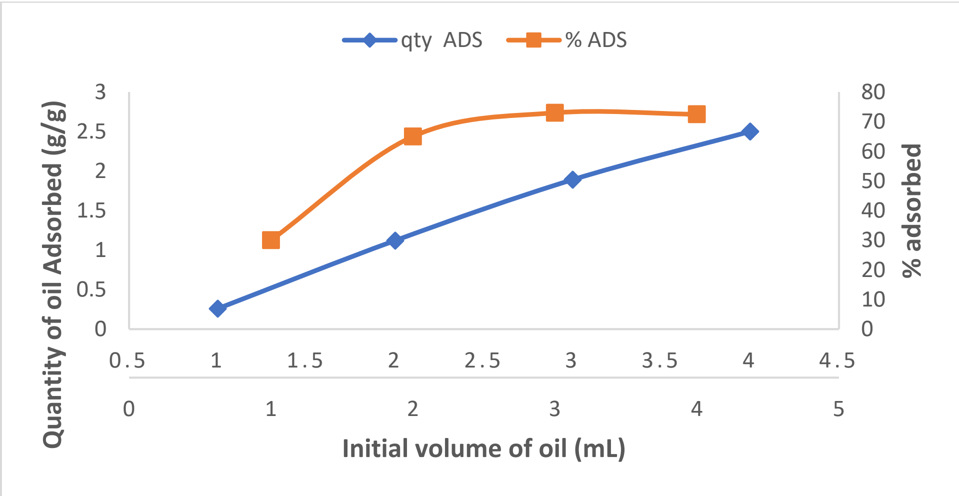


Figure 10: Effect of initial volume of crude oil on the quantity of oil adsorbed by Ag-MOF

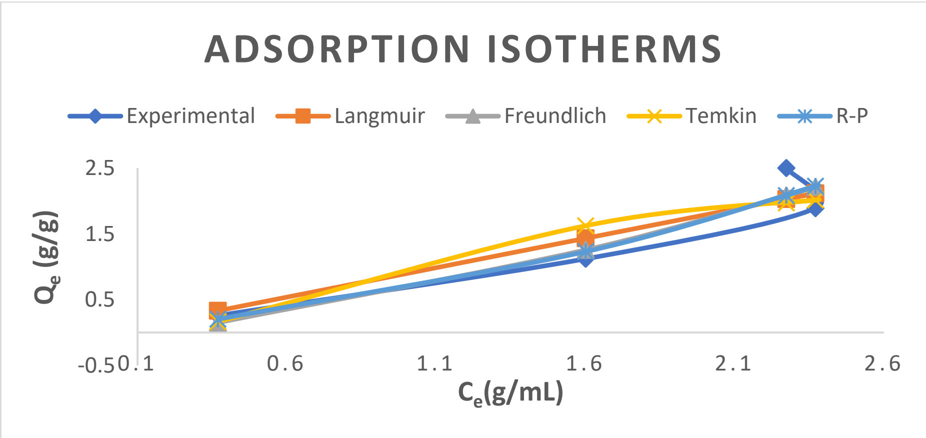


Figure 11: Isotherm plots for the adsorption of crude oil by Ag-MOF

4. Conclusion

Ag-MOF was successfully synthesized by a solvothermal protocol. FTIR, SEM, and EDX were used to characterize the as- synthesized Ag-MOF. Characterization results revealed chemical functional groups and porous morphology that could enhance adsorption of crude oil by Ag-MOF. Sorption analysis showed that the silver MOF could absorbed 100% volume of the crude oil for all measurements except for the 4 mL, where about 92.5% was adsorbed. Forming a composite of Ag-MOF and charcoal has been shown to be innovative and cost effective for adsorption. The composite with clay was good, but not as good as charcoal for adsorption of crude oil. Quantity of oil adsorbed increased with increase in initial volume of crude oil, while percent adsorption increased with initial volume of oil used to a maximum. Isotherm study showed that physisorption may have been the prevailing process of the adsorption. An optimized quantity of Ag-MOF can be utilized in crude oil spill remediation in our environment.

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