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# *PREPARATION, AND UTILIZATION OF CHROMIUM METAL ORGANIC FRAMEWORK FOR CRUDE OIL REMEDIATION*

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***Keywords:*** Cr-MOF, Adsorption, Charcoal, Composite, Remediation

***Abstract:*** Chromium-metal organic framework (Cr-MOF) was synthesized by solvothermal method. It was characterized using Fourier Transform Infrared (FTIR) spectrometer, Scanning Electron Microscope and Energy Dispersive X-ray (EDX) Spectroscopy. Composites of Cr-MOF/Clay and Cr-MOF/charcoal were also prepared. The as-synthesized MOF and the composites were all applied for the adsorption of crude oil on water media. Characterization results showed the presence of unsaturated C=C, C=O vibrations as well as metal-oxygen and OH group vibrations which confirmed the formation of the Cr-MOF. EDX spectra also confirmed formation of the MOF with the observed peaks of Cr, C and O. Adsorption results showed the oil in water could be adsorbed by as-synthesized Cr-MOF, though very slight the adsorption of the crude oil increased almost linearly with an increase in adsorbent dose. Adsorption of crude oil by Cr-MOF ranged from 10 - 70% for various doses from 0.2-1.0 g. However, the adsorption of the crude oil was greatly enhanced in the Cr-MOF/charcoal composite, whose sorption ranged from 80-100%. The effect of pH tipped in the acid range and increased with adsorption in the alkaline region for the pHs considered.

## 1. INTRODUCTION

Metal organic frameworks (MOFs), also known as porous co-ordination polymers (PCPs), were discovered about a decade ago as a new class of porous materials which vary in their structures, Claudio, Fabio, Nello, Glovanni and Andrei (2017). MOFs are crystalline materials that are made up of organic-inorganic hybrid compounds whereby coordinated bonds link metal ions and multidentate ligands together. Remya and Kurian (2018). Since 1964, the research field has had lots of interest or attention from a lot of people who specifically focused on investigating every one of the series of Hoffman clathrates and Prussian blue compounds because of what their complexes possessed in terms of properties (irreversible sorption and other wonderful properties), Abdulraheem, Hitler, Saud, Adejoke, Oluwatobi, Amos, (2018).

Claudio et al. (2017) explain that porosity is the main importance of MOFs, which makes the organic-inorganic hybrid compounds more like zeolites. Historically, MOF and its branches might have trailed

into the renowned area of zeolite (coordination chemistry), Abdulraheem, *et al*, (2018). People focused on the research of Hoffman clathrates and Prussian blue until about 1989-1990 when Robson and Hoskins came up with an idealistic aspect of the formation of a crystal-based porous material in which the catalytic, sorption, and ion exchange properties elevate more improved functional groups after synthesis. Through these ideas of Robson and Hoskins, MOF was birthed and this area of research has been improved over time, Abdulraheem *et al.* (2018). There are different methods of synthesizing MOFs, which are; Diffusion, Solvo-thermal or hydrothermal, Mechano-chemical, Microwave heating, Sonochemical, and Spry-drying method.

Almost all of these methods occur in a liquid phase, where a solvent is added to a mixture of salt and ligand. MOFs can be used in the adsorption of transition elements, actinides, etc. Another possible application is in gas purification, Kurian *et al.* (2018).

Chromium (Cr), is a transition element with an atomic number of 24. It is a group 6 element in the periodic table. Cr has the most common oxidation states of +2 and +3, with the electronic structure of [Ar] $3d^5$ $4s^1$ and a relative atomic mass of 52.0. Lee, (2013). The word chromium was derived from the Greek word "chroma", meaning colour, which means chromium compounds are strictly colourful. They are very necessary nutrient and highly toxic metals depending on the valence, and their primary source is the mineral chromite, $FeCr_2O_4$. Zahra, Mohammad, and Hamid (2017). The hydrothermal method was used to synthesize a new metal-organic framework with zinc as the metal ion and benzene-1,3-dicarboxylic acid as the organic linker, which was then used as a selective nano-adsorbent for the extraction and preconcentration of trace amounts of cadmium using a solid-phase extraction method.

Several metal-organic frameworks may be created, according to Furukawa, Ko, Go, Aratani, Choi, Choi, Yazaydin, Snurr, O'Keeffe, Kim, and Yaghi (2010), due to the ability of transition and lanthanide metal ions with a broad variety of coordination geometries and organic linkers to join via synthesis. Katalin, Marton, Adel, Belteky, Zoltan, Kukovecz, Sipos, and Palinko (2021) used a mechanochemical approach to create nanocomposites of Nickel-Copper-Tin (dimetallic and trimetallics) using a range of chemical additives. Xiaoli, Rongli, and Feng (2021) developed dinuclear cobalt/nickel metal-organic frameworks, which they described and investigated for magnetic characteristics. The results they presented revealed weak antiferromagnetism in triple and double complexes. Micro-porous materials (i.e. MOFs) that form organic linkers bonded by metal atoms, forming a repeating molecular cage-like structure, are the most suitable for storing gases. Highly porous materials developed as future fuel tanks for hydrogen or methane powered vehicles may be able to store more gas than previously thought, and MOFs have a high capacity for storing gas with a very high surface area of about 14.600$m^2$/g. In their research, Hussein, Okoro, Stephen, Ayika, and Tella (2018) discussed that a submerging characteristic of MOF is found on the surface area, which is much larger than the well-known best activated carbons and zeolites. This explains the amazing high demand for the application of MOFs for a great number of environmental uses; they are used for capturing and separating various unacceptable or even environmentally harmful chemical elements or materials.

According to Esfahaian, Ghasemzadeh, and Razavian, (2019), MOFs for the distribution of drugs have been revised widely, and the novel magnetic framework including $Fe_3O_4$@PAA@ZIF-8 for the delivery of ciprofloxacin (CIP). At the end of the research, they concluded that 93% of CIP was loaded on the synthesis framework and drug distribution was done at pH: 7.4 and pH: 5 within 2 days, resulting in about 73% release of the drug, confirmed by FTIR, SEM, BET, EDX, UV-Vis, and XRD. Ren, Langmi, North, Musyoka, Segakweng, Mathe, and Kang (2014) reviewed that MOFs have allured much interest as porous hydrogen storage materials in the transition from laboratory to commercial application. MOFs are frequently obtained as loose powders with low packing densities and low thermal conductivities, but it is necessary to increase the properties of the powders to

facilitate the transition of the MOF materials, so they can form part of a practical hydrogen storage system.
According to Simagina, Polynski, Vinogradov, and Pidko (2018), MOFs contain one kind of chemical and physical property, but due to the high surface area, biocompatibility, and stability in biological media, MOF materials are the best candidates for the improvement of new dosage forms, especially for drug delivery systems. Chromium is a toxic heavy metal found in the earth's crust, and its most stable oxidation numbers (+3 and +6) are more focused on in their research because +3 (trivalent) chromium has very poor absorption inside of the cell compared to +6 (hexavalent) chromium. It was concluded that chromium causes primary health hazards such as bronchial asthma, lung and nasal ulcers and cancers, skin allergies, and reproductive and developmental problems when it is excessively taken into the body of a living organism. It may cause death because of its carcinogenic nature. Orodu and Dikio (2021) used Cu-MOF for crude oil waste remediation, and it performed admirably in all aspects of the study.Junhua Luo, Hongwu Xu, Yun Liu, Yusheng Zhao, Luke L. Daemen, Craig Brown, Tatiana V. Timofeeva, Shengqian Ma, and Hong-Cai Zhou.(2008),did sorption and diffraction studies on MOFs.

## 2. METHOD AND MATERIAL

### 2.1 MATERIALS

The materials used for process included, thermometer, Magnetic heating mantle, Magnetic stirrers, Reflux kit, Electronic scale, Spatula, Filter paper, measuring cylinder, Separating funnel, Pipette Reciprocating shaker, Beakers and centrifuge. Were gotten from Onitsha market in Anambra, Nigeria.

### 2.2 REAGENTS USED

Metal salt (chromium nitrate)**,** Dimethyl formamide (DMF)**,** methanol**,** Benzene-1, 4-dicarboxylic acid (BDA)**,** from South Africa. Crude oil, from LNG, Bayelsa State. Nigeria.**,** Distilled water. Charcoal and Clay was gotten from Warri, Delta State.

### 2.3 METHOD

Solvothermal method or synthesis is a method in the production of chemical compounds, it has a common feature with that of hydrothermal method. Solvothermal method grants a definite and accurate influence over the size, shape distribution, and crystallinity of metal oxide (nano particles or nanostructure products). These features can be changed by changing certain experimental parameters, which involves reaction temperature, reaction time, solvent type, surfactant type and precursor type. Solvothermal method was used to synthesize chromium metal organic frameworks (Cr-MOFs). 4.0031 g of Cr $(NO_3)_2$ and 1.663 g benzene-1,4- dicarboxylic acid were separately weighed on an electronic balance and delivered into a round bottom flask (reflux condenser). These were dissolved in 50 mL DMF and was mildly stirred. The solution was sealed and refluxed for 5 hours at 105˚C. The resulting green gelatinous substance was then centrifuged and separated for 20 minutes. It was decanted and washed with methanol 4 times. The obtained gelatinous substance was dried at 60˚C for 7 hours and was preserved for further experiments. Below is the experimental set-up fpr the synthesis.

Figure 1. Solvothermal method

## 2.4 CHARACTERIZATION

A Fourier-transform infrared spectroscopy (FTIR) method was used to characterized the Cr-MOF. This was used to identify the functional groups present in the product. Scanning electron microscopy (SEM) was used to study the morphology of the as-synthesized MOFs. Energy Dispersive X-ray (EDX) Spectroscopy which gave the elemental compositions

## 2.5 ADSORPTION PROCEDURE

1.0 g of Cr-MOF was weighed on an electronic scale and transferred into a beaker. 50 mL of distilled water and 1mL of crude oil were added to the MOF, then a reciprocating shaker was used to shake the mixture for 30 minutes and was decanted. 0.2, 0.4, 0.6 and 0.8 g, of MOF were respectively weighed and put into different conical flasks alongside distilled water to the 50 mL mark for adsorbent dosage study. 1 mL of crude oil was then added to it. The mixture was then put in the shaker for 30 minutes. The composite was prepared by weighing 1:1 ratio of both MOF/clay and MOF/charcoal i.e. 0.1g of each to make 0.2 g and other weights. Volume concentration was done by varying the crude oil volume using 1.0, 2.0, 3.0 and 4.0 mL. For the masses of MOF, clay and charcoal, 1.0 g of each was used. Effect of pH on adsorption was determined at pH 4.4, 6.85 and 9.0 for the study. The oil was thereafter separated from the water using a 250 mL separating funnel, and 10 mL pipette was used to obtain the amount of oil that was not adsorbed.

## 3. RESULTS AND DISCUSSION

The results of the characterization of the Cr-MOF are shown in figures 3a,3b,4a and 4b

Figure 2. picture of a synthesized Cr-MOF.

A green crystalline Cr-MOF was obtained at the end of the synthesis, which was used for further experiments.

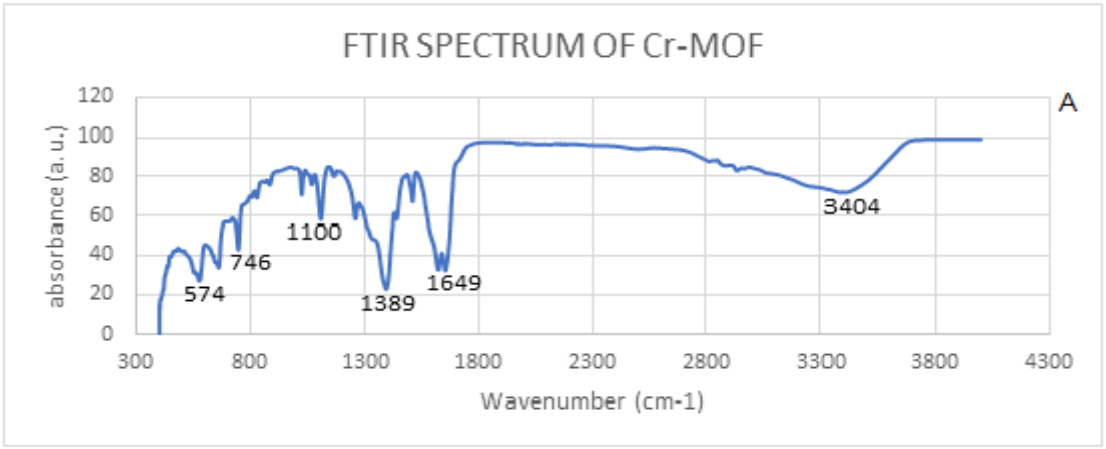



Figure 3a. FTIR spectrum of Cr-MOF

Figure 3a is an FTIR spectrum of Cr-MOF readings in a plot of absorbance against wavenumber. The peak at 574cm$^{-1}$ represents a ring in and out of plane bending, having a C=C-H which shows the bond is strong. This peak could be assigned to the benzene ring of the linker BDA. The peak at 746cm$^{-1}$ represents a C-C skeletal vibration which means the bond is weak, and the peak at 1100cm$^{-1}$ are assigned to a C-O stretch in the metal-bonded carboxyl group, which shows that the bond is variable. The peak at 1389cm$^{-1}$ represents an aliphatic C-H in-plane bending vibrations in the benzene ring of the BDA, which means the bond is variable; the peak at 1649cm$^{-1}$ corresponds to a C=O stretch in which means the bond is variable. The peak at 3404cm$^{-1}$ represents a free O-H stretch which means it is very sharp.

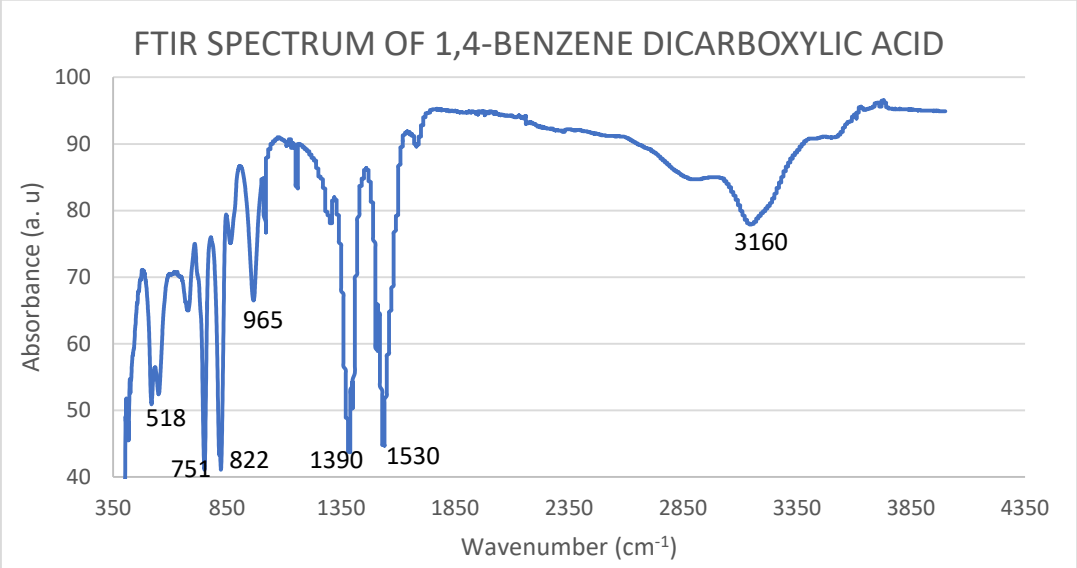



Figure 3b. FTIR Spectrum of 1,4-benzene dicaboxylic acid

Figure 3b is an FTIR spectrum of the Benzene Dicarboxylic Acid (BDA) readings in a plot of absorbance against wavenumber. The peak 518cm$^{-1}$ represent a ring in and out plane bending having C=C-H stretch which shows that the bond at that peak is variable, the peak 751cm$^{-1}$ represent C-C skeletal vibration which indicates that the bond at that peak is weak. The peak 822cm$^{-1}$ represent C-H bending, the peak 965cm$^{-1}$ represent C-O stretch which means that the bond at that peak is variable, the peak 1390cm$^{-1}$ represent C-H bending, aliphatic which shows that the bond at that peak is variable, the peak 1530cm$^{-1}$ represent C=O stretch which indicates that the bond at that peak is variable. The peak 3160cm$^{-1}$ represent a free O-H stretch.

Table 1. vibration and wavelength number.

| 1,4-benzene diacarboxylic acid (BDA)cm$^{-1}$ | Chromium metal organic frameworks (Cr-MOF)cm$^{-1}$ | ASSIGNMENT (V)cm$^{-1}$ |
|---|---|---|
| 518cm$^{-1}$ | 574cm$^{-1}$ | Ring in and out of plane bending (V) |
| 751cm$^{-1}$ | 746cm$^{-1}$ | C-C skeletal vibration |
| 822cm$^{-1}$ | 1100cm$^{-1}$ | Metal oxygen bond formation |
| 965cm$^{-1}$ | _ | C-O stretch (V) |
| 1390cm$^{-1}$ | 1389cm$^{-1}$ | C-H bending (V) |
| 1530cm$^{-1}$ | 1649cm$^{-1}$ | C=O stretch (V) |

| | | |
|---|---|---|
| 3160cm$^{-1}$ | 3404cm$^{-1}$ | O-H stretch (Sh) |

Comparing the two bonds, a new wavenumber is seen in the Cr-MOF spectrum which is 1100. This signifies the presence of an O-metal linkage, which implies that an O-Cr bond formed. This corresponds to the C-O stretch.

The SEM images of the synthesized Cr-MOF are shown in Figures 4a and 4b. Several pores can be seen with different sizes. The image of Chromium MOF as observed is wax-like, with broad sheets. It appears as thick, flakey platelets with conspicuous voids and some degree of roughness on the surface.

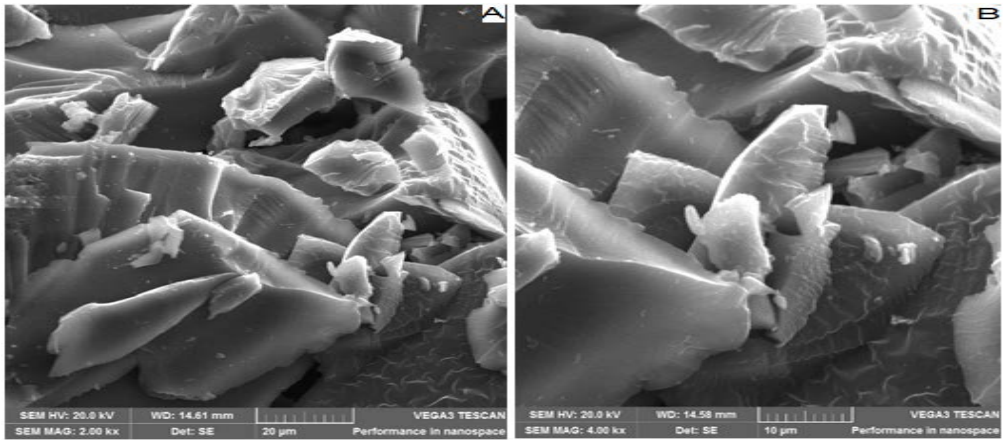



Figure 4a & 4b. Scanning Electron Microscopic (SEM) Image for Cr-MOF. (A) x20 µm (B)x10 µm.

The EDXS of Chromium MOF (figure 4C), shows the elements Carbon, Oxygen, and Chromium only. Elemental composition of Cr = 30.9%, C = 46.1% and O = 23.0%. chromium has two peaks at 0.6 and 5.5 keV. Isotopes of Cr may be present.

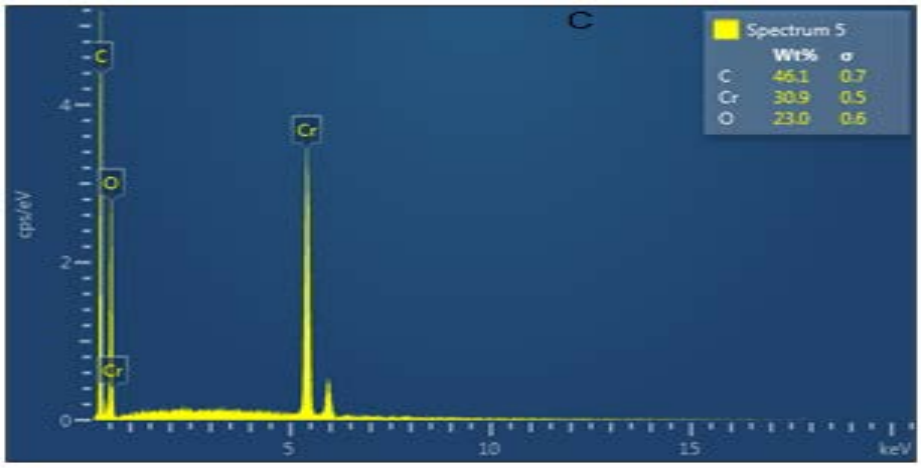



Figure 4c. Energy Dispersive X-ray Spectroscopy. (EDX) of Chromium Metal Organic Framework (Cr-MOF) with Benzene-1,4- dicarboxylic acid (BDA) (Terephthalic acid) linker.

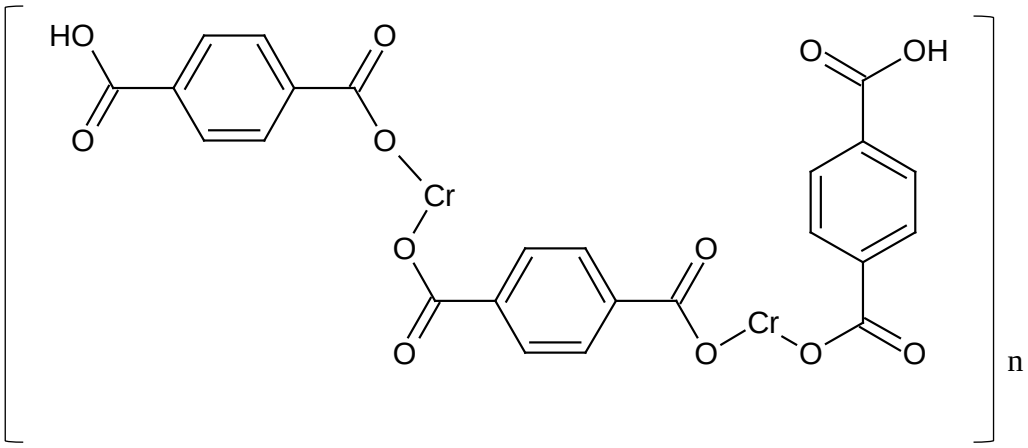



Figure 4d. Cr-MOF possible bonding and repeating units in Chromium organic framework.

## 3.1 ADSORPTION RESULT

Adsorption result for Chromium Metal Organic Framework (Cr-MOF) or (Cr-BDA) of Benzene-1,4-dicarboxylic acid presented in Figure 5a showed from the curve, that, the adsorption of the crude oil increased almost linearly with increase in adsorbent dose. Though there was an increase in the amount of oil removed with respect to MOF dose used, the adsorption of the crude oil was quantitatively low. Zero sorption was recorded at mass 0.2 g, 0.4 g adsorbed 10%, 0.6 g adsorbed 20%, 0.8 g adsorbed 40% and 1.0 g adsorbed 70%. The implication is that more of the Cr-MOF will be required for remediation, hence more expenses and longer time before a good cleaning of the environment will be achieved.

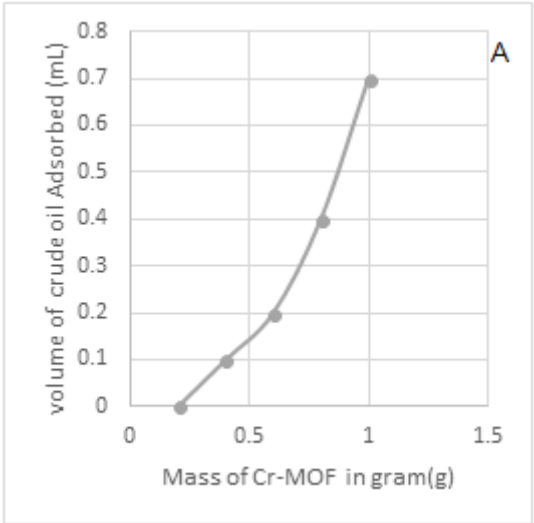



Figure 5a. Dosage adsorption result.

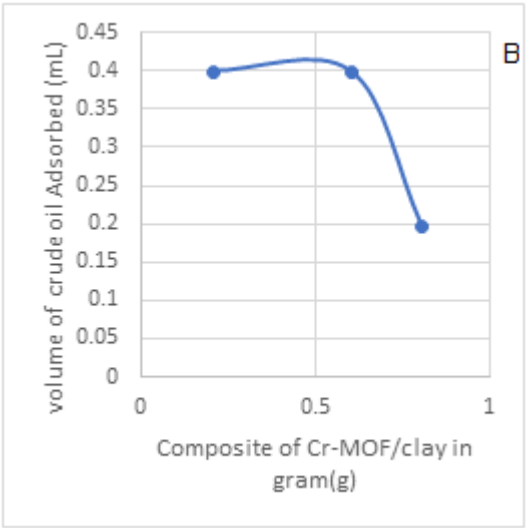
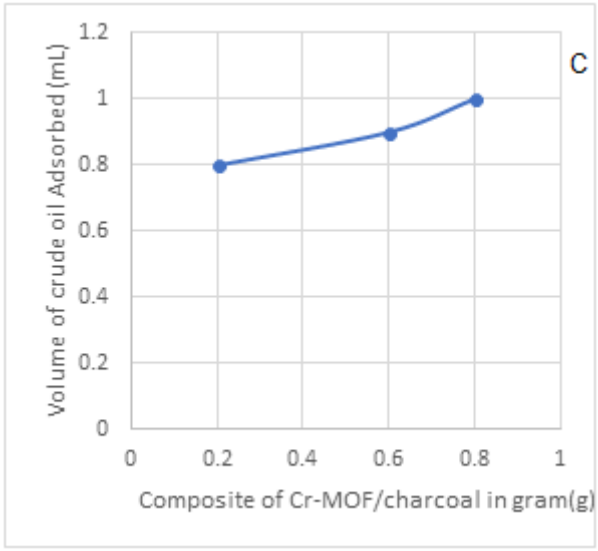



Figure 5b. Composite of Cr-BDA/clay

Composite of Cr-MOF/clay in the ratio 1:1 adsorption results are presented in figure 5B. The 0.2 g and 0.6 g adsorbed 40% of 1 mL crude oil. The adsorption dropped to 20% at 0.8 g. The result is poor when compared to using the Cr-MOF alone.

Composite of Cr-MOF/charcoal in the ratio 1:1 adsorption results are presented in figure 5C. The values obtained for sorption of crude oil ranged from 80-100%. This shows that the adsorptive property of the Cr-MOF was improved by the charcoal.



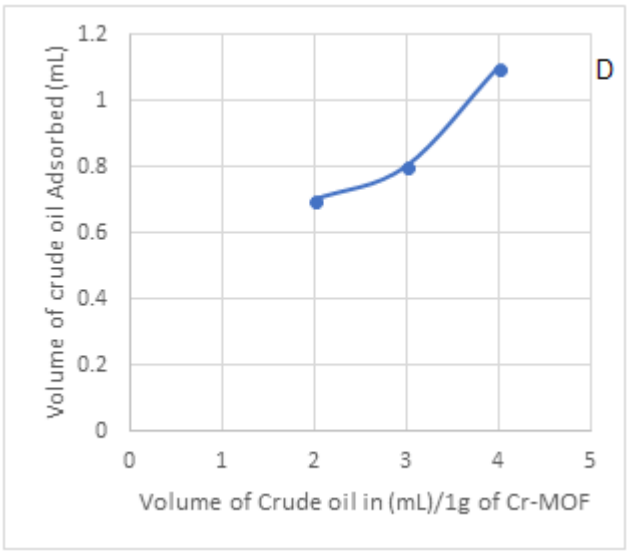




Figure 5c. Result of the composite of Cr-MOF/charcoal in gram(g). Figure 5d. Volume concentration of crude oil in mL/1g of Cr-MOF & the quantity of crude oil that was adsorbed.

The effect of pH for Cr-MOF on adsorption capacity is presented in Figure 5e. Looking at the figure, at pH 4.4, 90% of the crude oil was adsorbed. The graph then slopped down to 80% at pH 6.85 but increased to 100% at pH 9.

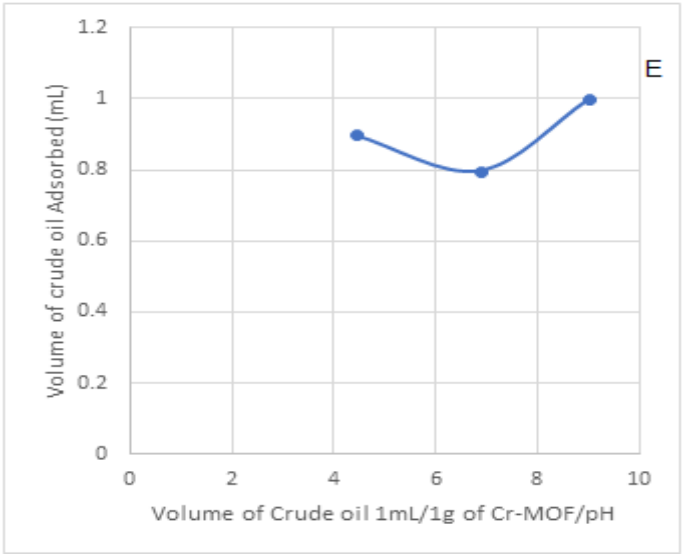



Figure 5e. Result of pH effect on the adsorption property of Cr-MOF.

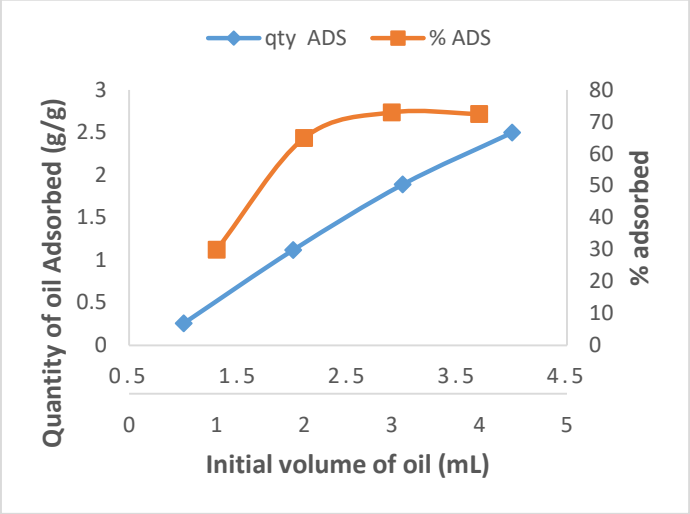



Figure 6a. Effect of initial volume on the quantity of adsorbed and percent adsorbed of crude oil by Cr-MOF

## 3.2 ADSORPTION MODELLING

The quantity of crude oil removed from the mixture was first determined by using the equation (2) according to Kelle, (2018). The quantity, qe, removed is given by

$$q = \frac{(m_i - m_f)g}{M(g)}$$

where, $m_i$ is the initial weight of crude oil (g), $m_f$ is the final weight of crude oil (g) and M is the mass of sorbent used.

The performance and parameters of applied models for the adsorption are shown in Figure 6b and table 2

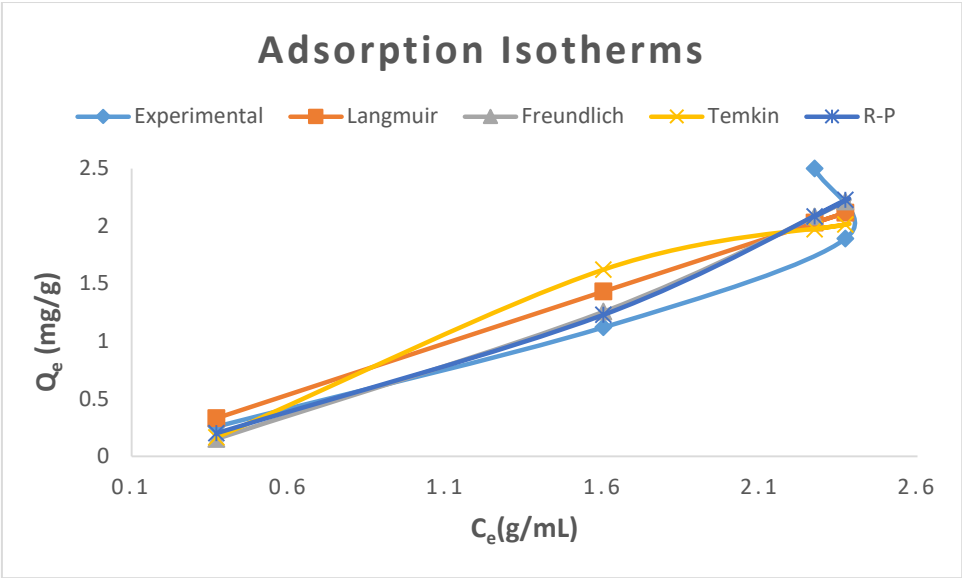



Figure 6b. Applied non-linear isotherms for the adsorption of crude oil by Cr-MOF

The results from the Langmuir isotherm model shows that maximum adsorption capacity of the MOF for the crude is 276.25 mg/g of adsorbent. The models applied did not correlate the data perfectly, but the regression coefficients are all above 0.8 which represents 80% of the measure. The correlation constant of the Freundlich plot ranks the highest among others, implying that it is best correlated

among the other isotherms applied. A Freundlich affinity parameter, n between 1 and 10 or its reciprocal, 1/n, between 0 and 1 for the adsorption, indicates a beneficial adsorption process (Kadirvelu and Namasivayam,2000) and a predominant heterogeneous adsorbent surface (Olu-Owolabi, Diagboya and Adebowale, 2014) which the isotherm models. The affinity parameter n, for this adsorption is 0.6929, therefore, there is a high affinity of the MOF for the crude oil.

Table 2. Non-linear Equilibrium Parameters for the Adsorption of Crude oil by Cr-MOF

| ISOTHERM | PARAMETERS | VALUES |
|---|---|---|
| **Langmuir** | $q_{max}$ (mg/g) | 276.245 |
| | $K_L$ (L/g) | 0.00326 |
| | $R^2$ | 0.8672 |
| **Freundlich** | $K_F$ (L/g) | 0.6369 |
| | n | 0.6929 |
| | $R^2$ | 0.8909 |
| **Temkin** | B | 0.9938 |
| | $K_T$(J/mol) | 3.1951 |
| | $R^2$ | 0.8033 |
| **Redlich-Peterson** | $K_{RP}$ | 0.5048 |
| | $a_{RP}$ | 0.1446 |
| | g | 2.2737 |
| | $R^2$ | 0.8931 |

## 4. CONCLUSION

MOFs are class of porous materials and their importance is based on their features and applications; they can be synthesized with different methods of synthesis. The synthesis Cr-MOF was done by the solvothermal method. Cr-MOF characterization was done using the FTIR, SEM, and EDX. The characterization results indicated from the observed functional groups, elemental composition and the crystalline morphology that the MOF was successfully formed. The adsorption of crude oil by the as-synthesized Cr-MOF was done. Adsorption result which showed that the synthesized MOF could be used to remove crude oil to a maximum of 70%. Composite with charcoal and pH gave an improved adsorption prowess for crude oil rectification by Cr-MOF. Four equilibrium isotherms were applied to the adsorption; though the data was not perfectly correlated, the maximum adsorption capacity of the MOF for the crude oil was determined from the Langmuir isotherm to be 276.25mg/g of adsorbent. Affinity parameter from the Freundlich isotherm showed that the adsorbent (MOF) has a high affinity for the adsorbate (crude oil), thus a real -time process can be initiated after further studies.

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