

Synthesis, Characterization, and Sorption study of Fe-MOF on Crude oil Remediation in Niger Delta Region of Nigeria

Orodu Victor Enearepuadoh*, Iyabi Deborah, Dikio Ezekiel Dixon

Department of Chemical Sciences, Faculty of Science, Niger Delta University, Wilberforce Island, P.M.B 071, Amassoma, Bayelsa State.

**Corresponding Author Email: lv.rodu@yahoo.com*

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Abstract: A Metal-Organic framework was prepared from iron nitrate[Fe(NO₃)₃] and benzene-1,4-dicarboxylic acid with the aid of dimethylformamide using the solvothermal method of preparation. The structure and properties of the resultant MOF were then investigated using the Fourier Transform Infra-Red Spectroscopy (FTIR), the elemental composition was analyzed using energy dispersive spectroscopy, and scanning electron microscopy, to know how crystalline or amorphous the MOFs is. The result shows that the resultant MOF has a very good crystalline structure with abundant micropores which suggests a high specific surface area. The FTIR spectrum of the Fe-MOF indicated the presence of various functional groups and also suggests the formation of a new functional group peak. The new functional group indicates the formation of the Fe-MOF in comparison to the pure Spectra of the benzene-1,4-dicarboxylic acid. This new wavenumber for the new functional group found can be seen at 618cm⁻¹ which is a Metal –Oxygen (M-O) band corresponding to the C-C skeletal vibrational band. Adsorption studies carried out showed the efficiency of crude oil adsorption to be 70%. pH effect, composite with clay and charcoal was done for which it was proved that its effectiveness can improve with pH and charcoal to be a good adsorbent.

1. Introduction

For years, porous materials have gained consideration in chemistry due to their versatility says Sing *et al.*, (1985). These porous solids exhibit properties that are unique such as proficient surface area and largest volumes, Kitagawa, Kitaura, Noro, (2004). MOFs have nanopores that are very tuneable and this places them higher than zeolites and other metal oxides. This class of materials is important because it is possible to tailor their pore size, topologies, and structure by careful selection of their organic linkers/ligands (Furukawa *et al.*, 2010). A broad range of MOF can be made due to the ability of transition and lanthanide metal ions to form a large range of coordination geometries with organic linkers.

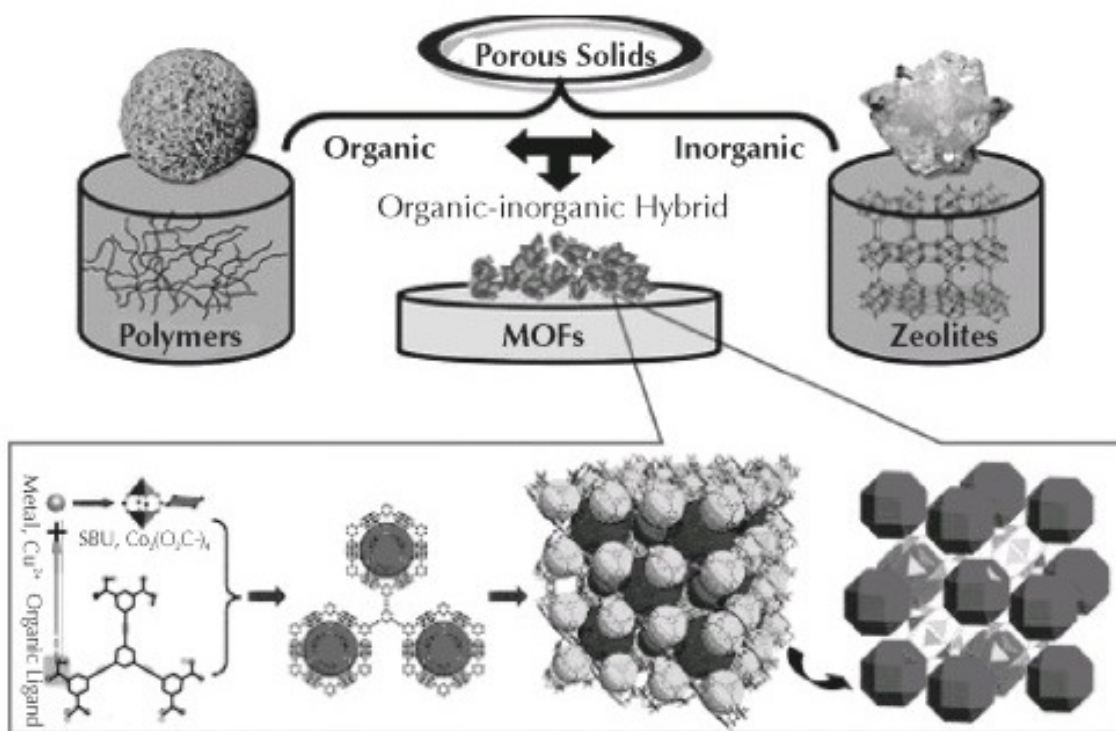


Fig 1. Diagrammatic representations of porous solids' general categorization. The bottom panel shows a typical MOF construction technique. J. R. Li et al., Chem Rev 112, 869–932, 2012.

So far, only a few catalytic MOF uses have been described. All of the reports are on metal-organic frameworks with unsaturated sites. Aromatic dicarboxylates, triazolates, tetrazolates, and pyrazolates are examples of linking molecules for MOFs, according to Aroma, Barrois, Robeau, and Gamez (2011). The key distinction of MOFs is their extensive structural diversity and unpredictability, along with lesser topological constraints on the development of porous three-dimensional frameworks. Every year, a large number of novel MOF structures are synthesized, confirming their variety and piqueing interest in their prospective applications. MOFs are one-dimensional, two-dimensional, or three-dimensional compounds with a large pore volume. Owing to their porous structure, larger specific surface area, stability and ability to be functionalized, Cejka J, ed., (2011) said MOFs are good candidates for use in gas separation, catalysis, and ion exchange reactions where zeolites are commonly used. J.D Lee (1996), said Iron (Fe) with atomic number 26 and mass number 55.845 belongs to group 8 and a d-block first series transition metal with electronic configuration $[Ar] 3d^6 4s^2$. Iron has the oxidation states of +2, +3, +4, and +6. It is used in the manufacture of many important metals. Iron is the fourth most abundant element on the earth's crust. Shooto, Dikio, Donbebe, and Sikhwivhilu, (2015), synthesized MOFs and applied them in Pb^{2+} absorption. Heavy metals are increasingly polluting the environment from industrial sources like dyes, pesticides, fertilizers, mining, and the making of batteries. Nigam and Srivastava, (2003). MOF is said to be a new class of porous material with a huge surface area. Yaghi and Rowsell, (2005). MOFs are good absorbents and can be used for storing of hydrogen., Rosi, Eckert, Edaoudi, Vodak., (2003). They are made up of inorganic units and organic bridging ligands. Civalleri, Napoli, Noel, Roetti, and Dovesi (2006).

Li, Yaghi, and Li., (1999) designed MOF-5 that can be utilized in several applications like gas storage and separation. Civalleri *et al.*, (2006), said MOFs received interest in the area of hydrogen and methane adsorption. Jahan *et al* prepared a graphene-MOF hybrid material which were used for Catalytic studies and were found to be very efficient. Rene et al. reported the preparation of and

selective drug delivery by a folate-MOF hybrid, demonstrating the potential for synthetic MOF materials to interact with biochemical pathways. Ibrahim, Sabouni, and Husseini (2017) said MOF structures have additional characteristics that make them attractive candidates for use as drug carriers in biomedicine.

This research seeks to successfully synthesize a Fe-MOF from $\text{Fe}(\text{NO}_3)_3$ and benzene-1,4-dicarboxylic acid for use in crude oil waste adsorption.

Synthetic methods include electrochemical, mechanochemical, microwave, and sonochemical processes, among others. (Xamena and Gascon, 2013) said heating could lead to the collapse of the framework, especially when guest molecules and the framework are closely bound together. Formation of MOFs is strongly affected by the solvents used and also by the presence of different additives (Li *et al.* 1999).

Solvothermal synthesis was proposed by Yaghi and the Nalco chemical business in 1995 which involves mixing the reactants and solvent, in a reaction vessel, closing it, and then heating the mixture to generate an insoluble framework and crystals. This method will be employed in my Iron and BDA MOF synthesis. Under autogenous pressure, the mixture will react above the solvent's boiling point. Furthermore, the majority of products are flawless crystals that can be examined using the single crystal XRD technique (Pachfule, Das, Podder, Banerjee, 2011). The reaction temperature has a significant impact on product formation (Forster, Stock, Cheetham, 2005).

The main idea of MOF synthesis using the electrochemical method is that metal ions are introduced as a result of electrochemical processes and not from a solution of corresponding salt or even through formation of these ions during reactions of a metal with an acid. (Stock, 2012). Microwave synthesis produces a high yield of desired product that can be neatly isolated without residues of other products, as well as a shorter reaction time and quick kinetics for crystal formation and development (Horikoshi, 2013). Microwave synthesis has been proven in several trials to assist shorten the time it takes to make MOFs (Jhung, 2005). Orodu and Dikio (2021) utilized a composite of MOF, charcoal, and clay for crude oil sorption. The results obtained showed that the composite with charcoal is adourable.

2. MATERIALS AND METHODS

2.1 MATERIALS USED

Filter paper, centrifuge, measuring cylinder/micro pipette, Refluxing kit, Electromagnetic stirrer, Thermometer, Fume cupboard, water that has been distilled, Oven, and Masking Tape X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Fourier Transform Infrared (FTIR) are all examples of analytical weighing balances (FTIR).

2.2 REAGENTS USED

DMF (Dimethyl formamide), Methanol, Iron(III)trioxonitrate (V), $[\text{Fe}(\text{NO}_3)_3]$, Benzene 1,4-dicarboxylic acid (BDA).

Except for terephthalic acid, which was obtained from a commercial source in South Africa, all of the chemicals were obtained at a chemical store in Onitsha, Anambra State, Nigeria. The clay and charcoal were obtained from Warri in Delta State, while the crude oil was obtained from LNG in Gbarain, Bayelsa State. Nigeria.

2.3 METHODS

2.3.1 Synthesis

Solvothermal procedures were used to make iron-MOFs. In the weighing scale, 4.04 g of iron nitrate salt was measured and deposited in the round bottom flask with 1.6613 g of BDA. The round bottom flask was also filled with 50 mL of DMF, which serves as the solvent. The reactants were heated to 76°C in the electromagnetic heating mantle for 3 hours while stirring was done with the magnetic stirrer. The solution changed from a dark brown to an orange creamy thick solution within the reaction time. After the solvothermal heating process, the solution was centrifuged at 4,000rpm for 20 minutes and rinsed numerous times with methanol. It was then dried in the oven. The Iron MOF that had been synthesized was then sent to be characterized.

2.3.2 Characterization of the synthesized MOFs.

The as-synthesized MOFs were characterized with Fourier Transform Infrared (FTIR), Fig 2a, Scanning Electron Microscopy (SEM), Fig 2b, and Energy Dispersive X-ray Spectroscopy (EDS). Fig 2c

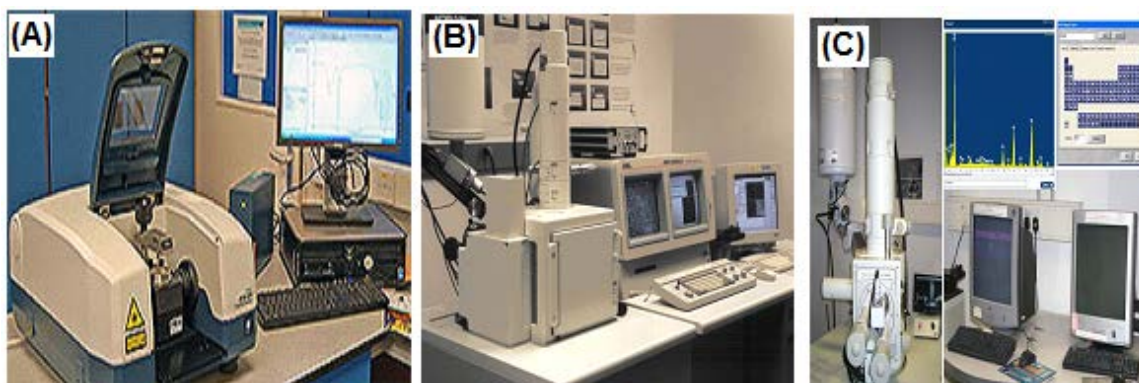


Fig 2: (a) Fourier transform infrared spectroscopy (b) Scanning electron microscope (c) Energy dispersive X-ray spectroscopy

2.4.2 Adsorption Procedures (Experimental)

Its efficacy in the adsorption of crude oil was carried out. The reciprocating stirrer, separating funnel, measuring cylinder, 10 mL pipette, and conical flask were all used. For the adsorbent dose study, 0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1.0 g of MOF were weighed and placed in separate conical flasks with distilled water to the 50 mL mark. After that, 1mL of crude oil was poured to it. After that, the mixture was shaken for 30 minutes. The composite was made by weighing MOF/clay and MOF/charcoal in a 50-50 ratio, i.e. 0.1/0.1 to make 0.2 g, and so on. The volume concentration was carried out. The crude oil volume was varied between 1.0, 2.0, 3.0, and 4.0 mL to achieve this. A total of 1.0 g of MOF, clay, and charcoal were used. pH 4.4, 6.85, and 9.0 were used to test the effect of pH on adsorption.

3. RESULTS AND DISCUSSION

Table 1. Vibration and wavelength number

1,4-BDA cm^{-1}	Fe-MOF cm^{-1}	ASSIGNMENT (V) cm^{-1}
518 cm^{-1}	533 cm^{-1}	Ring in and out plane bending (v)
	618 cm^{-1}	Metal oxygen bond formation
674 cm^{-1}	660 cm^{-1}	C-C Skeletal vibrational
751 cm^{-1}	747 cm^{-1}	C-H Bending
1160 cm^{-1}	1100 cm^{-1}	C-O Stretch
1390 cm^{-1}	1380 cm^{-1}	C-H Bending, Aromatic
3160 cm^{-1}	3434 cm^{-1}	O-H Stretch, COOH dimers

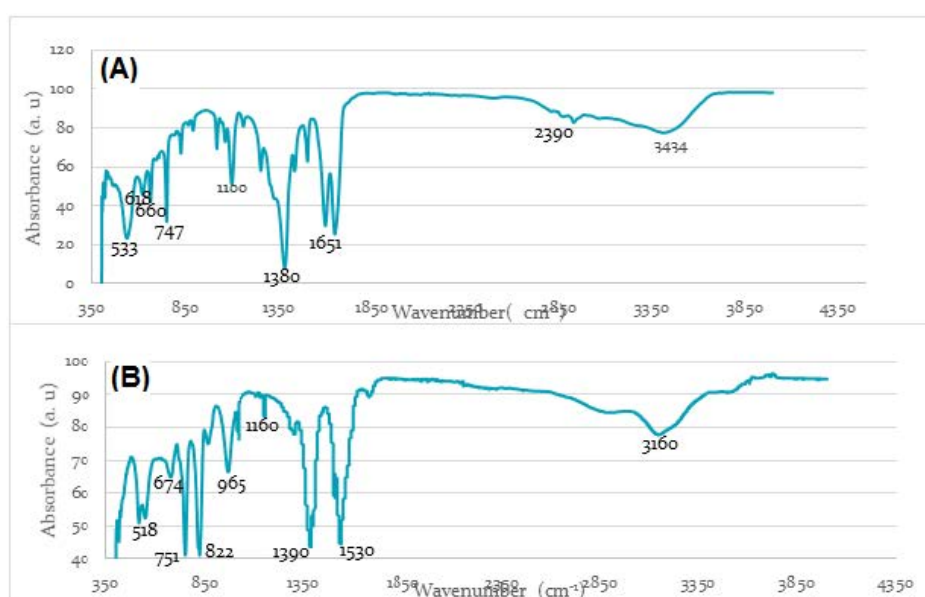


Figure 3. (A) FTIR spectrum of Fe-MOF (B) FTIR spectrum of 1,4-Benzenedicarboxylic acid.

In the presence of N, N-dimethylformamide, the metal-organic framework of Iron was synthesized with 1,4-dicarboxylic acid. Iron was obtained as a solid orange crystalline metal-organic framework. The absorbance of the Fe-MOF is plotted against its wavenumber in the FTIR spectrum shown in fig 3a. The synthesized MOF exhibits a weak C-C vibration bond at 660 cm^{-1} and a ring in and out bending at 533 cm^{-1} . A C-H bending ($\text{C}=\text{C}-\text{H}$) is detected at 747 cm^{-1} , with a medium to strong strength. At 1100 cm^{-1} , there is a variable C-O stretch observed. At the 1380 cm^{-1} wavenumber (frequency), a variable aliphatic C-H bond is observed. At the 1651 cm^{-1} wavelength position, the $\text{C}=\text{C}$ aromatic strength is found to be present. At the 3434 cm^{-1} position, there is a presence of an O-H bond which suggests the presence of water molecules in the compound.

The above graph is an FTIR graph in Fig 3b showing the absorbance against wavenumber of the benzene-1,4-dicarboxylic acid. The organic compound, has a ring in and out bending at 518 cm^{-1} , 674 cm^{-1} having a C-H bending and a C-C skeletal vibration of weak strength at 751 cm^{-1} . At the 822 cm^{-1} wavenumber, the same C-H bond is found to be present. At the 965 cm^{-1} , there is a C-O stretch which is variable. At the 1160 cm^{-1} point, there is still observed to be a C-O stretch. At 1390 cm^{-1} , there is a C-H aliphatic bending. At the 1530 cm^{-1} wavenumber, there is still a C-H bending present. At the 1680 cm^{-1} , there is a $\text{C}=\text{C}$ functional group present and at 3160 cm^{-1} , there is a presence of O-H functional group which signifies the presence of water molecules in the compound.

In comparison of the two bonds, a new wavenumber is seen in the Fe-MOF which is 618 cm^{-1} . This signifies the presence of an O-Metal bond which is an O-Fe bond formed. It corresponds to the C-H bending.

3.1 ADSORPTION RESULT

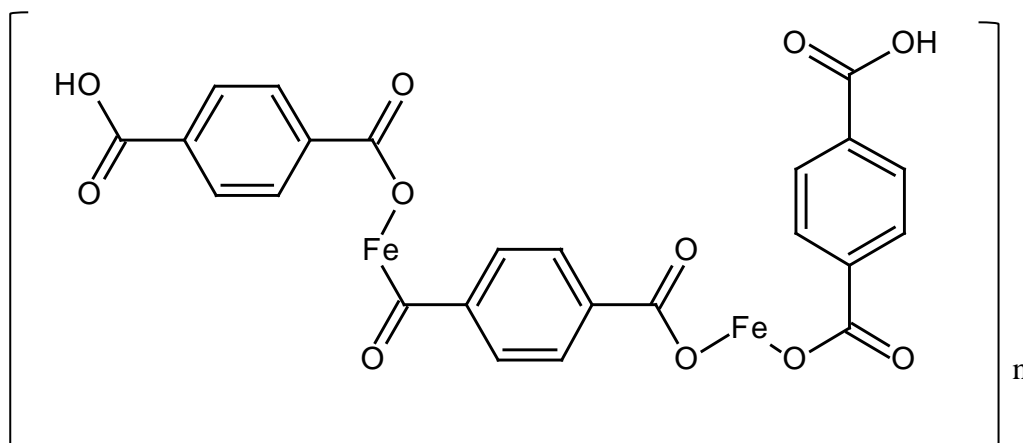


Figure 4. Fe-MOF possible bonding and repeating units in iron organic framework.



Figure 5. Fe-MOF obtained after synthesis and oven dried. It has a brownish colour.

3.2 SCANNING ELECTRON MICROSCOPIC (SEM) SPECTRUM.

The SEM image of the as-synthesized Iron MOF reveals crystals with a variety of pore diameters, uneven surfaces, and rough surfaces.

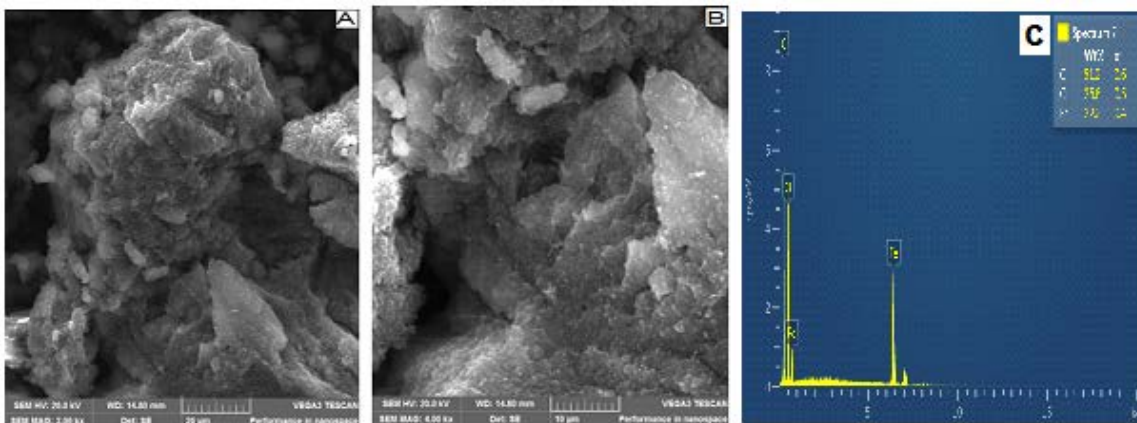


Figure 6. Scanning electron micrograph of Fe-MOF (A), (B) & Energy dispersive graph of Fe-MOF(C)

3.3 ENERGY DISPERSIVE X-RAY SPECTROSCOPY. (EDX).

Energy Dispersive X-ray spectroscopy (EDXS) is a strong characterisation technique that reveals the metal elements present in the as-synthesised material. Figure 6(C), is a clear indication of the material's successful synthesis and, more importantly, its purity. Only the elements Carbon, C, Oxygen, O, and Iron, Fe are seen in the EDXS of Iron MOF (figure 6c). Iron 22.2 percent, Carbon 51.2 percent, and Oxygen 26.6 percent are the elemental compositions shown. Iron exhibits two peaks at 0.8 and 6.5 keV, indicating the presence of its isotopes. The carbon peak was 0.1 keV while the oxygen peak was 0.5 keV.

3.4 ADSORPTION RESULTS

The curve for crude oil adsorption in an Iron Metal-Organic Framework (Fe-MOF) or (Fe-BDA) (adsorbent) dosage was not a straight line, as shown in Figure 7a. 0.2 g of the adsorbent (Fe-MOF) adsorbed 20%, 0.4 g, and 0.6 g each adsorbed 30%. The curve dropped at 0.8 g, which absorbed 20% of the crude oil, whereas 1.0 g adsorbed 70%.

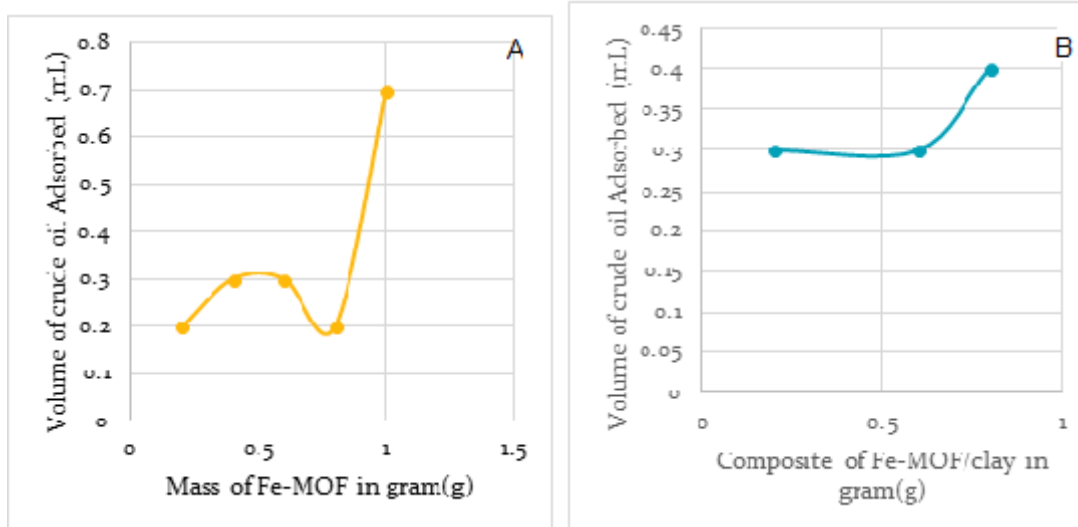


Figure 7 (A) dosage adsorption result for Fe-MOF.

Figure 7 (B) composite of Fe-MOF/clay

3.5 COMPOSITE RESULT FOR ADSORPTION OF CRUDE OIL IN RATIO 1:1 WITH CLAY.

The term composite refers to the process of combining substances or materials to improve or modify their physical or chemical qualities. If the intended outcomes are accomplished, composite also aids in cost reduction.

Figure 7b shows the adsorption results of a composite of Fe-MOF/clay in a 1:1 ratio. 30% of the crude oil was absorbed by the 0.2 g and 0.6 g. 0.8 g adsorbed at a rate of 40%. The end outcome is not good. It was not even close to 50%.

3.6 COMPOSITE RESULT FOR ADSORPTION OF CRUDE OIL IN RATIO 1:1 WITH CHARCOAL.

Figure 7c shows the findings of crude oil adsorption by a composite of metal-organic framework with charcoal. The percentage of success ranged from 80 to 100 percent. This is a one-of-a-kind and exceptional method.

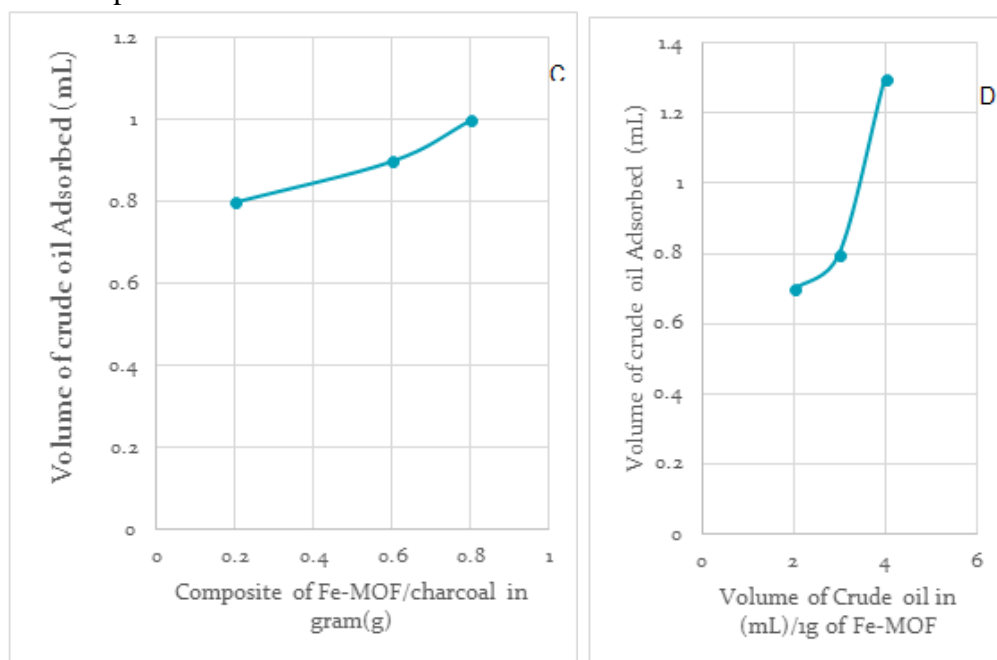


Figure 7(C) showing result of the composite of Fe-MOF/charcoal in gram(g). Figure 7(D) volume concentration

3.8 VOLUME CONCENTRATION OF CRUDE OIL IN (mL)/ 1 g OF THE ADSORBENT.

The greatest amount of crude oil that the adsorbent could adsorb was determined in this section of the study. This was accomplished by boosting crude oil production. 2 mL, 3 mL, and 4 mL of adsorbate were employed, with the mass of the adsorbent remaining constant at 1.0 g. Figure 7(D), show the results achieved.

1 g of the adsorbent, adsorbed 32.5 percent of 2 mL, 26.7 percent of 3 mL, and 35 percent of 4 mL. The ability of Fe-MOF is restricted, as evidenced by the results.

3.9 pH EFFECT on Fe-MOF.

The pH of the solution influences the charge density of the adsorbate and adsorbent. A pH is a number that, on a logarithmic scale, represents the acidity or alkalinity of a solution, with 7 being neutral, lower numbers representing more acid, and higher values signifying more alkaline. The pH is equal to $-\log_{10} H$, where H is the concentration of hydrogen ions in moles per litre. The effect of pH on the adsorption of crude oil on the as-synthesized Iron metal organic framework is presented in figure 7(E).

The effect of pH for Fe-MOF on adsorption capacity is presented in figure 3.9.1. At pH 4.4, 70% of the crude oil was adsorbed. 90% were adsorbed at pH 6.85 and pH 9.

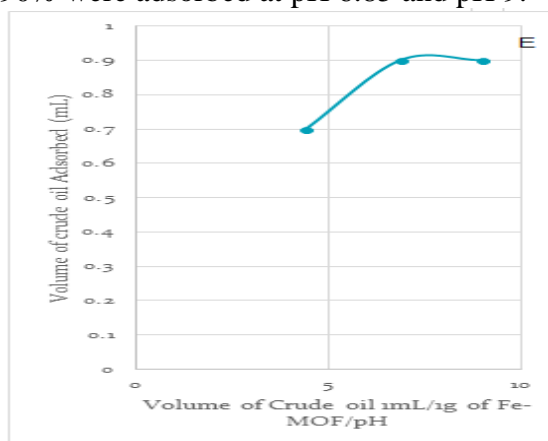


Figure 7 (E), Result of pH effect on the adsorption property of Fe-MOF.

4. Conclusion and Recommendation

4.1 Conclusion

The synthesis, characterization, and adsorption of iron and benzene-1,4-dicarboxylic acid by the metal-organic framework were carried out. Dimethylformamide was used as the solvent for the synthesis. In about 6 hours, the MOF was successfully synthesized and characterized. The effective production of the MOF was demonstrated by FTIR analysis, which also revealed that the structure is extremely crystalline. Adsorption results for the synthesized Fe-MOF dose were 70% for 1 g of composite with charcoal, a good crude oil adsorbent with an efficiency of 80–100%. Its adsorptive activity was regulated by the pH. At pH 6.85 and pH 9, 90% were absorbed.

4.2 Recommendation

We urge that both the business and public sectors involved in oil exploration in oil-producing areas consider this research as an alternative to cleaning up oil spills in our environment. Further research into the use of MOFs for crude oil remediation on-field is also encouraged.

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