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Synthesis, Characterization and Adsorption Study of Metal Organic Framework of Copper (II) benzene-1, 4-dicarboxylate (Cu-MOF) on Crude oil

Orodu Victor Enearepuadoh and Dikio Ezekiel Dixon

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

Keywords: Cu-MOF, simulation, Benzene-1, 4-dicarboxylic acid, crude oil.

Abstract: Metal organic framework (MOFs) of copper was synthesized using benzene 1, 4-dicarboxylic acid as a linker and N, N-dimethylformamide as a solvent. The Synthesis of copper MOFs was carried out using solvothermal method. The synthesized Cu-MOFs was characterized using the Fourier transform infra-red spectroscopy(FTIR), Scanning electron microscopy SEM, and Energy Dispersive X-ray spectroscopy, EDX, was utilized for morphology and elemental analysis respectively. The elemental composition was Cu = 23.6 %, C= 54.1% & O= 22.3 %. Synthesized Cu-MOF was used in crude oil adsorption study by simulation of spillage with 50 mL of distilled water. The result showed that Cu-MOFs is an effective adsorbent for crude oil.

1. INTRODUCTION

Copper exhibits one S electron outside its completely filled d orbital. It is a good conductor of electricity and heat. Copper (II) ion, Cu^{2+} is the only copper ion that exists in solution apart from complexes. Biologically, photosynthesis and the movement of oxygen onto the vertebrate with the help of oxidize enzyme need copper as an essential enzyme which act as the oxygen carrier. Copper is a superconductor in several mixed oxides. (Lee 1996). The atom of copper is much smaller in size compared to the group 1 element this is due to the poor screening by the d electrons. Though not common but copper also possess isotope which are naturally abundant in the percentages of 69.17% for (63 cu) and 30.83% for (65cu). (Cotton and wikinson 1972). Copper is essential to human health but has been known to be an element that causes health hazard to human. Benzaoui, selatnia and Djabali (2017). The oxides of copper are mostly insoluble and also weakly basic in water. (Lee *et al* 1996). Copper is used as a conductor of electricity and in all gauge's wire for circuits, also explored in electroplating, in fertilizer industry, In analytical reagents, in pigment. In agriculture, Bordeaux mixture is an essential copper hydroxide and is product from $CuSO_4$ and $Ca(OH)_2$. It is an important spray for preventing fungus attack on the leaves of potato. Copper is an essential catalyst, hence is used in direct process for the manufacturing of alkylchlorosilanes $(CH_3)_2SiCl_2$ which is an important tool in making silicones. Lee *et. al.* (1996).

MOF are class of porous materials because of their high surface area, low densities, thermal stabilities, high porosity and adjustable chemical functionalities, it has attracted massive attention.

MOF’s have various way it is applied to enhance industrial efficiency in gas sorption, gas separation, biomedical application and catalysis. Eram Sharmin and Fahmina Zafar, (2015). Years back research was carried out and facts where gotten that MOF display permanent porosity and also exhibits pore windows, ranging from 5 to 25A^{o}. MOF was defined by Yaghi *et al*. (1998) as a porous structure, constructed from the coordinative bonding between metal ion and organic linkers or bridging ligands.

Metal organic frame work (MOF) comprises of both the organic and the inorganic units or groups. Also, the organic units which are the linkers or bridging ligands contain carboxylated or anions which are the phosphoratesulfonate and the heterocyclic compound. For the past ten years, materials from zeolitescoordination polymers to metal frame works (MOFs) have achieve significant attention. (See Figure 1 below)

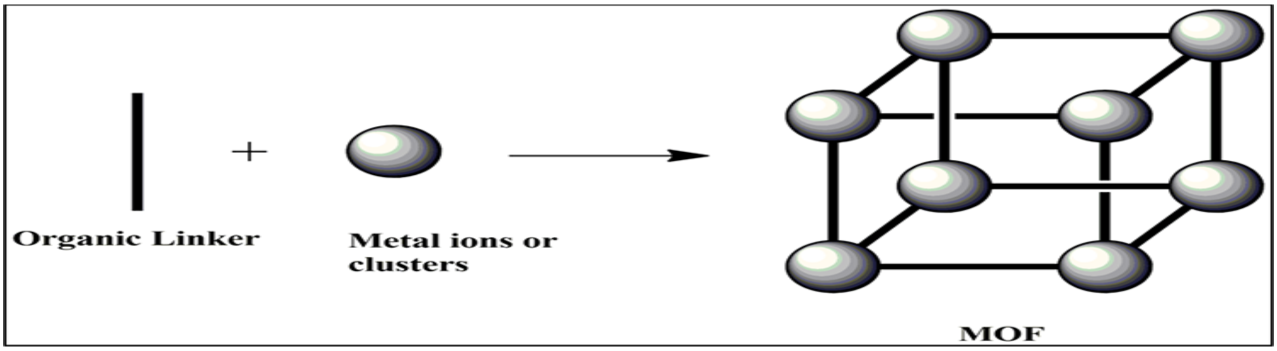
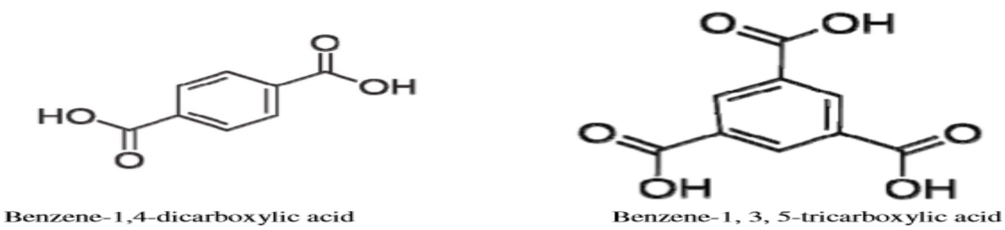


Figure 1 Structure of MOF

The MOFs have some inter linking centres which are the transition metals and it possess an empty d orbital which behaves as an electron acceptor in Lewis acid from ligands to produce a coordination bond. Contrary, a bridging ligand react with others metals ions that possess more than one valent or unstable site. Eram *et al*. (2015). MOFs interacts with organic compounds that have Monovalent, Divalent and Trivalent linkers to form MOFs. The most common way of its preparation, is by hydrothermal or solvothermal method in DEF medium, which will decompose on heating and will produce bases that are able to deprotonate organic linkers molecule. Keskin and Kizilel, (2010). The assembling process, referred to as molecular building block, (MBB) allows access to MOFs with easy topological process such as the border-transit net. The uni-modal and bimodal net with high connectivity n>8 are good target in crystal chemistry, as it present acceptable net for the putting together of their related connected MBBs. Vincent, Dong Wook, Janod, Ryan, Vintang Liu, KarimAdil, Young, and Mohammed, (2016). Molecular building block (MBB) of MOF can also be assembled by choosing ligand that has accurate geometry to form polyhedral (SBB) super molecular building block Rasha Adullahi (2016). Due to the rigidity and alternating tendency to form rigid metal carboxylate clusters, Benzene-carboxylate have been chosen as the main source of ligand. The cubic and square planar MOFs are ligand that possesses linear orientation (Xin Liu 2015) (See Scheme 1).

The basic set back of methane is the problem of its low volume energy density. It is important to develop suitable no-board methane storage solutions that is close to room temperature. This is important for a successful deployment of methane as an alternative fuel for transport application (Rasha *et al*. 2016). In the oxidation of Co, which has been investigated in the heterogeneous or different field of catalysis which is due to its fundamental interest and necessary practical application. Like the gas sensors for discovering trace amount of Co, automotive exhaust gas treatment and also polymer electrolytes, fuel. (Wenlong Xiang, Yuepingzhang, Hongfeilinand Chang-jun Lis, 2017). MOFs are used as drugs delivery material because their properties can adjust the functional group of the frame work and by finely tuning the pore size. Highly degradable Nano particles base on nanoscale coordination polymer containing Pt exhibit high anticancer efficiency *in- vitro* towards the human Colon carcinoma cell line (HT-29). As reported by Liu, Xin, (2015). MOFs have a characteristic porosity, which have a large range of applications industrially; most especially for the adsorption process and for catalysis. Hoskins and Robson activated the attention in porous coordination polymer and MOFs. They found out that zeolite is extremely important when it comes to crystalline aluminosilicate materials with incomparable pore of 4~13A° around 1990.



Scheme 1 Selected organic ligands with carboxylate groups

Solvothermal method is the most common method used for the synthetic process of MOFs. But there are also limiting factors that affect this method and that is, the time taken in the process is always time consuming. To speed up the discovery of MOFs, high –throughput method which were at first developed in pharmaceutical research have been developed. Norbert Stock and Shyam Biswas, (2012). Copper (II) metal organic framework CU-MOF based on the ligand of 5-aminoisophthalic acid (AIPA) was synthesized and Single crystals X-ray structural analysis confirmed the formation of the compound, [CU (AIPA). DMFn. The crystal structure exhibits a 2D sheet which generate a 3D framework through non-classical hydrogen bond interactions. TGA, IR and VT-PXRD were carried out to characterize the compounds thermal stability and purity. The sample was activated by removal of the coordination DMF solvent to afford porous framework CU-MOF without degradation of the original crystallinity. Wei-Qin, Shan He, Chun-Cheng, Yan-Xuan, Xiao-Jun, TaoJiang, Wen-Ting, Xiu-Lian, Zhang andJi-Jun, (2018). A novel metal organic framework, CU-BDC was synthesized by static hydrothermal method using innocuous solvent such as powder XRD, ESR, TG-DTA, elemental analysis, ICP-AES, SEM, EDXS, FT-IR, BET surface area, pore volume and pore size. The catalytic performance of CU-BDC was explored for 6-acetylation of alcohol under solvent –free conditions at room temperature. The catalyst exhibited remarkable activity and reusability affording the desired products in wonderful yield. Savita, Sandip, Manoj and Velhinho, (2014). Many researches on MOFs focus mainly on crystallographic and adsorption properties of synthesized material, with zinc and copper the most common metal studied as metal-organic frameworks. Dikio Ezekiel Dixon and Abdullahi Farah, (2013). The synthesis and structural characterization of a novel copper MOF: STAM-NMe2 was developed using the linker 5-dimethylamino isophthalic acid. The structure was examined using single crystal X-ray diffraction, variable temperature powder X-ray diffraction was used to ascertain the thermal stability of the MOF, and nitrogen BET adsorption was employed to determine the porosity of the material. Lauren Nicole, Paul Stewart, Leonardo Perez, David Cordes, (2019).

A copper glycinate (Bio-MOF-29), [CU $(C_2H_4NO_2)_2(H_2O)$] was synthesized by the hydrothermal method and characterized by single crystals XRD analysis. Tabinda Sattar and Muhammed Athar, (2017) Bio-MOF-29 crystallized in orthorhombic crystals system with P212121 space group. Tabinda Sattar *et al*, (2017), did *Invit*ro adsorption studies of four different drugs, terazosinehyrochlorie, telmisartan, glimepiride and rosuvastatin. The adsorption estimation for drug loaded to Bio-MOF-29 was analyzed through high performance liquid chromatography (HPLC), which revealed that these drugs were successfully adsorbed in it. Also, the slow release of adsorbed drugs after intervals was observed using HPLC. Thermograms and powder XRD pattern of Bio-MOF -29 before and after drugs adsorption were also recorded to develop in details the process of drug adsorption in Bio-MOF 29. Tabinda Sattar *et al,* (2017).

Shooto, Ntaoet, Dikio, Wankasi and Sikhwivhilu, (2015), synthesized and characterized MOF of copper and cobalt with the use of 1, 2, 4, 5- tetrabenzenecarboxylates, as linker and utilized them in metal adsorption studies. The result for the characterization was acquired by scanning electron microscopy, energy dispersive x-ray, thermogravimetric analysis and x-ray diffraction spectroscopy. They observed that the morphological forms of copper and cobalt MOF presented highly crystalline material as bestowed by the SEM micrographs. EDX spectra detected other constituent that was present in this metal organic frame work which are the C, O, and OH atom. Shooto *et al*, (2015) Studied thermodynamic, equilibrium and isotherm batch adsorption experiments for Pb^{+2} ion. The acquired result showed Cu-MOFs were more effective than Co-MOFs. Three different MOFs, (Cu $(Br_2$ BDC$)_2$(HTEA$)_{2,}$ (Co (BrBDC) (HCOO$)_2$(DMF$)_2$), Zn_2 (BrBDC) $(Tr_2)_2$ $3H_2O$. (Br BDC = 2, 5 – dibromoterepthalicate; DMF = Dimethylformamideand TEA = trimethylamine and TRz – 1, 2,4triazole), were Synthesized and their end results showed that the first two compounds which are the Cu and Co MOF have two-dimensional structures, while the last which is Zn MOF contained three dimensional channels with opening over 4.7A^o. (Xin *et al*.2015). Brinda, Rajan and John Bosco Balaguru Rayappan (2015), synthesized, MOF -199 under room temperature using benzenetricarboxylic acid and a 1:1:1 mixture of DMF/ethanol/copper (ii) acetate, in the cause of the synthesis, trimethylamine (0.5mL) was added to the reaction mixture and the resultant mixture was stirred for up to 23hr which was followed by drying to obtain a bluish crystalline material of MOF - 199 which was further characterized using various analytical and microscopic techniques. The porosity of the MOF material has tunable sizes, structure diversity and other importance. MOF have been observed by researchers that it can be synthesized by self-assembly of organic ligands and metal ions. It is known that the first transition metals such as Zn, Cu and Co are able to cope with carboxylate group under hydro and solvo thermal conditions to produce crystals. Liu, Xin. (2015). In recent time MOFs have also been synthesized from nontoxic products that are generated from cation such as Calcium, Magnesium, Iron and Zinc and ligands that possesses naturally occurring derivatives or bimolecular, such as amino acids, peptide, proteins nucleobases, carbohydrates and other natural product such as cyclodextrins, morphine's and some carboxylic acid which acts as newly formed building blocks for the designs and model of metal-bimolecular framework with novel and interesting qualities and applications which cannot be obtained or achieved through the use of traditional organic linkers (See Figure 2 below).

2. MATERIALS AND METHODS

2.1 MATERIALS

Thermometer, Magnetic stirrer, Magnetic heating mantle, Reflux kits, Reflux condenser, centrifuging machine, oven, retort stand, electrical weighing balance, beaker, centrifuge bottle, filter paper, measuring cylinder, pipette, conical flask, reciprocating shaker, separating funnel.

2.2 CHEMICAL/REAGENTS

Benzene-l, 4-dicarboxylic acid (BDA), Dimethylformamide (DMF) it's a solvent, methanol used for washing instead of water, Copper nitrate, distilled water. Clay and charcoal used were gotten from Warri in Delta State, Crude oil was from LNG, Gbarain in Bayelsa State. Nigeria.

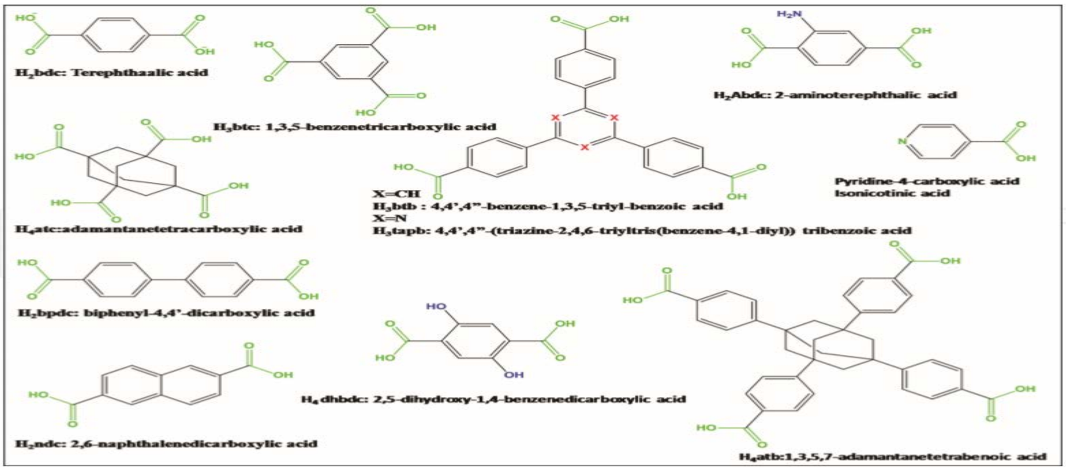


Figure 2 Some examples of organic ligands with carboxylic functionality used for the preparation of MOFs

2.3 THE SYNTHESIS

First the calculated nitrate salt of 2.4155g $Cu(NO_3)_2.3H_2O$ and Benzene-1,4-dicaboxylic acid of (1.6613g), was weighed and transferred into a 250mL round bottom flasks containing the 50mL dimethylformamide. The biro blue solution was stirred and heated with the reflux kits for about 3hr: 10mins at 100°C. While the solution was still stirring, at about 2hr: 20mins, a pale milky blue colour was observed, but refluxing continued for more 50mins to enable more crystal formation. The synthesized MOF was allowed to cool for some minute and then decanted into the centrifuge bottle and transferred into the centrifuging machine. The machine was set for 40 RPM X 100 in 20mins. (i.e. 4000 spins in 20mins). The pale blue crystals were obtained and isolated from the supernatant. It was washed with methanol severally. The obtained crystals were then oven dried at 60°C for 4hr 23mins and use for further experiment. Picture of Cu-MOF obtained before & after drying below.

2.4 EQUIPMENT USED FOR CHARACTERIZATION

FTIR (Fourier transform infrared spectroscopy); this is a device used to identify organic, polymeric and in some cases, inorganic material. It also uses infra-red light to scan test samples and observe chemical properties and functional groups present in the spectrum. Fourier transform infrared spectroscopy by Perkin Elmer attached with FT-IR/FT-NIR spectrometer, spectrum 400. Range of measurement was from 4000 to 520cm^{-1}.

SEM (Scanning electron microscope); this is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electron interacts with atoms in the sample, producing various signs that contain information about the surface topography and composition of the sample.

EDXS (Energy dispersive X-ray Spectroscopy); It is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum. For surface morphology and EDX result, JOEL 7500F scanning electron microscope was used for the analysis.

2.5 ADSORPTION STUDY PROCEDURE

0.2g,0.4g, 0.6g, 0.8g,1.0g of copper MOF was weighed with analytical balance and 50mL of distilled water was measured using a measuring cylinder and were transferred into the conical flask. 1mL of crude oil was added to the mixture with the use of a pipette and shaken for 30minutes using a reciprocating shaker. The supernatant was decanted into a 250mL separating funnel, to separate the two mixtures in order to get the volume of crude oil adsorbed by the MOF. Volume concentration was done in order know the capacity to which 1gram of Cu-MOF can adsorb. This was carried out by varying the volume of the crude oil using, 2.0, 3.0 and 4.0mL. The composite was prepared by weighing 50-50% ratio of both MOF/clay and MOF/charcoal i.e 0.1/0.1 to make 0.2g etc. The mass of MOF, clay and charcoal, 1g of each was used. Effect of pH on adsorption was carried out by using pH 4.4, 6.85 and 9.0 for the study.

3. RESULT AND DISCUSSION

Table 3.1 The(Cu-MOF) were characterized using Fourier transformed infrared spectroscopy.

1,4 BDAcm^{-1}	Cu-MOFcm^{-1}	ASSIGNMENT (V)cm^{-1}
3160cm^{-1}	3439cm^{-1}	O-H Stretch vibration(sh)
1540cm^{-1}	1604cm^{-1}	C=C Aromatic stretch vibration(m)
1390cm^{-1}	1380cm^{-1}	C-O-C Asymmetric vibration (vs)
1160cm^{-1}	1103cm^{-1}	C-O Stretch vibration (v)
750cm^{-1}	675cm^{-1}	Metal Oxygen bond formation

519cm^{-1}	563cm^{-1}	Ring in and out of plane bending (v)

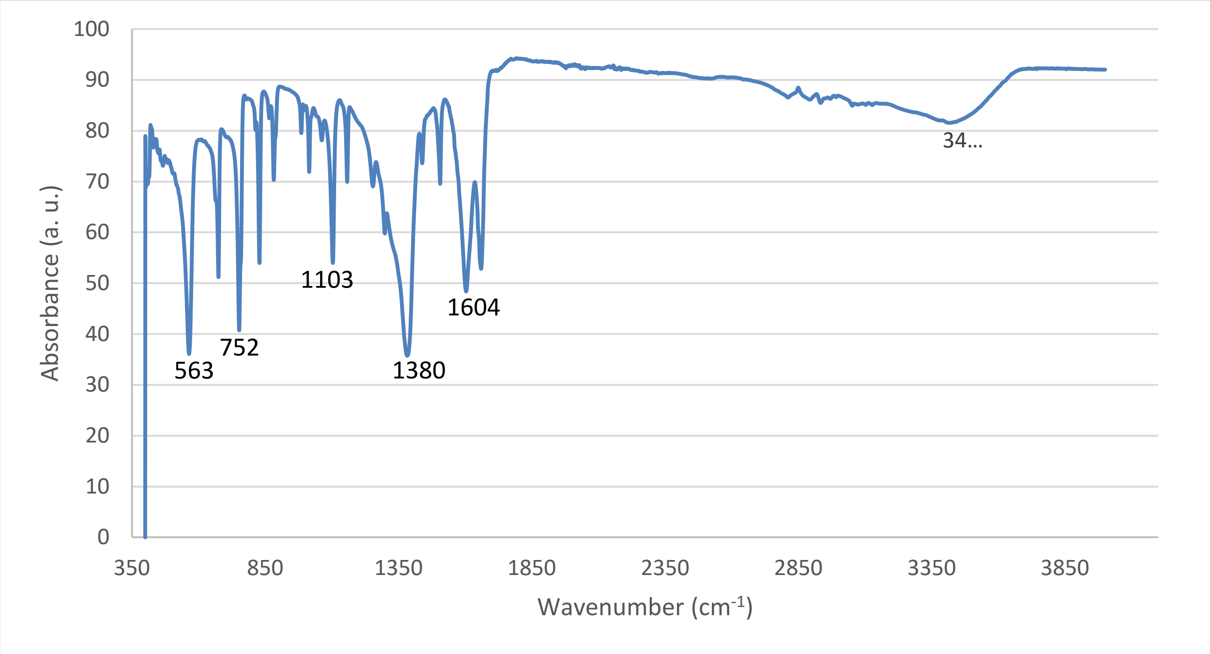


Figure 3a Fourier transform infrared spectra of copper metal organic framework.

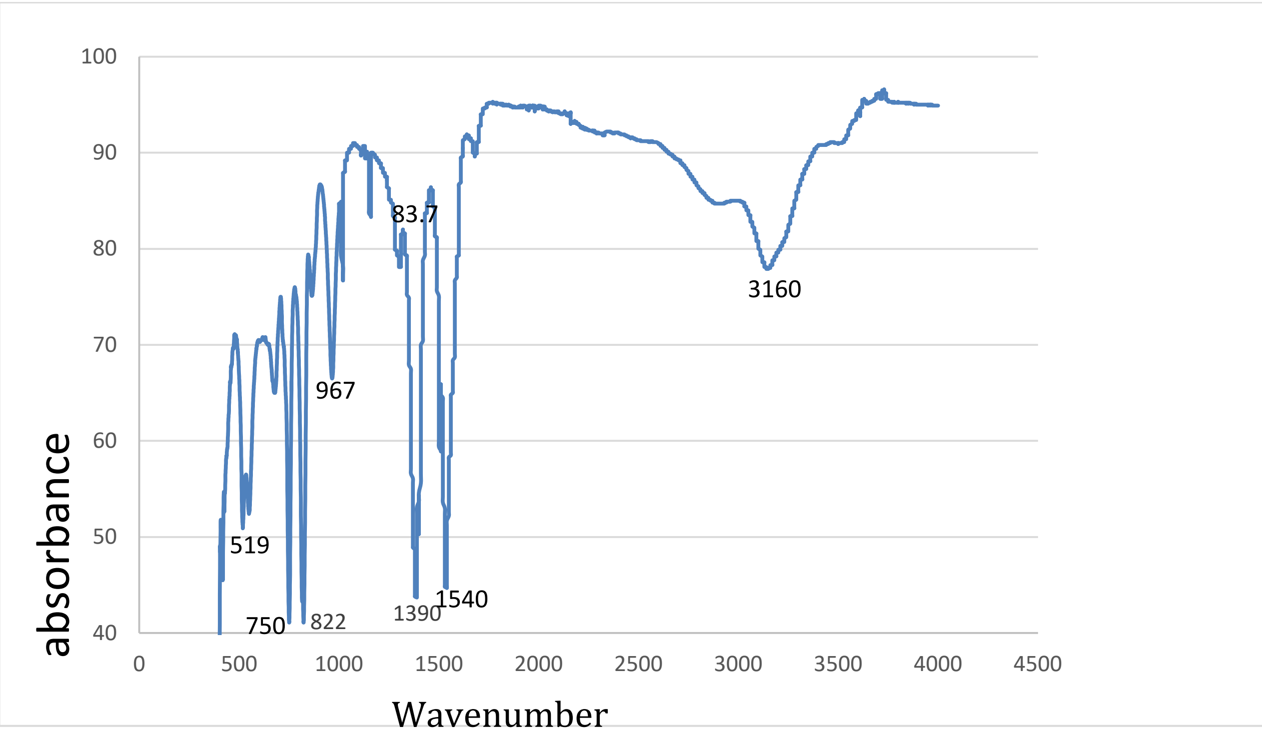


Figure 3b Fourier transform infra-red spectrum of 1, 4-benzene dicarboxylic acid

The absorption band in the region 3439cm^{-1} in the spectra figure 3 are assigned to the free O-H stretching vibration originating from the 1, 4- benzene dicarboxylic acid. The weak and medium band at 1662cm^{-1} to 1507cm^{-1} respectively are assigned as residue of C=C aromatic stretching vibration originating from the 1, 4-benzenedicarboxylic acid. The variable band centered at 1380cm^{-1} to 1158cm^{-1} correspond to the C-O stretching vibration and the C-O-C asymmetric stretching vibration unreacted 1, 4- benzene dicarboxylic acid. From the region of 828 to 752cm^{-1} of the weak, medium and strong band can be assigned to C-C skeletal vibration and C=C-H bending vibration. The strong band at675cm^{-1} is assigned to C-H bending vibration where the metal-oxygen bond reacted. This is because, in comparison of 1, 4-benezenedicarboxylic acid spectrum and (Cu-MOF) spectrum, there is no similar peak found. The region 563cm^{-1} is assigned as ring in-and-out of plane bending vibration of the aromatic ring.

3.1 SCANNING ELECTRON MICROSCOPY (SEM)

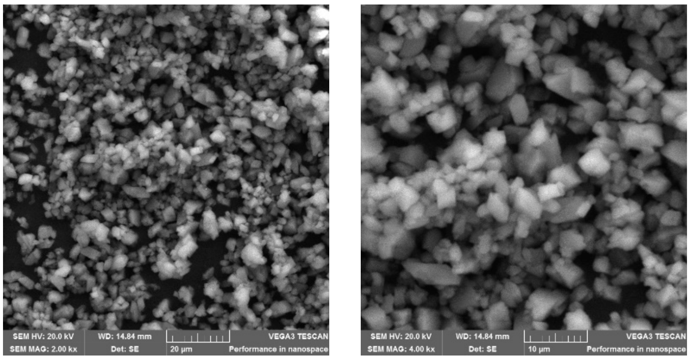


Figure 3.1 SEM image of Cu-MOF obtained. The scanning electron micrograph present irregular shaped crystals.

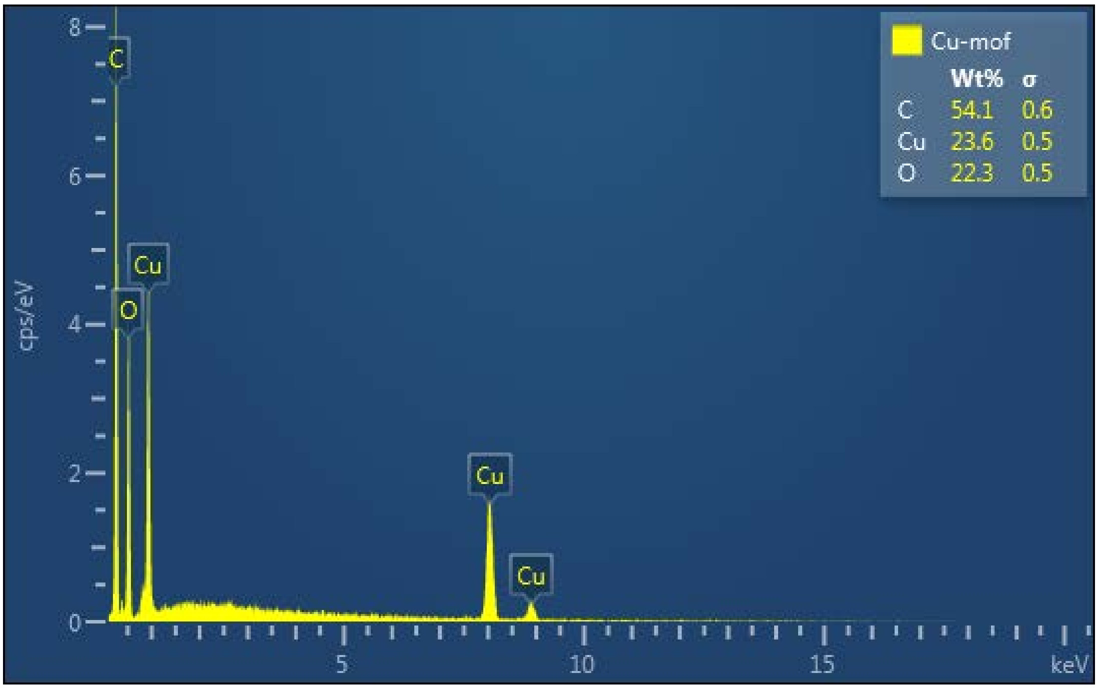


Figure 3.2 Energy Dispersive X-ray Spectroscopy (EDX) for Cu-MOF. The elemental analysis as observed from the EDX spectrograph shows the presence of Cu at 1, 8 and 9keV (kilo electron volt) and have 23.6% elemental composition in the Cu-MOF formed. Carbon (C), appeared 0.01keV and 54.1% elemental composition. Oxygen was identified at 0.5keV and have elemental composition of

22.3%. This shows the Cu-MOF was formed. The different peaks for Cu is as a result of the presence of its isotopes.

3.2 ADSORPTION STUDY REPORT

Table3.3a showing adsorption result by Cu-MOF

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

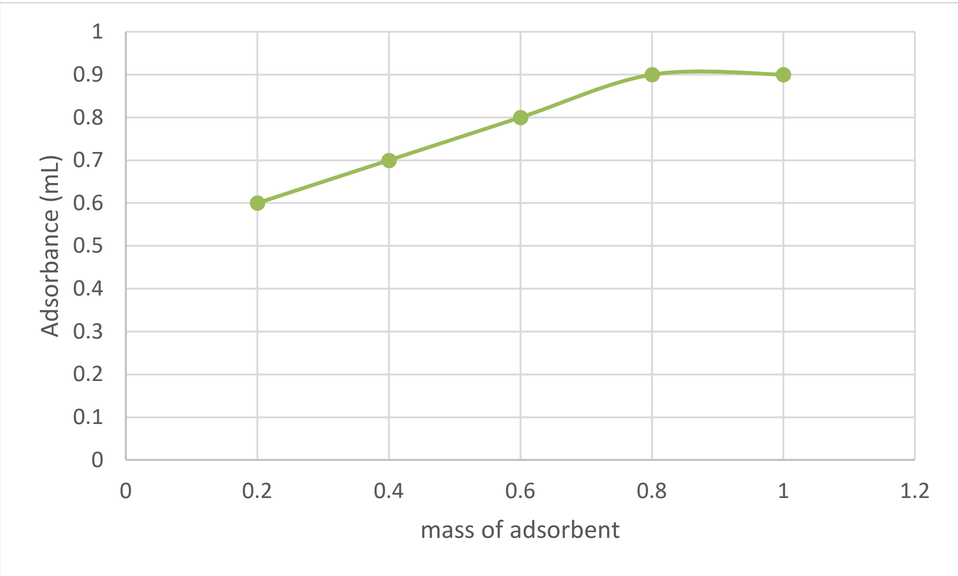


Figure 3.3a adsorption graph for Cu-MOF. From the table and the graph (3.3) section, the capacity for adsorption of the crude oil was seen be increasing with increasing mass (dosage) of Cu-MOF. The observation was quite intriguing. As a result, more analysis was done to truly ascertain the extent to which Cu-MOF can adsorb the crude oil by varying the volume of the crude oil and leaving the mass of Cu-MOF constant at 1gram. The result obtained is given as follows:

Table 3.3b The result

Volume of Crude oil in (mL)/1g of Cu-MOF	volume of crude oil Adsorbed (mL)
2.0	2.0
3.0	2.8
4.0	3.2

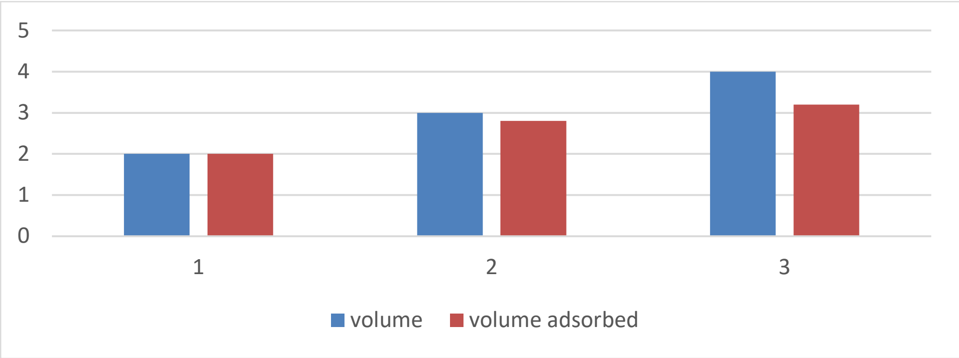


Figure 3.3b comparing the volume of crude adsorbed by varying the volume/1gram of Cu-MOF. Blue colour= original volume used. Red colour= volume adsorbed. The result has shown that Cu-MOF as the capacity to adsorb crude oil. 1gram Cu-MOF adsorbed 80% of the 4mL crude oil. This ability is credited to the properties such as large surface area etc. that are exhibited by MOFs.

Table 3.3c Composite of Cu-MOF/clay in gram(g)

Composite of Cu-MOF/clay in gram(g)	Volume of crude oil Adsorbed (mL)
0.2g	0.4
0.6g	0.4
0.8g	0.5

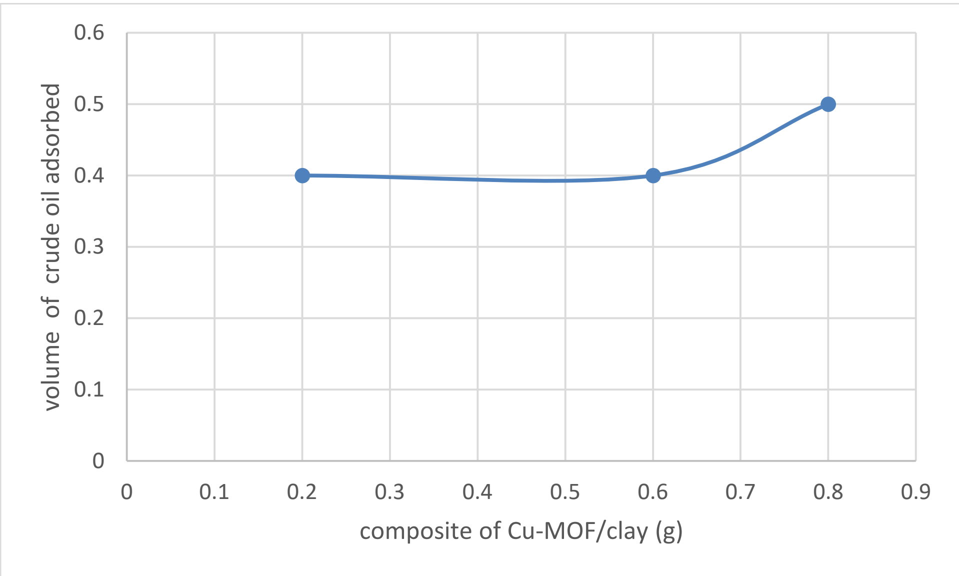


Figure 3.3c showing the adsorption of crude oil by composite of Cu-MOF/clay. The result obtained showed that 0.2 & 0.6g adsorbed 40% of the crude oil while 0.8g adsorbed 50% of crude oil. The performance as composite (Cu-MOF/clay) is poor, taking into consideration the performance of Cu-MOF alone. Clay did not improve on the capability of the Cu-MOF.

Table 3.3d Composite of Cu-MOF/charcoal in gram (g)

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

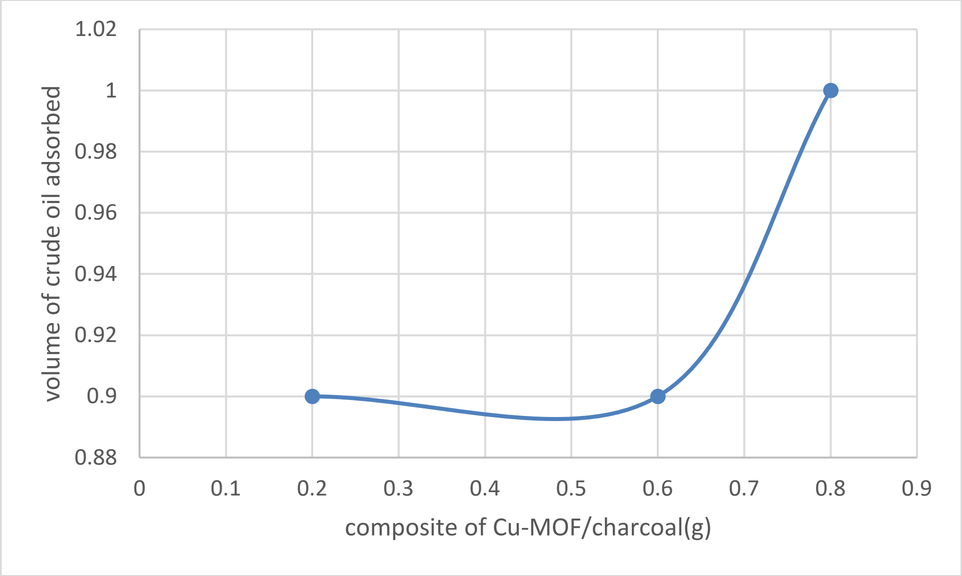


Figure3.3d showing the performance of Cu-MOF/charcoal composite. The result is uniquely outstanding. 0.2 & 0.6g in ratio 50/50 adsorbed 90% of the crude oil. 0.8g adsorbed 100% of the crude oil. The synthesis of MOFs is time consuming and expensive. With the result, it is cheaper to apply Cu-MOF/charcoal composite for the treatment/cleaning of crude oil spill on our water/river. It is cost friendly, hence cost effective.

Table 3.3e Volume of Crude oil 1mL/1g of Cu-MOF/pH

Volume of Crude oil 1mL/1g of Cu-MOF/pH	volume of crude oil Adsorbed (mL)
pH4.4	0.6
pH6.85	0.9
pH9.0	0.8

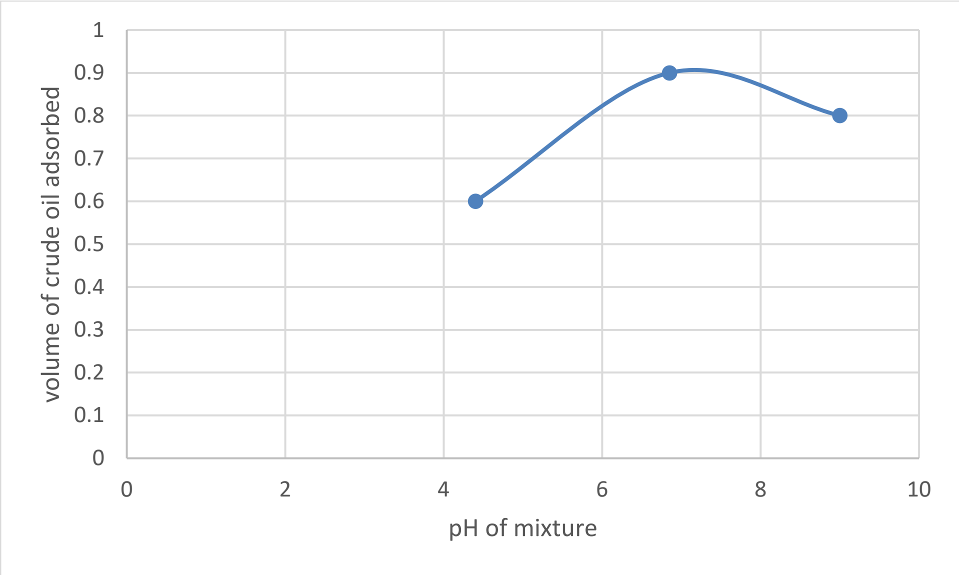


Figure 3.3e showing the effect of pH on the adsorption of crude oil. Looking at the curve, at pH4.4, 60% of the crude oil was adsorbed. As the pH increases to 6.85, 90% of the crude oil was adsorbed. Adsorption was observed to be decreasing towards pH9, although 80% of the crude oil was adsorbed at pH9. Lower pH (acidity) did not favour the adsorption of the crude oil as compared to high pH6.85 (weak acidity). Alkalinity (pH9), adsorbed better than lower (pH4.4).

4. CONCLUSION AND RECOMMENDATION

4.1 CONCLUSION

(Cu- MOF) was solvothermally synthesized using N, N-dimethylformamide as solvent and 1, 4-benzenedicarboxylic acid as the ligand. The solid crystalline metal organic framework of copper was characterized and compared with the 1, 4-benzenedicarboxylic acid spectrum. The spectrum showed there are changes in the wavenumbers when compared. The different functional group at different wavenumbers were influenced by the presence of the metal in the compound formed. The adsorption result for Cu-MOF as observed, have shown it to be a very efficient adsorbent for crude oil remediation. 1gram of Cu-MOF adsorbed 80% of the four-milliliter crude oil in the water. The composite of Cu-MOF/charcoal had an excellent sorption of the crude oil.

4.2 RECOMMENDATION

Cu-MOFs can be used for the cleansing of crude oil spillage. The importance of this study cannot be overemphasized as removal of crude oil from water bodies is crucial for controlling the effect of crude oil on human health and other toxicological effect associated with oil spillage.

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APPENDIX

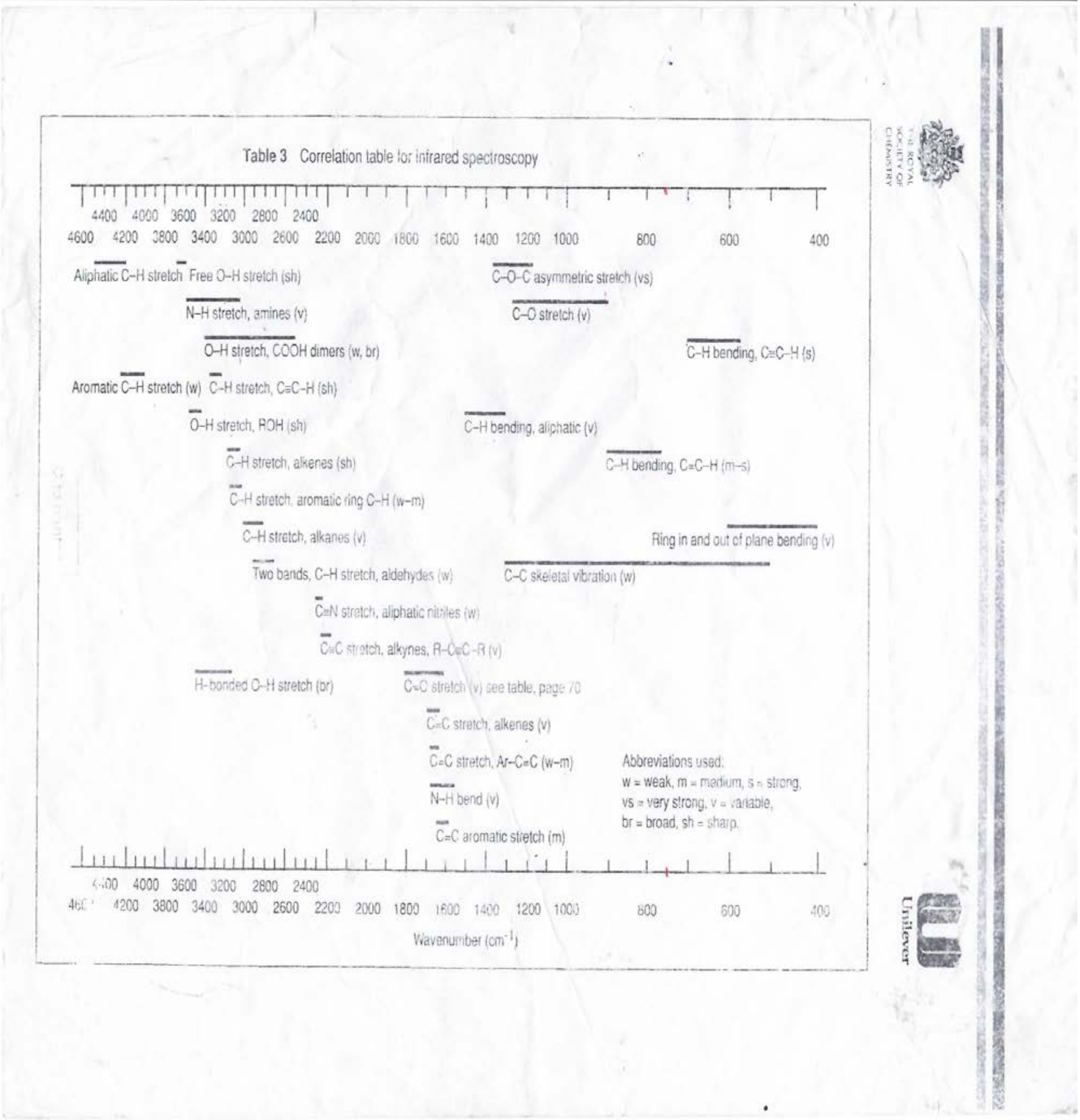
Table 3 Correlation table for infrared spectroscopy
4400 4000 3600 3200 2800 2400
4600 4200 3800 3400 3000 2600 2200 2000 1800 1600 1400 1200 1000 800 600 400
Aliphatic C–H stretch
Free O–H stretch (sh)
C–O–C asymmetric stretch (vs)
N–H stretch, amines (v)
C–O stretch (v)
O–H stretch, COOH dimers (w, br)
C–H bending, C≡C–H (s)
Aromatic C–H stretch (w)
C–H stretch, C≡C–H (sh)
O–H stretch, ROH (sh)
C–H bending, aliphatic (v)
C–H stretch, alkenes (sh)
C–H bending, C=C–H (m–s)
C–H stretch, aromatic ring C–H (w–m)
C–H stretch, alkanes (v)
Ring in and out of plane bending (v)
Two bands, C–H stretch, aldehydes (w)
C–C skeletal vibration (w)
C≡N stretch, aliphatic nitriles (w)
C≡C stretch, alkynes, R–C≡C–R (v)
H-bonded O–H stretch (br)
C=O stretch (v) see table, page 70
C=C stretch, alkenes (v)
C=C stretch, Ar–C=C (w–m)
Abbreviations used:
w = weak, m = medium, s = strong,
vs = very strong, v = variable,
br = broad, sh = sharp.
N–H bend (v)
C=C aromatic stretch (m)
Wavenumber (cm⁻¹)
Unilever