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A Preliminary Study on Removal of Metal Ions from Laboratory used Solution and Adsorption of CO2 by 1,4-Benzene di-carboxylic Acid MOF'S

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***Abstract*: MOFs have gained extensive explorations as a highly versatile platform for the development of novel materials with effective adsorption of metals from used up solutions (like volumetric solution) from chemical laboratory at educational institutions level, high carbon dioxide adsorption capacity and selectivity is becoming increasingly appealing for use in clean energy and pollution control applications. MOFs are sensitive and selective to particular pollutants and follow adsorption techniques to recover the pollutant particles. We have synthesized a new metal-organic frameworks (MOF) under mild hydrothermal routes using 1,4-Benzene di carboxylic acid as ligand. The prepared MOFs were analyzed by various techniques and adsorption studies were carried out using $KMnO_4$ solution and CO_2 gas adsorption.**

***Keywords*: CO_2 adsorption, 1,4-Benzene di carboxylic acid MOF, M – BDC, Adsorption metals from water**

I. INTRODUCTION

The steadily increasing CO_2 concentration in the earth's atmosphere has resulted in a slew of climate and environmental problems, necessitating the removal of this major greenhouse gas from the atmosphere (Changwei Chen et al., 2018). Along with this situation the contamination of water bodies also triggered in considerable rate by heavy metal ions and chemicals. This both conditions can be controlled by Metal Organic Frame Works (MOFs). Metal-organic frameworks (MOFs) are a relatively new class of porous, crystalline materials (Avery E. Baumann et al., 2019) formed by self-assembly of central metal ions or clusters and bridging organic ligand via coordination bonds (Luning Chenv et al., 2020), in which bivalent or trivalent aromatic carboxylic acids or N-containing aromatics are frequently used to form frameworks with zinc, copper, chromium, aluminum, zirconium, and other elements (Yu-Ri Lee et al., 2013). A large number of different metal ions and organic linkers can be used to make MOFs, resulting in an enormous number of different structures of varying pore dimensions, geometry and functionality (Pablo Cubillas et al., 2014). MOFs are Featured with extremely high surface area (typically ranging from 1000 to 10,000 m2/g), large porosity, tunable pore size, and flexible functionality, MOFs have gained extensive explorations as a highly versatile platform for functional applications in many research fields (Long Jiao et al., 2020).With this interest we studied the interaction and stability of bonds between metal clusters (like Nickel, Copper, Zinc, Zirconium, Cadmium, Aluminium) and ligand (1,4-Benzene di carboxylic acid) their stability in the Metal organic frame works and analyze the adsorption of metal ions in aqueous medium.

Experimental Session

Metals (Nickel(II) chloride hexahydrate, Copper (II) nitrate trihydrate, Zinc nitrate hexahydrate, Zirconium(IV) oxychloride, Cadmium(II) nitrate tetrahydrate, Aluminium nitrate monohydrate) and linker terepthalic acid (1,4-Benzene di carboxylic acid) were taken in 1: 2 ratio and dissolved in DMF. The pH was maintained at 8 and stirred for 12 hours. The precipitate was washed with ethanol and dried at 80˚C for 3 hours in a hot air oven, then kept in desiccator for few days to remove the unrevoked moisture content, after that it was stored in an air tight container[1]. All the six MOFs were prepared in the similar way: Ni - BDC, Cu - BDC, Zn - BDC, Cd - BDC, Zr - BDC, Al – BDC and structural properties of the synthesized

MOFs characterized using various techniques like FTIR (Shimadzu IR spectrometer), Thermo Gravimetric Analysis (TG/DTA - EXSTAR/6300), Powder X-Ray Diffraction Studied (X'Pert Pro PANalytical), Field Emission Scanning Electron Microscopy (Jeol JSM 6390 Scanning Electron Microscope.).

The CO_2 adsorption analysis was carried out by conventional method to study the CO_2 adsorption performance of Co-BDC MOF. Here, we have used Calcium carbonate and concentrated Hydrochloric acid to produce carbon dioxide gas.

II. Results and Discussion

FT-IR Spectral Analysis

The sharp peak with high intensity from 1400 cm^{-1} to 1600 cm^{-1} indicates the asymmetric and symmetric stretching modes of coordinated carboxylic acid. The mid intense bands at 700 to 800cm^{-1} were attributed to C-H bending modes of the aromatic ring. The characteristic coordination bonds of Metal-oxygen were observed at the lowest wavenumber from 400-600cm^{-1}. The broad peak in the spectral region of 3600-3800 cm^{-1} was due to acidic OH of carboxylic acid (Reda S. Salama et al., 2018), (Duyen Thi Cam Nguyen et al., 2019). The presence of bonding between organic linker and metal species is confirmed by the above FT-IR spectrum values, suggesting the development of MOF framework.

TABLE 1

FT-IR Spectroscopy of synthesized MOFs

Functional Groups / Synthesized MOFs	O-H	γas (C-O)	γs C-O	C-H	M-O
	Wavenumber(Cm-1)				
Cr-BDC	3700	1558.48	1411.89	740.67	462.92
Mn-BDC	3718.76	1558.48	1411.89	740.67	432.05
Fe-BDC	3446.79	1558.48	1411.89	740.67	520
Co-BDC	3633.89	1558.48	1411.89	740.67	493.78
Mg-BDC	3650	1558.48	1411.89	740.67	455.20
Sr-BDC	3564.45	1566.20	1411.89	740.67	516.92
Ni-MOF	3700	1558.48	1411	825	455
Cu-MOF	3657.04	1558.48	1396.46	825.53	462.92
Zn-MOF	3442.94	1562.34	1409.96	829.39	450.00
Cd-MOF	3603	1558	1411	825	470
Zr-MOF	3700.00	1558.48	1411.89	825.53	578.64
Al-MOF	3471	1558	1411	825	470

Powder X-RAY Difraction

The sharpness of the peak in the XRD pattern shows the sample's crystalline nature. The X-ray diffraction pattern of Co-BDC and Cu-BDC MOF is shown in Fig: 2 The relative crystallinity was calculated by using the diffraction peaks at 2Θ values at 17.20, 19.19, 30.78, 32.56, 38.08, 51.53, 58.02 and 61.76° of Co-BDC MOF and for Cu-BDC MOF 2Θ values at 30.7153, 9.2057, 17.1563. This infers about the coordination of metal with ligand to form complex (Omkaramurthy B M et al., 2020).

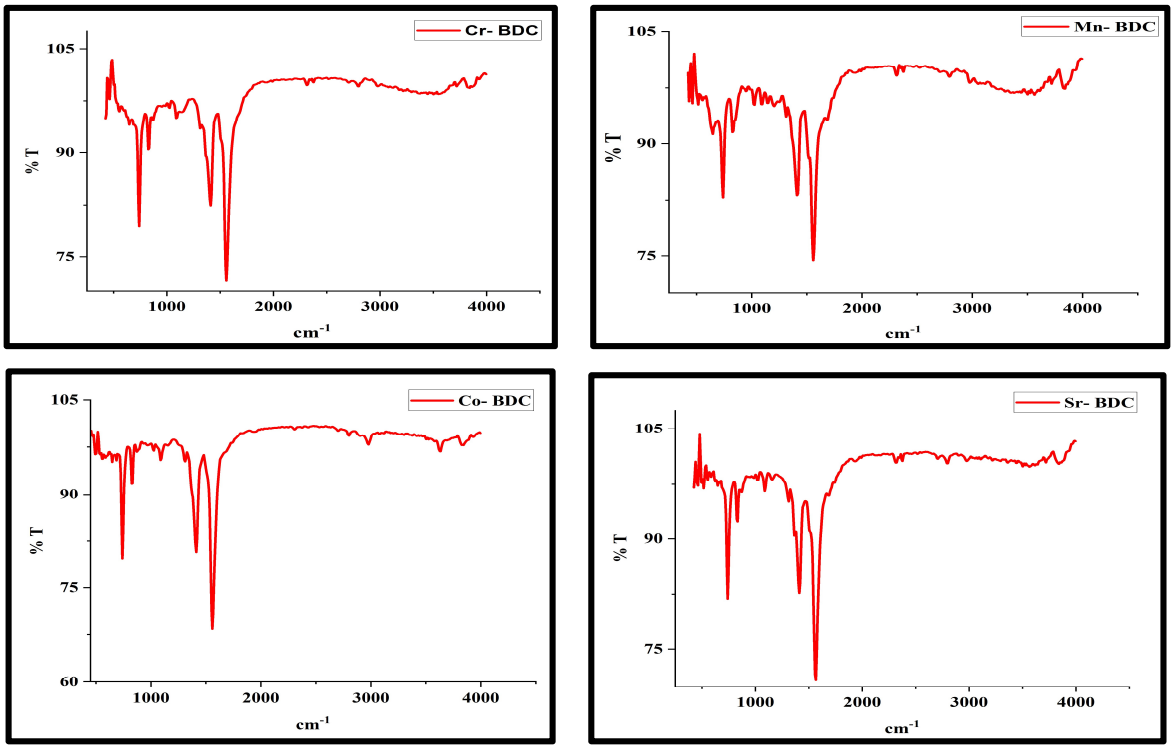

Fig. 1 FT-IR Spectra of Metal - BDC MOF

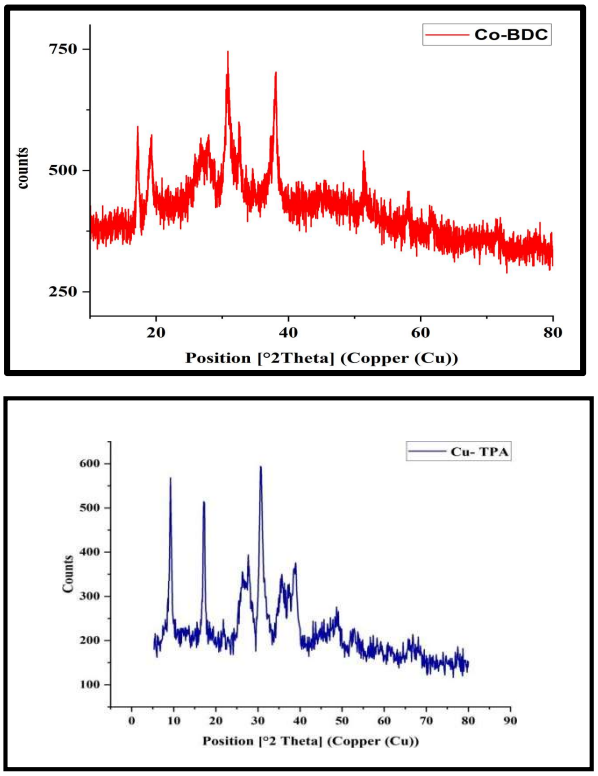

Fig. 2 P-XRD pattern of Co- BDC MOF and Cu-BDC MOF

These details can be enumerated from the peaks and values of the graph with the help of scherrer equation. The sharp peaks on the graph represent the crystalline nature of the analyte Co-BDC. The graph obtained from Powder XRD analysis of Cu based MOF holds few sharp peaks and many dwarf peaks represent that the analyte is a semi crystalline in nature.[110]

TABLE 2
Crystal Size Calculation

Position (2Θ)	FWHM (2Θ)	d-spacing(Å)	Crystalline size (nm)
P-XRD pattern of Co- BDC MOF			
17.2029	0.2676	5.15469	31.35
19.1933	0.5353	4.62438	15.71
30.7850	0.4684	2.90449	18.37
32.5670	0.2676	2.74952	32.29
38.0849	0.4015	2.36289	21.65
51.5344	0.4015	1.77343	22.73
58.0289	0.4015	1.58946	23.41
61.7694	0.8029	1.50189	12.03
P-XRD pattern of Cu-BDC			
30.7153	1.06030	2.90815	8.12
9.2057	0.86950	9.59748	9.58
17.1563	0.79260	5.16431	10.59

Thermogravimetric Analysis

Weight loss of MOF begins at 150°C indicating the framework of Co-BDC MOF and Cu-BDC MOF was stable below 150°C. The weight loss of MOF was from 150-210°C, which was ascribed to the loss of coordinated DMF molecules. A second weight loss between 360-420°C indicates the decomposition of dicarboxylate linker and another weight loss between 540-630°C is ascribed to the totally decomposition of the MOF structure, while the residual materials are converted into metal oxide (Ijlal Aamer et al., 2021), (Aisha Asghar et al., 2019)

TABLE 3
Range of Decomposition

Temperature range(˚C)	Compound eliminated
150 - 210	DMF(Solvent)
200 - 450	Organic linker(BDC)
500 - 800	Metals as oxides

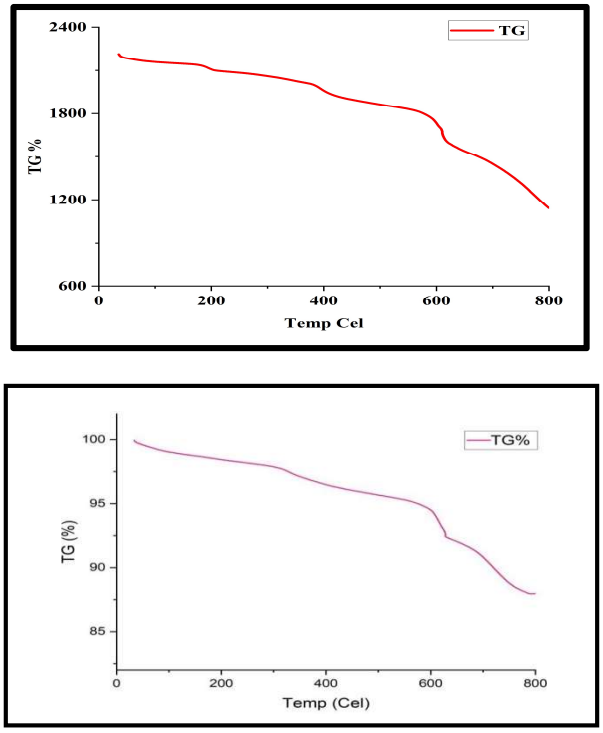

Fig 3 Thermogravimetric analysis of Co- BDC and Cu-BDC MOF

Field Emission Scanning Electron microscope (FESEM)

Scanning electron microscopy is a technique that enables the study of the microstructure of MOF. FE-SEM micrographs of Co- BDC MOF is presented in Fig: 4 (a, b, c, shows the distribution of particles in Co- BDC MOF with wide range of dimension. It can be identified from Fig: 4 (d & e) that the distribution of particles in Cobalt MOF is irregular shaped flakes arranged as flower- like clusters. (Ezekiel Dixon Dikio et al., 2013) The particle size was calculated as 2.7273 µm of Cu-BDC MOF

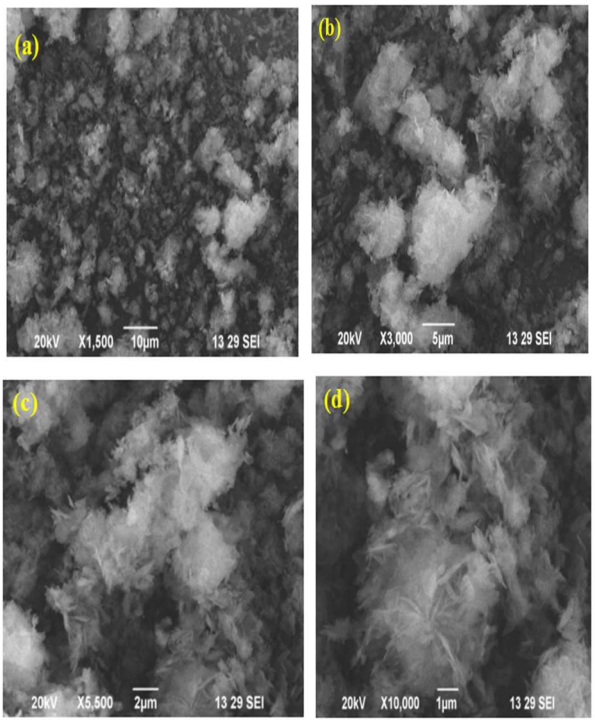

Fig. 4 FE-SEM micrographs of Co- BDC MOF with different magnifications

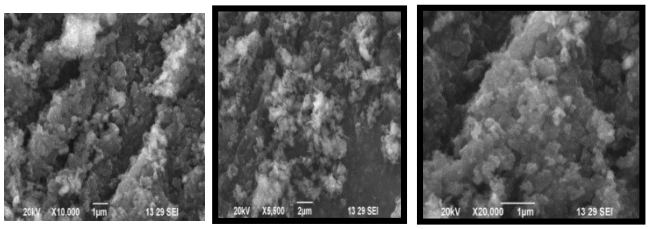

Fig. 4.1 FESEM images of Cu-BDC Metal Organic Frame work

Carbon Dioxide Adsorption Study

CO_2 adsorption into Co- BDC MOF was confirmed by observing the colour change from Dirty white to Pale dirty white and finally Distemper green on exposing it to CO_2 atmosphere for 5hrs. CO_2 adsorption into Co- BDC MOF is further confirmed by FT-IR, TGA and Weight gain method.

Fig. 5 Colour Change in Co- BDC MOF during CO_2 adsorption

The comparison of FT-IR spectrum of Co- BDC MOF before and after CO_2 treatment confirms the adsorption of CO_2 into Co- BDC MOF by CO_2 peak. The FT-IR spectrum of raw Co- BDC MOF displayed two characteristic band at 1558.48cm^{-1} and 1411.89cm^{-1} which corresponds to asymmetric and symmetric stretching mode of coordinated carboxylic acid. The band at 740.67cm^{-1} was attributed to C-H bending modes of aromatic ring. The characteristic coordination bond between metal-oxygen was observed at 493.78cm^{-1}. The broad band in the spectral region of 3633.89cm^{-1} was due to acidic OH of carboxylic acid (Duyen Thi Cam Nguyen et al., 2019)

The FT-IR spectrum of Co- BDC MOF after CO_2 adsorption displayed two characteristic band at 1674.21cm^{-1} and 1566.20cm^{-1}, related to asymmetric and symmetric stretching mode of carboxylic acid. The band at 732.95cm^{-1} was associated with C-H bending modes of aromatic ring, The characteristic band at 455.20cm^{-1} was due to metal-oxygen bond. The spectral band at 3700cm^{-1} was due to acidic OH of carboxylic acid (Duyen Thi Cam Nguyen et al., 2019)

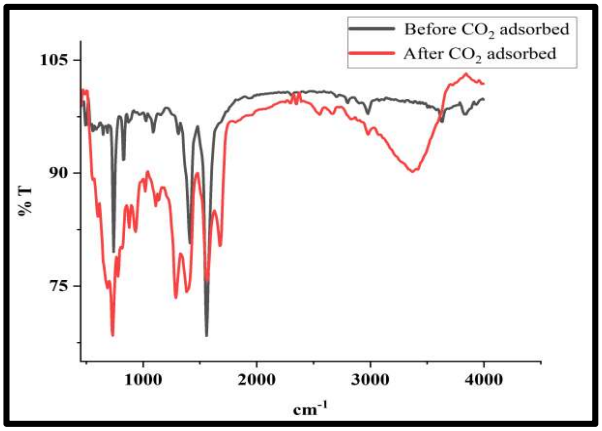

Fig. 6 FT-IR Spectrum of Co- BDC MOF before and after CO_2 adsorption

All of the characteristic peaks of raw Co- BDC MOF were retained in the FT-IR spectra of CO_2 adsorbed Co- BDC MOF. The asymmetric stretching mode of adsorbed CO_2, that was not seen in raw Co- BDC MOF FT-IR, was responsible for the formation of a new vibration band at 2353.16cm^{-1}. The occurrence of this peak was due to CO_2 interacting with the unsaturated metal centre through its oxygen atom (Nour Nijem et al., 2012). Thermal decomposition process for Co- BDC sample after exposing to CO_2 atmosphere for 5hours was examined using TGA technique.

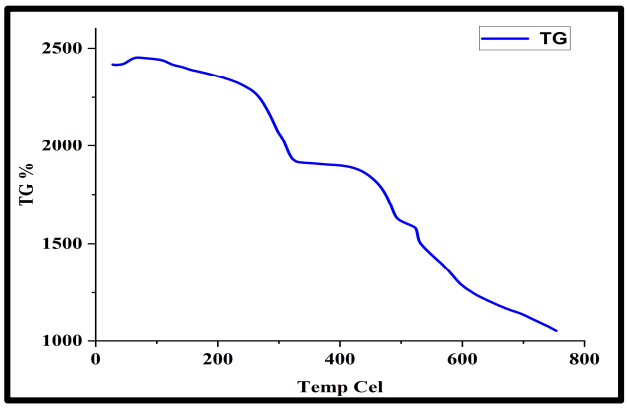

Fig. 7 Thermogravimetric analysis of CO_2- adsorbed Co- BDC MOF

The first weight loss between 50°C - 140°C is caused by the elimination of physically adsorbed DMF solvent. The second weight loss between 170°C - 310°C corresponds to the chemisorbed CO_2. The third thermal decomposition between 390°C - 480°C is due to the loss of dicarboxylate linker. Another weight loss between 500°C - 540°C is due to the complete metal- oxide formation, and at that temperature there will be complete regeneration of CO_2 (Gutierrez-Bonilla Elvira et al., 2016).

Weight Gain Method

Weight difference was noted before and after exposing the Co- BDC MOF for 5hrs. The difference between initial and final mass of MOF sample determine the CO_2 adsorption capacity of the MOF. Weight of Boiling tube with sample= 33.0213g. Weight of Boiling tube with sample after exposing to CO_2 gas for 5hrs= 33.0730g. Difference between initial and final mass= 0.0517g, thus this weight difference also confirms the presence of CO_2 in the MOF sample.

Removal of metals by adsorption technique

Adsorption studies were carried out with Potassium Permanganate Solution ($KMnO_4$). Their adsorption reaction was characterized by Ultra Violet Spectroscopy and Infrared Spectroscopy. The deep violet colour of Potassium Permanganate ($KMnO_4$) is due to MLCT (Metal Ligand Charge Transfer) effect, $KMnO_4$ absorb at 500-550nm.

Procedure for adsorption

By adding the MOF material of 0.5 g in 20 ml of 0.1N concentrated Potassium Permanganate ($KMnO_4$) solution then introduced to shake for 30mins using an electronic shaker and the solution was allowed to settle down for 1 hour. The MOF materials were completely settled down, violet colour Potassium Permanganate ($KMnO_4$) solution become colourless and transparent, which was centrifuged. This solution was taken to UV studies. There was absorbance at the region of 200nm - 400nm, not at visible region 400nm-800nm. Because all the metal ions of Potassium Permanganate ($KMnO_4$) were adsorbed by the MOF material. Adsorption was performed separately for each synthesized MOF in separate containers in the same time.

Fig. 3(a) Potassium Permanganate ($KMnO_4$) solution before addition of MOF

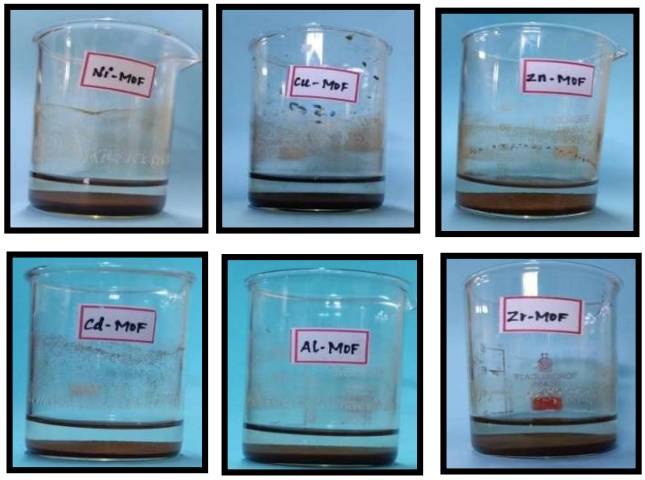

Fig. 3(b) $KMnO_4$ solutions after adsorption

UV Peaks for Potassium Permanganate ($KMnO_4$) solution after adsorption by addition of Ni-MOF, Cu-MOF, Zn-MOF, Cd-MOF, Zr-MOF and Al-MOF materials individually.

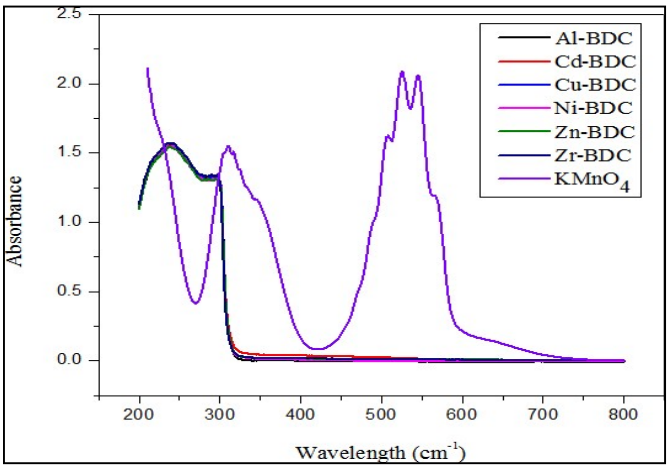

Fig. 4 Comparison of UV spectra of adsorption of $KMnO_4$ by Metal organic frameworks Ni-MOF, Cu-MOF, Zn-MOF, Cd-MOF, Zr-MOF and Al-MOF

UV graph for Potassium Permanganate ($KMnO_4$) without MOF contains higher absorbance at 400nm-800nm range for potassium ions and manganite ions (contains Manganese metal). But in the UV graph of Potassium Permanganate ($KMnO_4$) solution after mixing the MOF material has no absorbance at visible region, which confirms the adsorption of potassium and manganite ions by the MOF particles added to the Potassium Permanganate ($KMnO_4$) solution.

Absorption studies by Infrared Spectroscopy (FTIR)

In FTIR spectroscopic result of pure Potassium Permanganate ($KMnO_4$) solution shows transmittance peaks at 2800 cm^{-1}, 1450 cm^{-1} and 500- 600 cm^{-1}.Intense transmittance peak at 500-600 cm^{-1} indicates the Mn-O (metal- oxygen) strong bonding on $KMnO_4$.Transmittance peak at 1450 cm^{-1} is due to water molecules of the solvent. Transmittance peak at 2800 cm^{-1} is because of hydrogen bonding within the $KMnO_4$ solution.[8]

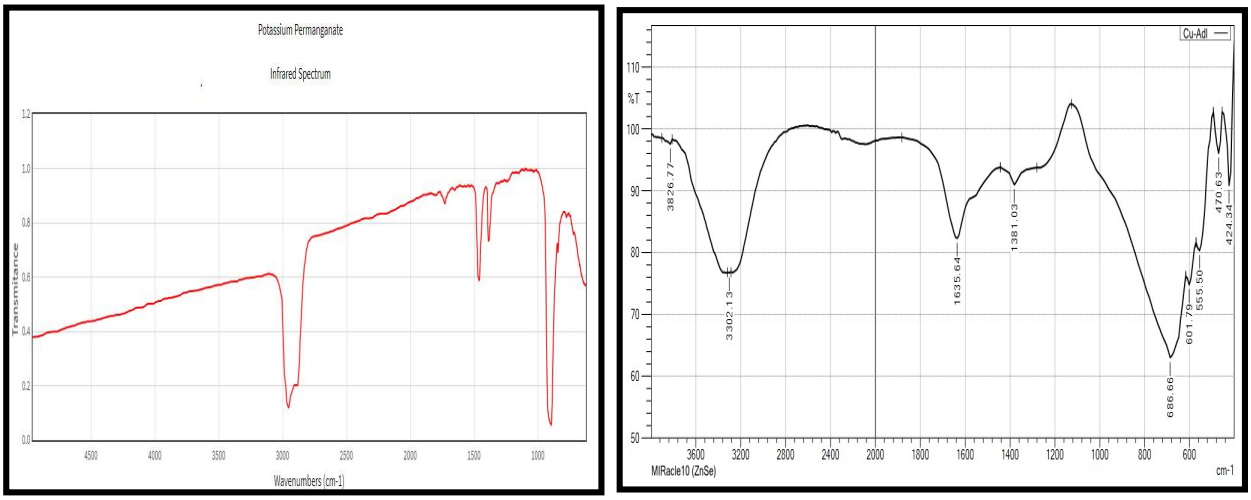

Fig. 5 (a) FTIR spectroscopy result for pure Potassium Permanganate ($KMnO_4$) solution. 2021 by the U.S. Secretary of Commerce on behalf of the United States of America. 5(b) FTIR spectroscopic result of Potassium Permanganate ($KMnO_4$) solution after the adsorption study done with the Metal Organic Frame work, Cu-BDC.

The FTIR result of MOF solution after adsorption of $KMnO_4$ does not show the peaks of manganite ions and potassium ions. This absence of FTIR peaks at exact position as in the result of pure Potassium Permanganate ($KMnO_4$) solution shows that there is no Potassium (K^+) and Manganate (MnO_4^-) ions remain in the Potassium Permanganate ($KMnO_4$) solution after the adsorption by synthesized Metal Organic Frame works. Thus we are confirming that, the metal adsorption taken place by the MOF materials.

III. Conclusion

The synthesized MOFs were highly water stable and insoluble in all commonly used solvents which confirm the formation of MOF. Presence of various functional groups like O-H, γ_{as} (C-O), γ_s C-O, C-H has been confirmed by FT-IR analysis. Further, the peaks around 400-550cm^{-1} indicates the formation of Metal-oxo bond between metal and the ligand. This results also confirms the formation of MOF. The semi-crystalline nature of Co- BDC MOF was confirmed by P-XRD results. The crystalline size of the MOF particle is calculated using Scherrer equation. During CO_2 adsorption process, characteristic colour change was noted from Dirty white to Pale Dirty white and finally Distemper green color which indicates the CO_2 adsorption into the framework.

FT-IR results after CO_2 adsorption showed a characteristic peak at 2353.16cm^{-1}. The occurence of this peak is due to the interaction of CO_2 with unsaturated metal centre, which confirms its adsorption into the framework. TGA result showed weight loss between 170 - 310°C which indicates the weight loss of chemisorbed CO_2. A weight difference of 0.01517g was observed in the Co- BDC MOF before and after CO_2 adsorption, indicating that CO_2 has been absorbed into the framework.

Conflicts of interest: All authors declare that they have no conflicts of interest.

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