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Metal Organic Frameworks of Ethylenediaminetetraacetic acid as Chemosensors for Heavy Metal Ions in Water

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ABSTRACT

Metal organic frameworks of zinc, copper and manganese with ethylenediaminetetraacetic acid have been synthesised using a solvothermal approach. They have been characterised using IR, PXRD, SEM, EDAX and UV spectral analyses. The efficiency of these MOFs in the sensing of toxic heavy metal ions such as cadmium, lead and chromium was analysed using the changes observed in the UV absorption spectra. Their efficiency in sensing these ions in water having a mixture of these ions have also been analysed.

Keywords: Metal organic frameworks, ethylenediamine tetraacetic acid, chemosensor,zinc, copper, manganese

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INTRODUCTION

Metal organic framework (MOF) materials are potential storage materials (energy carriers) suitable for gas uptake such as hydrogen, carbon dioxide, methane etc. The design of low-cost, light-weight metal organic framework (MOF) materials can probably reduce the escalating atmospheric level of carbon dioxide caused by fossil fuels. Increasing demand for timely and accurate environmental pollution monitoring and control requires new sensing techniques with outstanding performance, i.e., high sensitivity, high selectivity, and reliability. MOF-based sensing platforms have been reported for environmental contaminant detection including anions, heavy metal ions, organic compounds, and gases. [1-8]

Heavy metal ions are one of the non-biodegradable pollutants in the water environment. Some heavy metal ions including, lead (Pb), mercury (Hg), arsenic (As), chromium (Cr), and cadmium (Cd) are considered to be highly toxic and hazardous to human health even at trace level. MOFs have been widely utilized for chemical detection in an aqueous solution owing to their unique characteristics for selective capture and determination of analytes. Their porosity and large surface area enable the

reversible adsorption and release of target molecules. Therefore, many MOF-based sensors have been reported for heavy metal ion detection in water. [9] Residents of Flint, Michigan are suffering from high toxic levels of lead in their water due to incompetent governance. Unfortunately, water quality issues are not a recent development. Industrial dumping, pesticide runoff, leaky storage tanks, and government mandates have created big concern worldwide.

In the present work, we have synthesised metal organic frameworks of Zn, Cu and Mn with the ligand, ethylenediamine tetraacetic acid (EDTA) under solvothermal conditions for analysing the efficiency of these MOFs in sensing the toxic elements present in water.

MATERIALS AND TECHNIQUES

All the chemicals used for synthetic purpose were of analar grade. A.R quality Zinc Sulphate, Copper Acetate and Manganese Sulphate were used for the present investigation. Dimethyl Formamide was used as the solvent for the preparation of MOF. Ethylenediaminetetraacetic acid (EDTA) is used as the ligand in the present study.

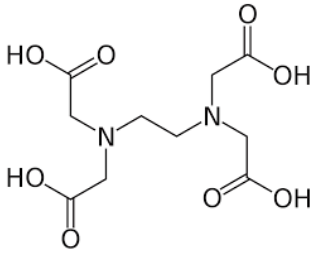

Figure 1: Ethylenediaminetetraacetic acid

Physico-Chemical Measurements

The IR analyses of the samples were carried out using KBr pellet method with Perkin-Elmer spectrometer at Department of Chemistry, MG College, Kesvadasapuram, Thiruvananthapuram, Kerala. PXRD studies were recorded using BRUKER D8 advanced X-ray Diffractometer at Department of Physics, TKM Arts and Science College, Kollam. The graph is obtained as intensity versus 2θ in accordance with Debye-Scherrer method.

$$D = 0.94\lambda / \beta \cos\theta$$

Where D= average crystal diameter, Beta (β) = full width at half maximum, theta (θ) = diffraction angle, Lambda (λ) = wavelength of incident radiation.

SEM images of samples have been recorded using FE-SEM, FEI Quanta FEG 200 at SAIF IIT Madras. EDX analyses of the samples were done using F E I Quanta FEG 200 with EDX at SAIF IIT Madras. The liquid UV studies for the present study were recorded using UV Schimadzu at the Department of Chemistry, TKM Arts and Science College, Kollam.

Methods of Preparation

Syntheses of MOFs of Zinc, Copper and Manganese with EDTA

Metal salt [Zinc sulphate for ZnEDTA MOF, Copper acetate for CuEDTA MOF and Manganese sulphate for MnEDTA MOF] and ethylenediaminetetraacetic acid in 1:1 ratio were mixed thoroughly with 10 ml of DMF. The mixture was transferred into an autoclave and heated at 150^0c for 72 hours. It is cooled, filtered and washed with DMF. The MOF was dried in a desiccator over silica crystals.

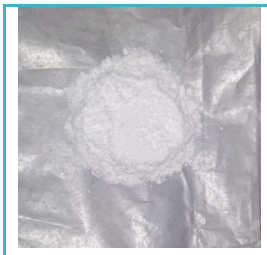

Figure 2: ZnEDTA MOF

Figure 3: CuEDTA MOF

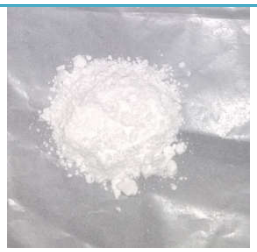

Figure 4: MnEDTA MOF

RESULTS AND DISCUSSION

Metal organic frameworks of zinc, copper and manganese with ethylenediaminetetraacetic acid have been prepared. They have been characterized using IR, UV, PXRD, FE-SEM, and EDX. Copper MOF is coloured and the other two are colourless. All the three are soluble in water.

Infrared Spectral Studies

In the IR spectrum of the ligand (EDTA) there is a strong band at 3027.67 cm^{-1} due to the O-H stretching of the carboxylic acid group in EDTA. Strong and intense band at 1611.99 cm^{-1} corresponds to the C=O stretching of carbonyls. C-H band of alkanes is shown at 1475 cm^{-1}. C-O stretching is obtained at 1315.1cm^{-1} while C-N stretching vibration is obtained at 1292.29 cm^{-1}. (Fig. 5).

In the IR spectra of the as synthesised MOFs, the peak corresponding to C=O stretching of the ligand undergoes an appreciable shift in frequency indicating the interaction of the metal ion with the carboxyl group of EDTA indicating the formation of MOFs as evidenced from EDX analysis. (Fig. 6-8, Table 1). Intense band around 710 cm^{-1} is a clear indication of O-M-O symmetric stretch in these MOFs. There is a reduction in the C-N stretching frequencies in the MOFs indicating the interaction of the metal ions with the N atom in EDTA.

Table 1: IR spectral data of MOFs

Assigned peaks	Ligand (EDTA)	ZnEDTA MOF	CuEDTA MOF	MnEDTA MOF
C=O	1611	1735.6, 1615.9	1588.5	1574.8
C-O	1315.51	1376.5	1314.9	1328.6
C-N	1292.29	1116.5	1109.7	1109.7
O-H bend	957	957	918.1	859.96
O-M-O	---	716.3	706.04	709.46

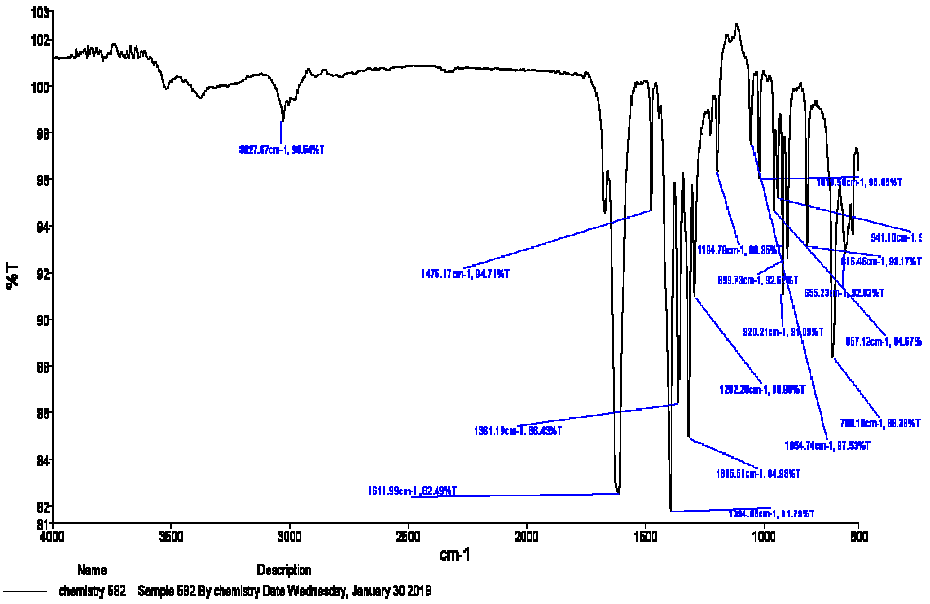

Figure 5: IR spectrum of EDTA ligand

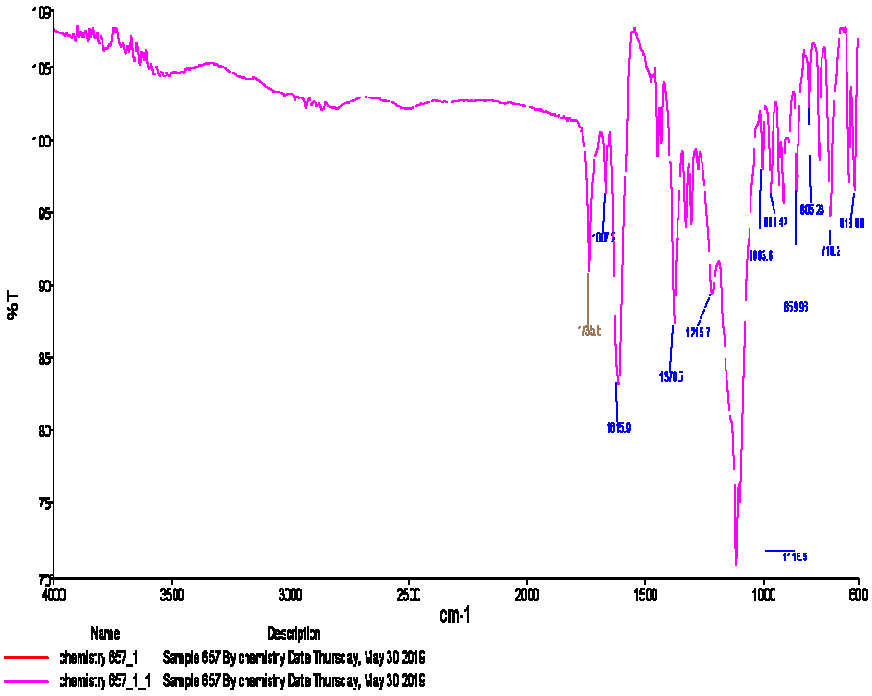

Figure 6: IR spectrum ZnEDTA MOF

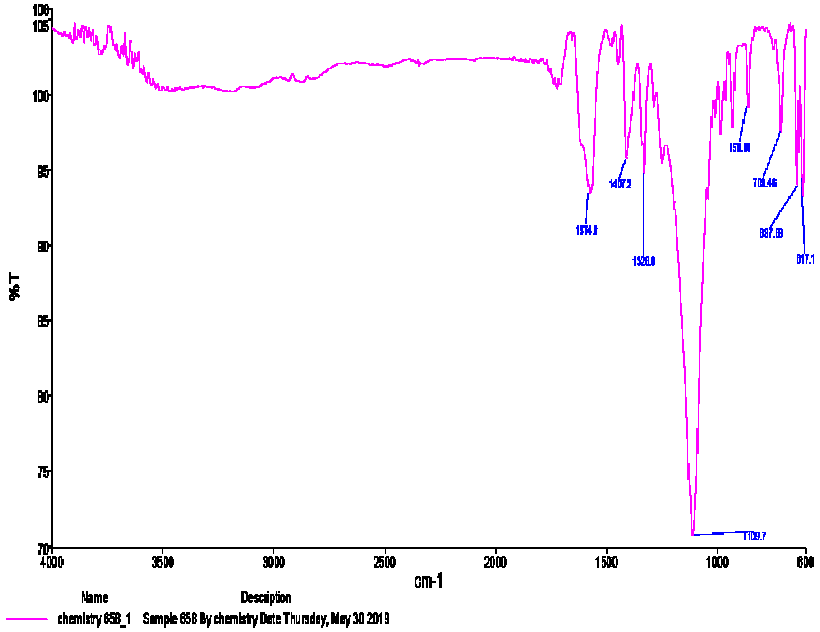

Figure 7: IR spectrum of MnEDTA MOF

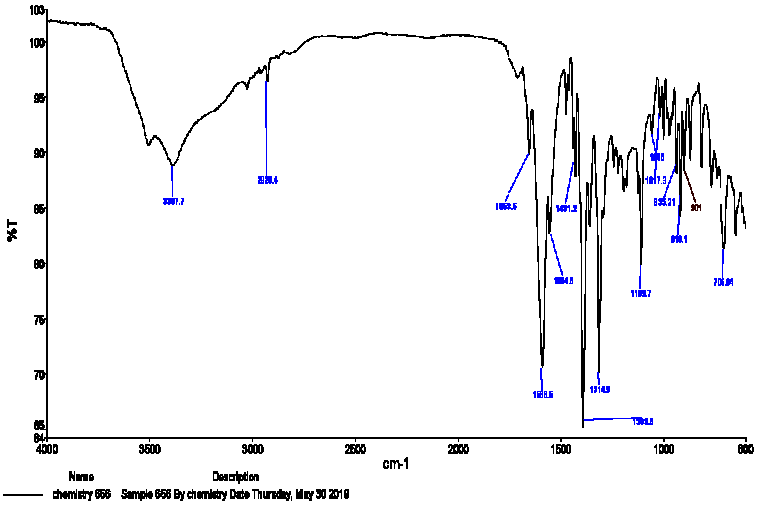

Figure 8: IR spectrum of CuEDTA MOF

Powder XRD Analysis

Powder XRD analyses of MOF samples have been carried out and the average grain sizes have been calculated with Debye Scherrer equation. The average crystallite sizes of ZnEDTA MOF, MnEDTA MOF and CuEDTA MOF are found to be 48.56 nm, 50.42 nm and 31.34 nm respectively. The sharp peaks in PXRD indicate the crystalline nature of all these MOFs.

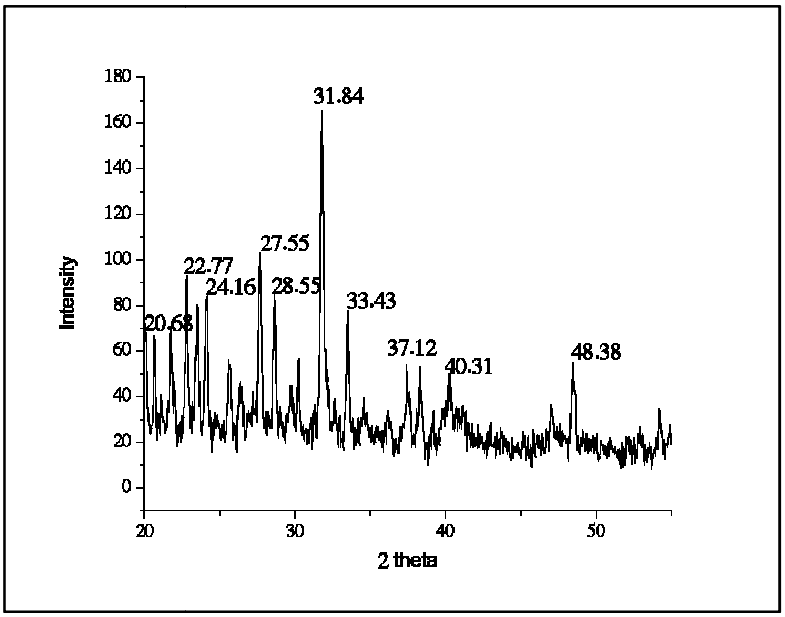

Figure 9: PXRD pattern of ZnEDTA MOF

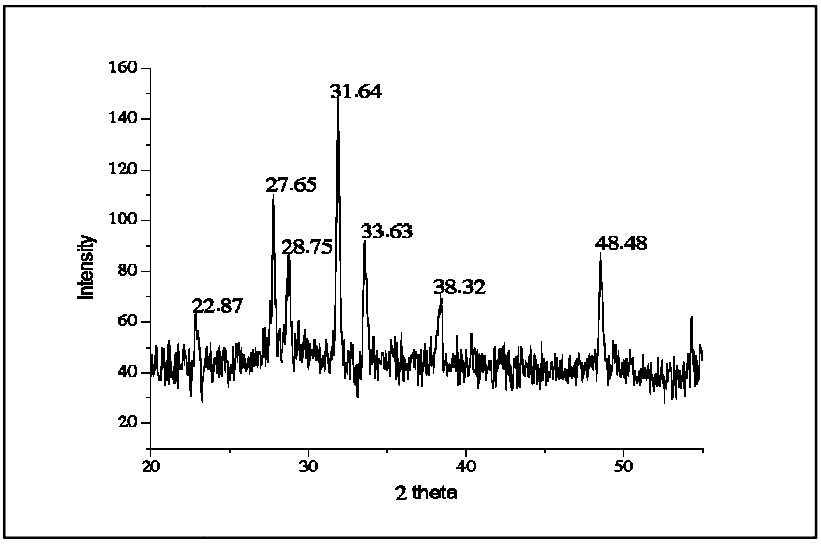

Figure 10: PXRD pattern of MnEDTA MOF

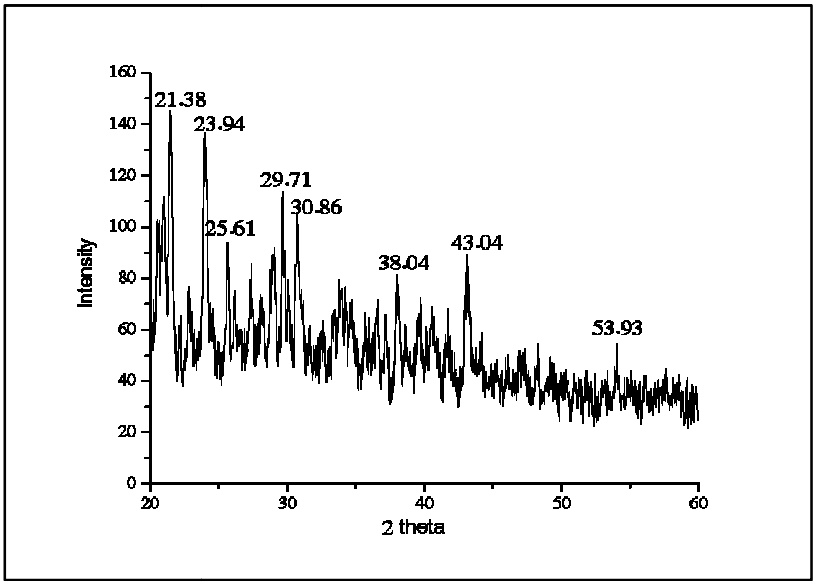

Figure 11: PXRD pattern of CuEDTA MOF

The powder XRD pattern of the synthesized MOFs are shown in Figs. 9-11. The high intensity Bragg diffraction peaks are obtained at 2Θ= 22.77, 27.55, 31.84, 33.43, 48.38° in ZnEDTA MOF (Fig. 9); at 2Θ= 27.65, 28.75, 31.64, 38.32, 48.48° in MnEDTA MOF (Fig.10) and at 2Θ= 21.38, 23.94, 29.71, 30.86, 43.04° in CuEDTA MOF (Fig. 11).

SEM Analysis

Size and morphology of the synthesized MOF are confirmed using FE-SEM studies. Figures from 12 to 14 show the SEM images of CuEDTA MOF, MnEDTAMOF and ZnEDTA MOF respectively. CuEDTA MOF shows hexagonal morphology; MnEDTA MOF shows rod-like structure and ZnEDTA MOF shows pointed rod-like morphology comparable to scattered nails.

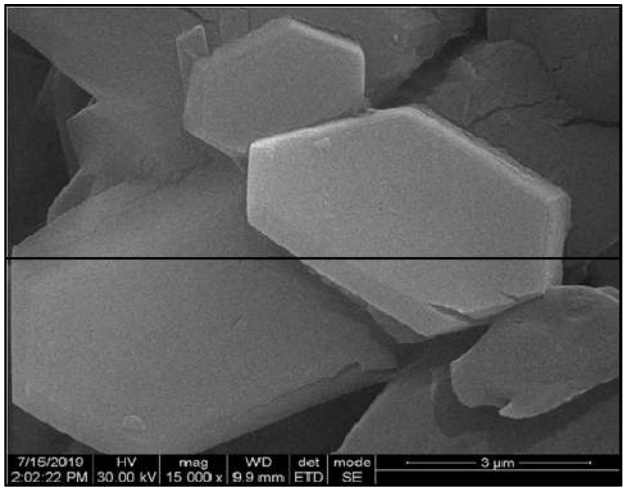

Figure 12: FE SEM images of CuEDTA MOF

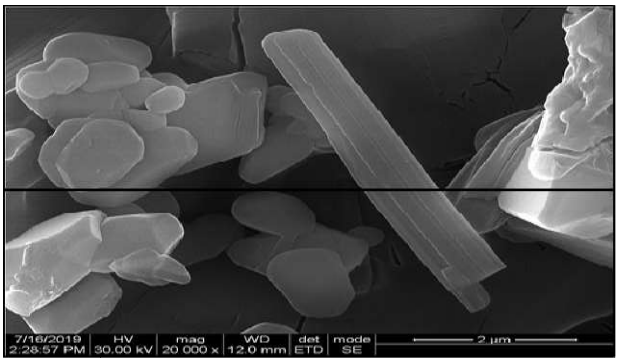

Figure 13: FE SEM image of MnEDTA MOF

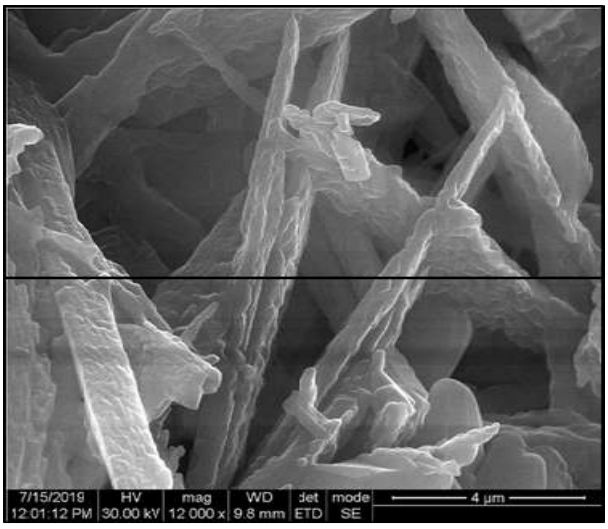

Figure 14: FE SEM image of ZnEDTA MOF

Energy Dispersive X-ray Spectroscopic Studies
EDX spectra of the as synthesised MOFs are shown in the figures from 15-17. The corresponding elemental composition in percentage is given in Tables 2-4. The MOF formation can be confirmed from the presence of expected elements in the spectra.

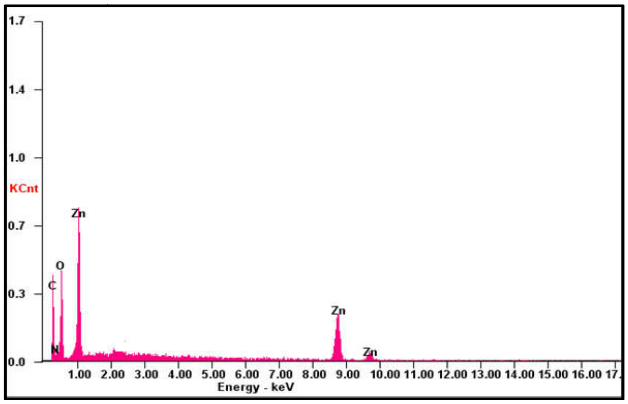

Figure 15: EDX spectrum of ZnEDTA MOF

Table 2: Percentage composition in ZnEDTA MOF

Element	Wt %	At%
CK	**43.79**	**55.34**
NK	**08.88**	**09.62**
OK	**33.70**	**31.97**
ZnK	**12.37**	**02.87**

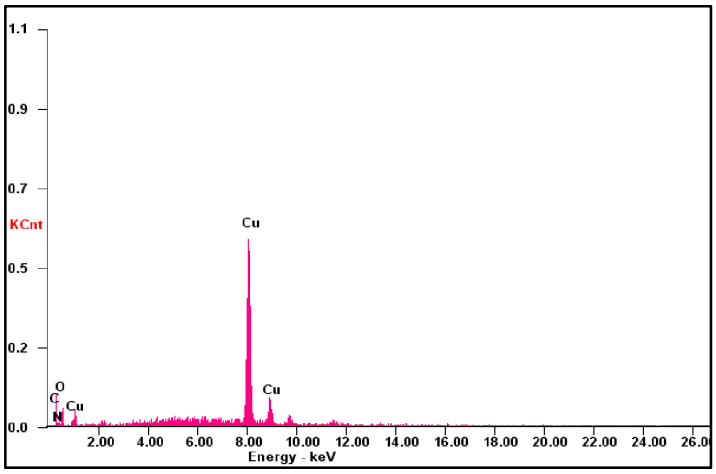

Figure 16: EDX spectrum of CuEDTA MOF

Table 3: Percentage composition of CuEDTA MOF

Element	Wt%	At%
CK	**27.25**	**54.58**
NK	**05.86**	**0.06**
OK	**08.91**	**3.4**
CuK	**57.98**	**21.96**

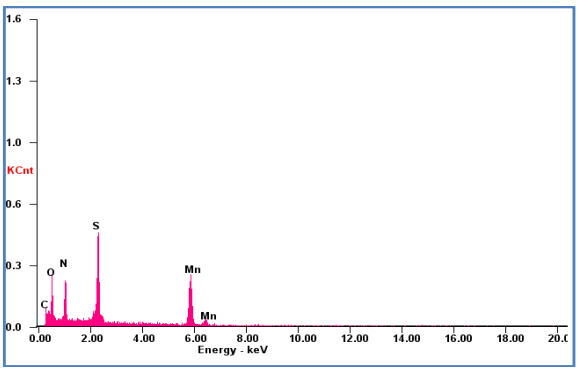

Figure 17: EDX spectrum of MnEDTA MOF

Table 4: Percentage composition of MnEDTA MOF

Element	Wt%	At%
CK	**41.16**	**57.39**
OK	**25.41**	**26.60**
NK	**11.87**	**08.65**
SK	**03.66**	**01.91**
MnK	**17.90**	**05.46**

Application of the as Synthesised MOFs in Sensing of Toxic ions in water - UV spectral studies

The UV Visible spectroscopic studies have been conducted for the synthesized MOFs. Efficiency of MOFs in the sensing of toxic metal ions was analysed based on changes in UV absorption spectrum.

Toxic metal ion sensing using ZnEDTA MOF

UV-Vis spectroscopic studies of ZnEDTA MOF indicated the absorption band at 232.5 nm. This is due to the transition of electrons from ligand EDTA to metal Zinc (Fig. 18). In Fig. 19, the maximum absorption peak was split into three such as 223.83, 259.90 and 350.76 nm on the addition of Cd metal ions. i.e. a bathochromic shift is observed from the ZnEDTA MOF. In the absorption spectrum of ZnEDTA MOF, after adding lead ions, a small shift at 238.5 nm is observed from that of ZnEDTA MOF as shown in Fig 20. While in the sensing of Cr with ZnEDTA MOF, three absorption peaks are observed at 223.83 nm, 255.90 nm and 350.76 nm (Fig 21). In the sensing of the mixture of Pb, Cd, Cr with ZnEDTA MOF, we could observe a red shift and their maximum absorptions were at 270.6, 378.96 nm respectively (Fig 22).

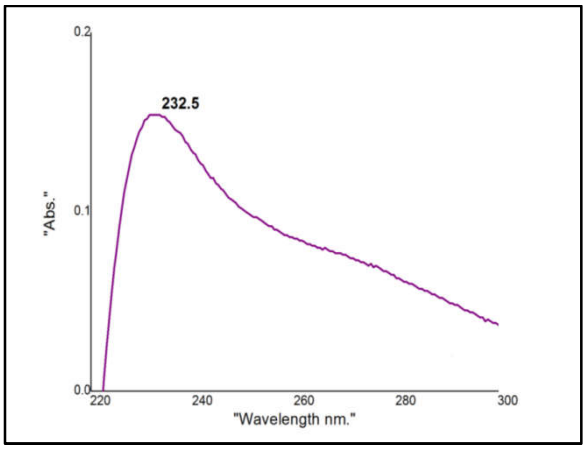

Figure 18: UV spectrum of ZnEDTA MOF in water

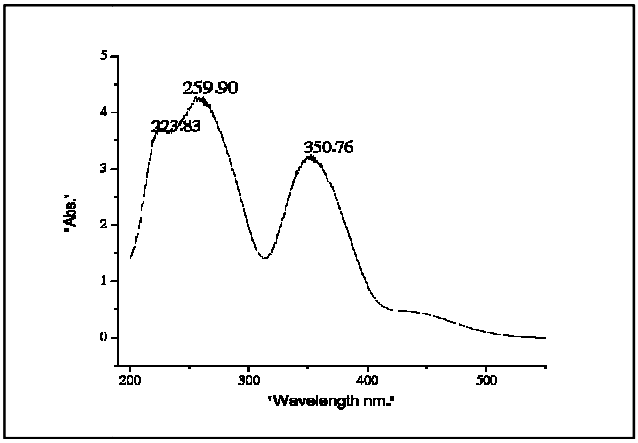

Figure 19: UV spectrum of water contaminated with Cd after the addition of ZnEDTA MOF

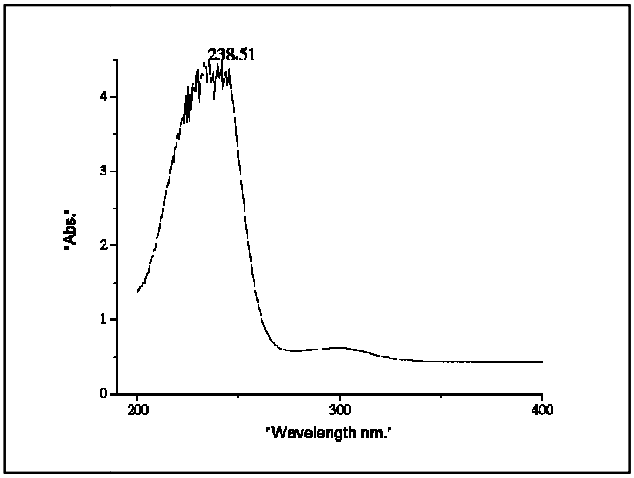

Figure 20: UV spectrum of water contaminated with Pb after the addition of ZnEDTA MOF

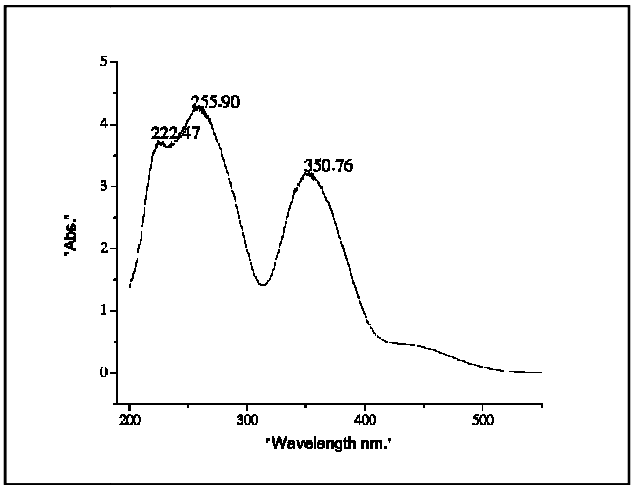

Figure 21: UV spectrum of water contaminated with Cr after the addition of ZnEDTA MOF

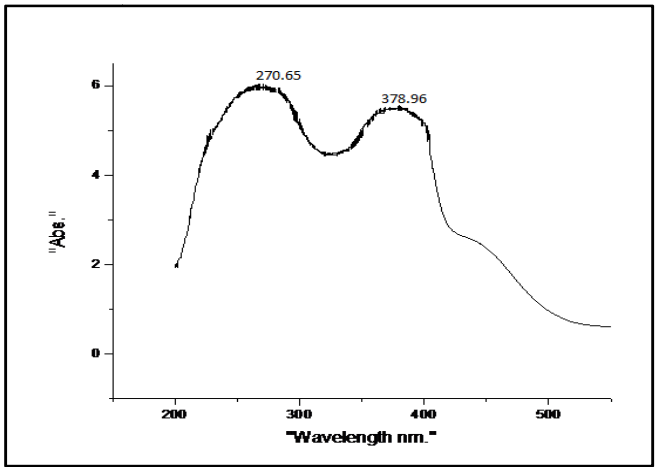

Figure 22: UV spectrum of water contaminated with mixture of Pb, Cd, and Cr after the addition of ZnEDTA MOF

The UV spectral studies indicate that using ZnEDTA MOF, toxic metal ions like Cd, Pb and Cr could be sensed separately while the MOF could sense Cd and Cr ions selectively from water containing a mixture of the three ions.

Toxic metal ion sensing using MnEDTA MOF

The MnEDTA MOF shows sensitive UV absorption maxima at 203.4 and 220 nm which can be ascribed to the transition of electrons from ligand EDTA to metal (fig 23). Fig 24 shows the absorption spectrum of water containing Cd with MnEDTA MOF, a small shift at 201.48 and 209.80 nm is observed from the MnEDTA MOF. While in the sensing of Pb with MnEDTA MOF, a bathochromic shift is observed from the MnEDTA MOF to 245.91 (fig. 25). In fig.26, the maximum absorption peak was split into two such as 259.32 nm and 393.76 nm on the addition of Cr metal ion. i.e. a bathochromic shift is observed from the MnEDTA MOF. In water containing a mixture of Pb, Cd, Cr ions, when MnEDTA MOF is added we could observe a red shift and their maximum absorptions are 245.5 and 397.2 nm respectively as shown in fig 27.

For MnEDTA MOF, a significant toxic metal ion sensing was observed with Pb and Cr compared to Cd.

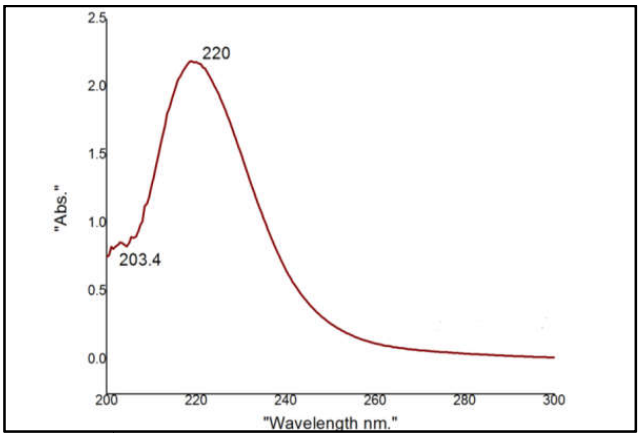

Figure 23: UV spectrum of MnEDTA MOFin water

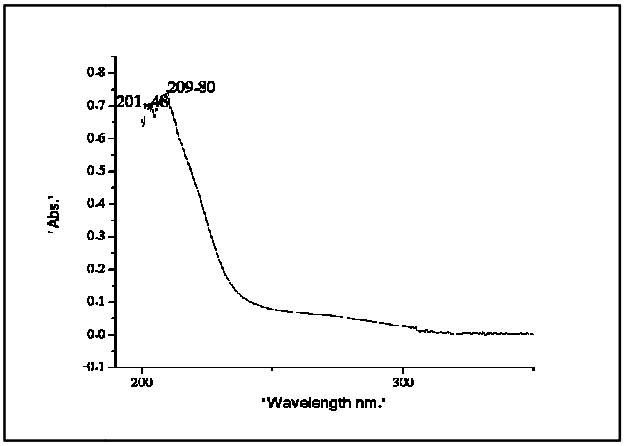

Figure 24: UV spectrum of water contaminated with Cd after the addition of MnEDTA MOF

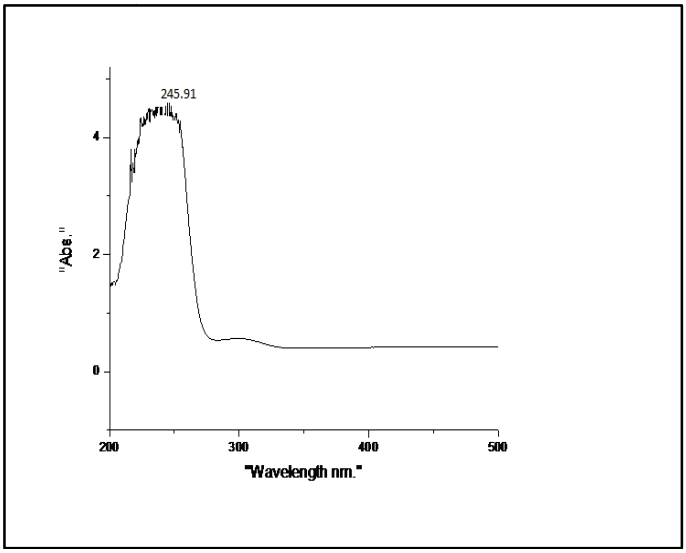

Figure 25: UV spectrum of water contaminated with Pb after the addition of MnEDTA MOF

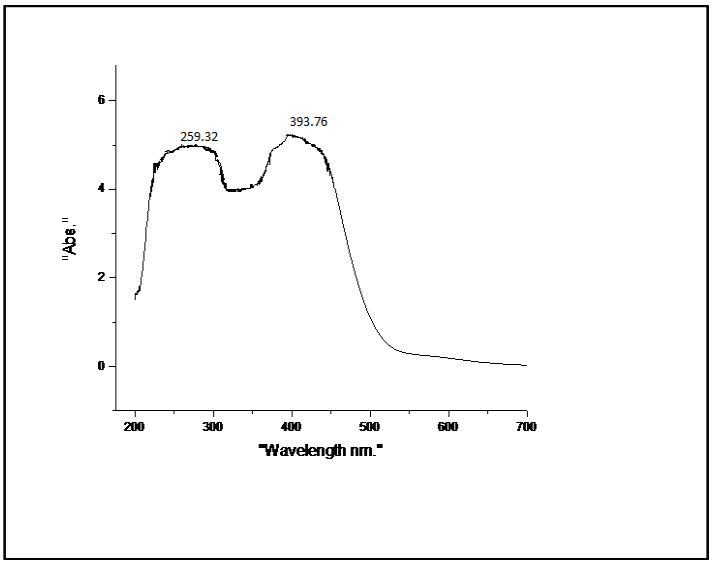

Figure 26: UV spectrum of water contaminated with Cr after the addition of MnEDTA MOF

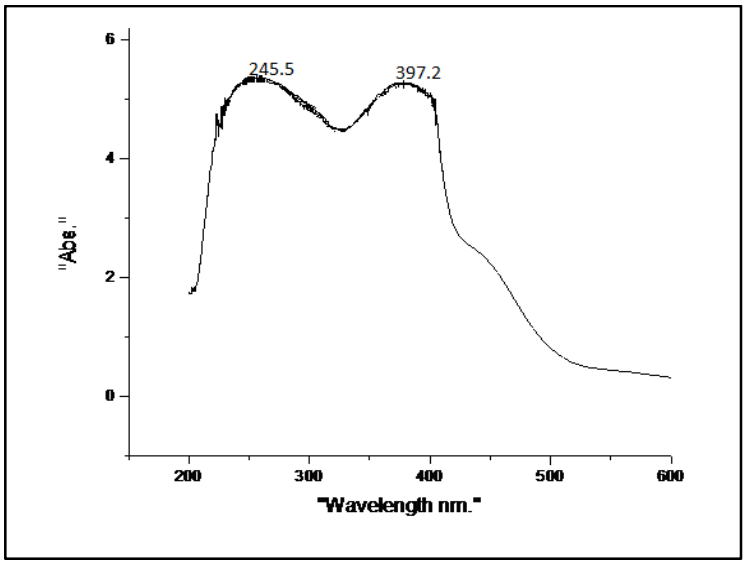

Figure 27: UV spectrum of water contaminated with mixture of Pb, Cd, and Cr after the addition of MnEDTA MOF

Toxic metal ion sensing using CuEDTA MOF

UV absorption maximum is observed at 255.9 nm in CuEDTA MOF due to the transition of electrons from ligand EDTA to copper (fig 28). In Fig. 29 absorption maxima at 238.2 nm, 263.98 and 300.36 nm is observed after the addition of MOF in water that contains Cd metal ion. In fig 30, the absorption spectrum of Pb with CuEDTA MOF, a valuable shift at 270.5 nm is observed from the MOF. While in the sensing of Cr with CuEDTA MOF, bathochromic shift in absorption peaks are observed at 257.28 nm, and 362.56 nm (fig 31). In the sensing of ions in water containing a mixture of Pb, Cd and Cr ions with CuEDTA MOF, we could observe that absorption maxima split into two such as 245.56 nm and 380.47nm respectively (fig 32).

UV spectral studies indicate that using CuEDTA MOF, toxic metal ions like Cd, Pb and Cr could be sensed separately while the MOF could sense Cd and Cr selectively than Pb from water containing a mixture of these ions.

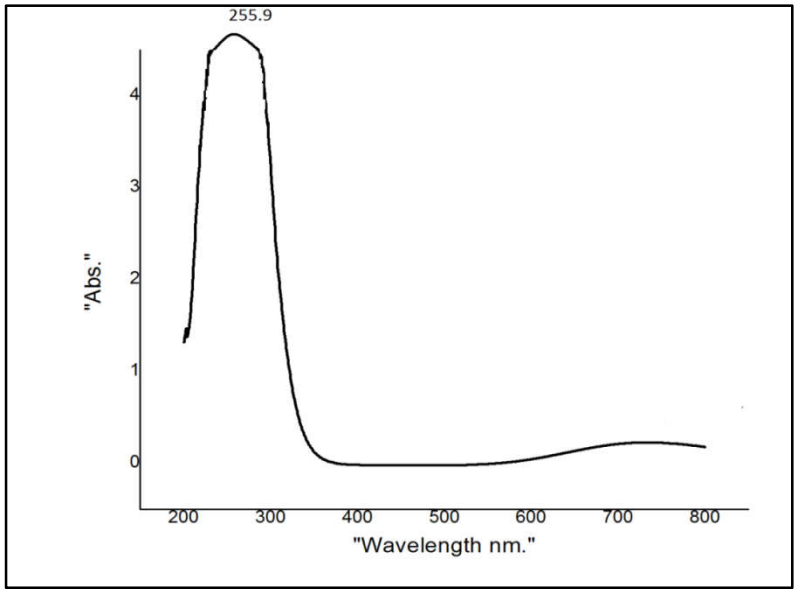

Figure 28: UV spectrum of CuEDTA MOF in water

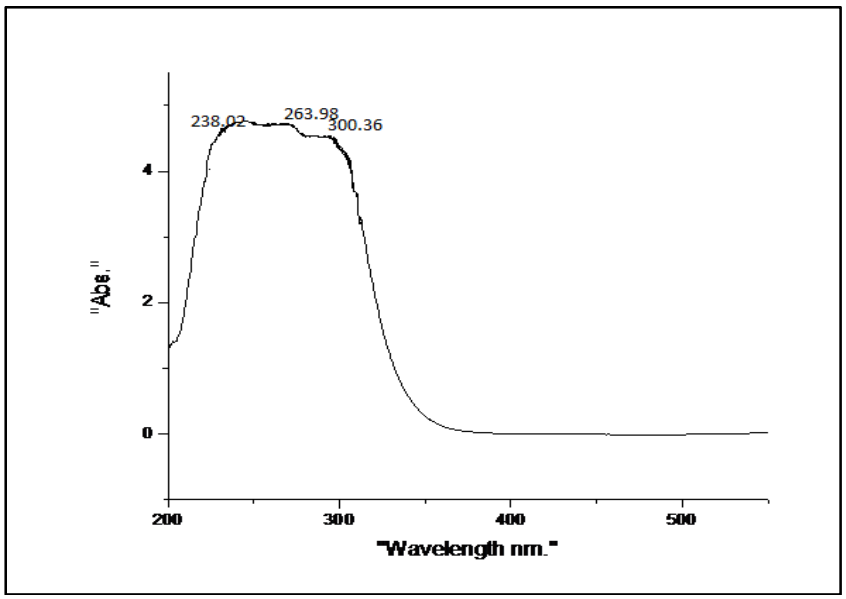

Figure 29: UV spectrum of water contaminated with Cd after the addition of CuEDTA MOF

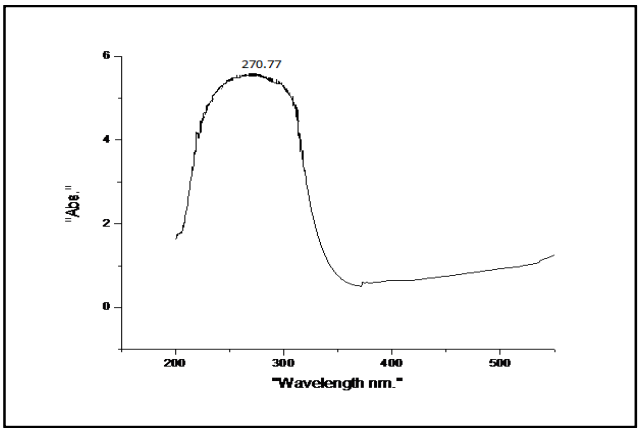

Figure 30: UV spectrum of water contaminated with Pb after the addition of CuEDTA MOF

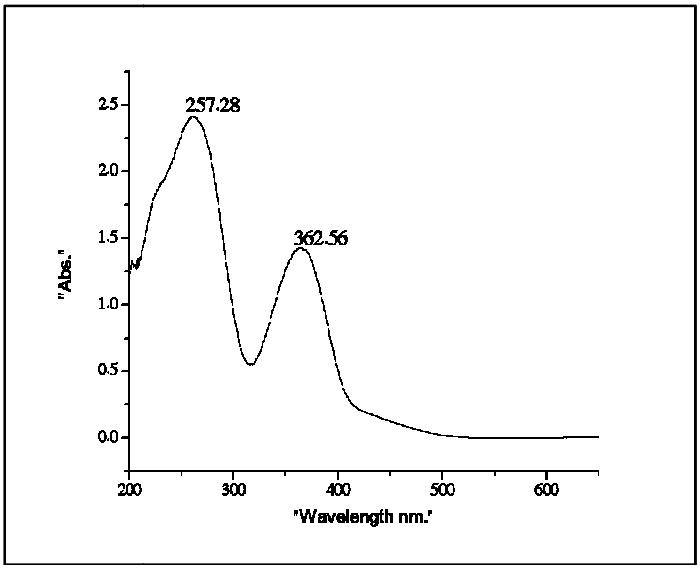

Figure 31: UV spectrum of water contaminated with Cr after the addition of CuEDTA MOF

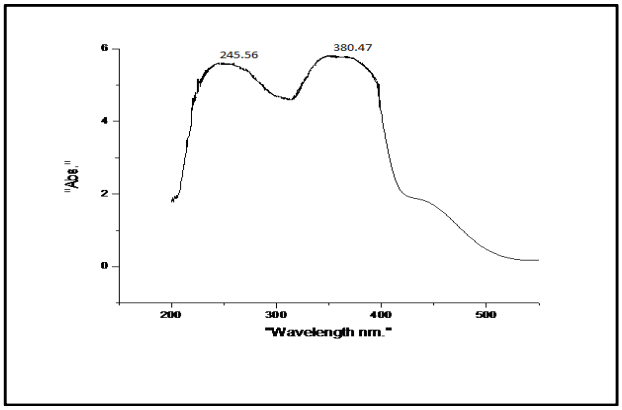

Figure 32: UV spectrum of water contaminated with mixture of Pb, Cd, and Cr after the addition of CuEDTA MOF

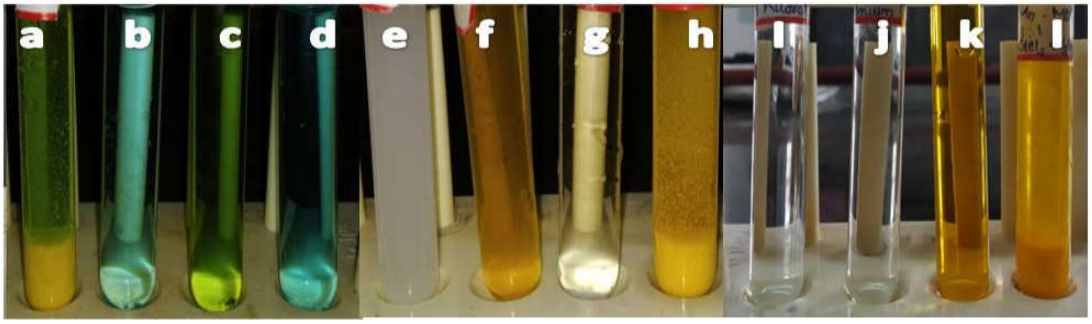

Figure 33: Images of sensing experiments of water-a,b,c,d- after adding CuEDTA MOF in water containing a mixture of ions of Cd, Cr and Pb; Cd, Cr, and Pb ions respectively. e,f,g,h- after adding MnEDTA MOF in water containing Pb, Cr, Cd and mixture of these ions respectively. i,j,k,l -after adding ZnEDTA MOF in water containing Pb, Cd, Cr and mixture of these ions respectively.

CONCLUSION

Nano crystalline metal organic frameworks of zinc (II), copper(II) and manganese(II) with ethylenediaminetetraacetic acid have been solvothermally synthesized and have been characterised using infrared spectroscopy (FT-IR), powder X-ray diffraction studies (PXRD), Scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS). Sensing applications using UV-Visible spectroscopic analysis have also been carried out. The shift in the vibrational frequencies observed in the FT-IR spectra in the MOFs when compared to that in the ligand confirms the formation of MOFs. The EDS indicates the presence of expected elements in the MOFs showing the successful synthesis of MOFs. From the UV Visible spectral studies, it is clear that the as synthesised MOFs, ZnEDTA MOF, CuEDTA MOF and MnEDTA MOF show remarkable sensing behaviour on toxic metal ions of Pb, Cr, Cd and their mixture. CuEDTA MOF and ZnEDTA MOF are suitable for sensing Cd and Cr selectively from a mixture of Cd, Cr and Pb in water. Also, MnEDTA MOF is suitable for sensing Pb and Cr selectively from a mixture of Cd, Cr and Pb in water. The synthesized metal organic frameworks may be developed into materials which may find application in sensors.

REFERENCES

1. Radha Kishan Motkuri, Jian Liu, A. Fernandez, Satish K. Nune, Praveen Thallapally, B. P M cGrail Citation Information, Pages 61–103.
2. Halian Li, Mohammed Eddaoudi, M.O Keeffe & O.M. Yaghi, (1999). Nature 402, 276-279.
3. John J Perry, Jason A Perman, Michael J. Zaworotko, (2009). Chem. Soc. Rev. 38, 1400-1417.
4. Hong-Cai Zhou, Jeffrey R.long, Omar M. Yaghi, (2012). Chem.Rev. 112(2), 673-674.
5. Amrita Chatterjee, Xijun Hu, Frank LeungYuk Lam, (2018). Catalysis today.
6. Adedibu C. Tella and Isaac. Y. (2012). Aaron Acta Chim. Pharm. Indica: 2(2), 75-81.
7. Tran Dinh Tuan, Nguyen Thi Hoai Phuong, Ninh Duc Ha, (2017). International Journal of Engineering Research, Volume no.6 Issue. 7, 349-352.
8. Jianwei Rena, Henrietta W.Langmia, Nicholas M Musyokka, Mkhulu Mathea, Xiangdong Kangb, Shijun Liaoc, (2015). Materials Today: Proceedings 2, 3964-3972.
9. Demin Liu, Kuangda Lu, Christopher Poon, Wenbin Lin (2014). *Inorg. Chem.* 534, 1916-1924.

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