CHROMATE ION ADSORPTION BY METAL ORGANIC FRAMEWORKS IN WATER

DISSERTATION

Submitted in partial fulfilment of the degree of M.Sc. in Physical Chemistry

By

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To

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STATEMENT

I hereby declare that the work presented in this dissertation entitled "**Chromate ion adsorption by metal organic frameworks in water**" is based on the investigations carried out by myself in the School of Chemical Sciences, Goa University under the supervision of Dr. Sandeep Kumar Dey and the same has not been submitted elsewhere for the award of a degree or diploma.

Miss Sarvesha S. Shetgaonka

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Chromate ion adsorption by metal organic frameworks in water

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1. INTRODUCTION

Metal-organic frameworks (MOFs) are organic-inorganic hybrid crystalline porous materials that consist of a regular array of positively charged metal ions surrounded by organic 'linker' molecules. Porous materials such as porous ceramics, zeolites, activated charcoals, porous metal, polymer foams and porous glass are being used in many ways in our daily lives. Due to their well known properties and wide range of applications, the field of porous materials, in particular the nano-porous materials has undergone rapid development in past two decades. Metal Organic Frameworks (MOFs) are among the recently developed porous materials, which are distinct from the other traditional porous materials above due to their high porosity and thermal stability. MOFs are composed of metal ions or clusters (called as Secondary building blocks), which act as joints, bound by multidirectional organic ligands which act as linkers in the network structure. These networks can be 1-D, 2-D or 3-D extended periodic structures. The joints and linkers assemble in such a way that regular arrays are formed resulting in robust (often porous) materials analogous to zeolites.

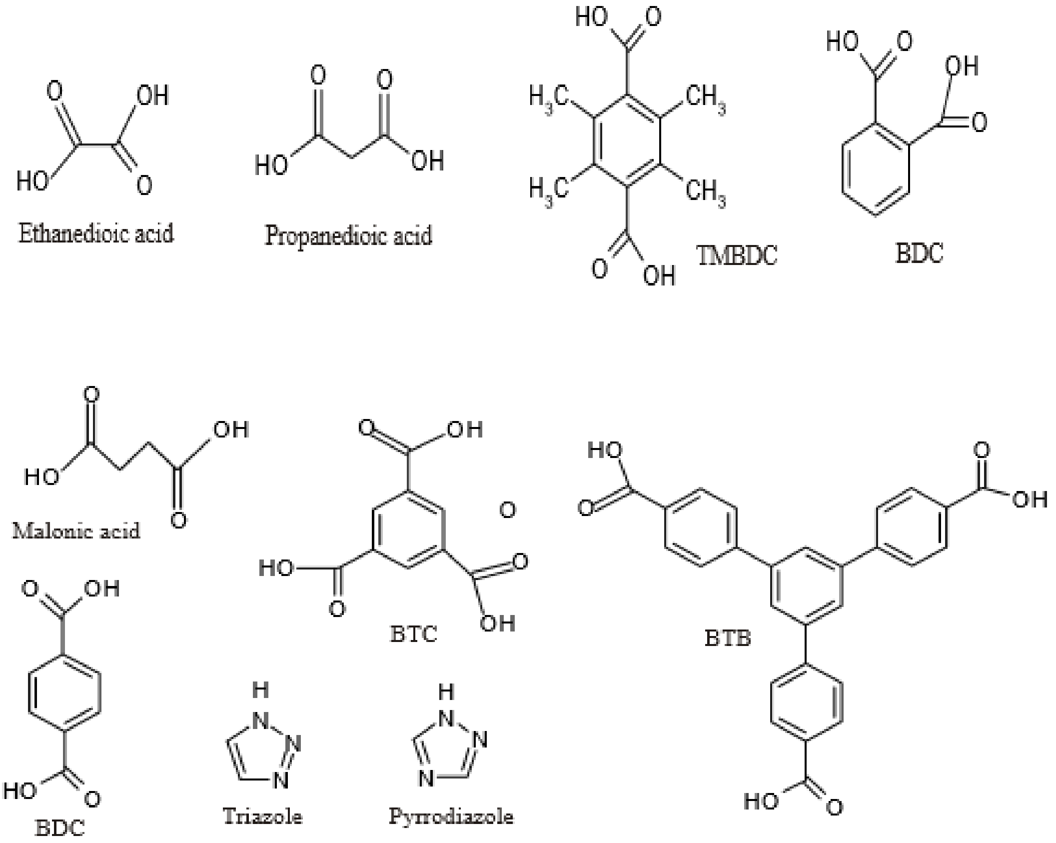


Figure: ORGANIC LINKERS

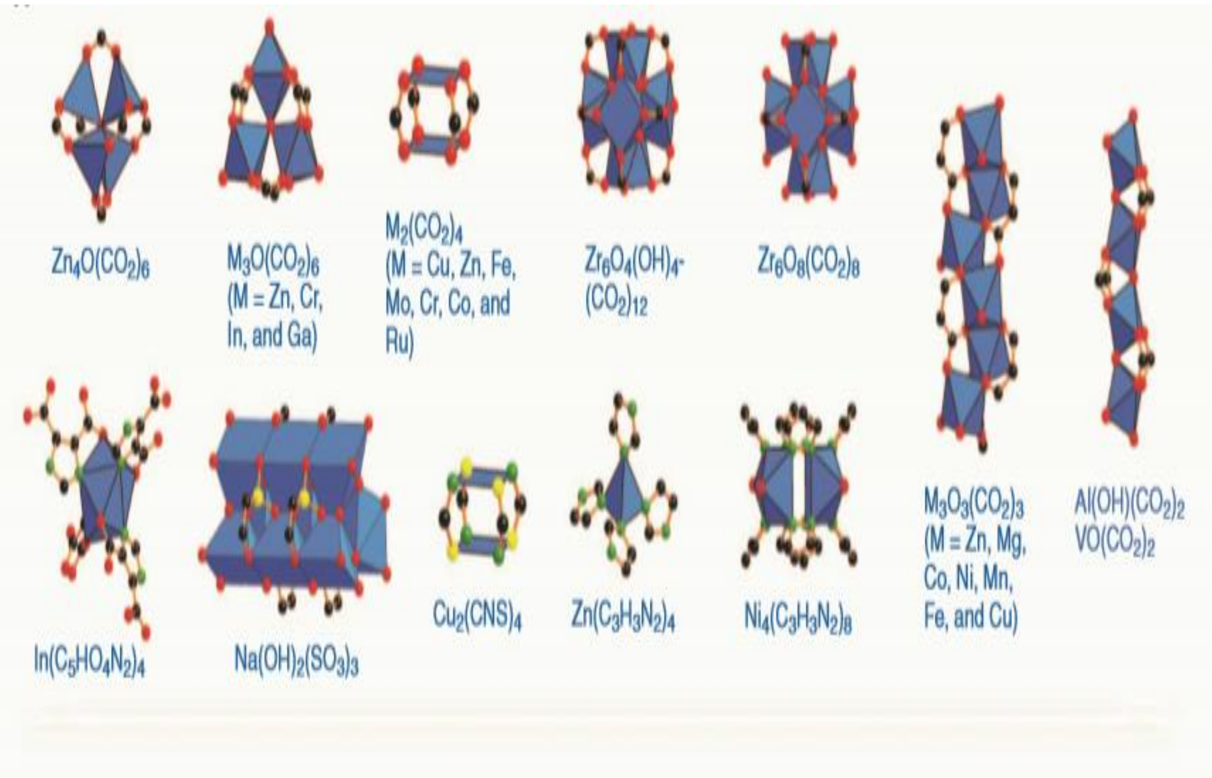


Figure: METAL CLUSTERS

The preparation of hollow structures, for technological applications, has long been a popular research field for chemists and materials scientists. However, the synthesis of porous or hollow-structured materials with controllable – and especially complex – structures and certain composition in a controlled manner has always been a challenge for scientists. The advent of Reticular chemistry, has made it possible to construct these porous materials, which can be synthesised by using topologically designed building blocks. Reticular chemistry is concerned with the connection of molecular building blocks via strong bonds to make predetermined extended structures (porous frameworks).

Metal Organic Frameworks are also known as porous coordination polymers (PCPs) i.e. they are a subclass of coordination polymers with the special feature that they are porous. Due to their structural and functional tunability, the area of MOFs has become one of the fastest growing fields in chemistry, since its discovery in 1990s by Omar Yaghi and co-workers. More than 20,000 MOFs have been reported. With the highly ordered framework of pores, MOFs exhibit the largest surface area per gram, known so far. The large surface area offers more space for chemical reactions and adsorption of molecules. Researchers have synthesized MOFs that feature a surface area of more than 7000 square meters per gram.

Some of the MOFs discovered initially were constructed from single metal-ion nodes. The incorporation of metal clusters into MOFs has led to significant improvements in porosity and stability. However, the metal-containing building units and coordination bonds are normally formed in situ, almost exclusively from a one-pot procedure. The linkers, on the other hand, are pre-designed and generally keep their integrity during MOF formation.

Amongst the thousands of MOF structures reported so far, the majority are built up from divalent cations (Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}...) and are typically based on carboxylates, phosphonates or N donating linkers, or a combination of them. This leads to MOFs with a wide range of structure types and pore sizes, from the micro to the meso domain and with or without functional groups on the organic spacer. MOFs built up from higher valence cations (+III, +IV...) are not very common, except may be for Ln^{3+} cations and more recently uranyl moieties. Such a discrepancy arises mainly from the differences in terms of chemical reactivity compared to lower valence metals; for example their higher charge density often results in less control over the crystallization process and/or in the formation of metal hydroxides or oxides. This makes the discovery of new topologies based on these cations and obtaining single crystals suitable for fast structure determination more difficult.

Many synthesized MOFs, however, have relatively weak thermal and chemical stability compared to zeolites which restricts their use in large scale industrial applications. It is possible to classify MOFs on the basis of framework robustness. In the first generation MOFs the framework undergoes irreversible collapse once the guest molecules are removed. The second generation MOFs have stable and rigid frameworks characterized by permanent porosity that remains even after the guest molecules are removed. Finally, third generation MOFs possess flexible and dynamic frameworks which can change their channels or pores reversibly in response to an external stimulus (radiation, light, pressure etc).

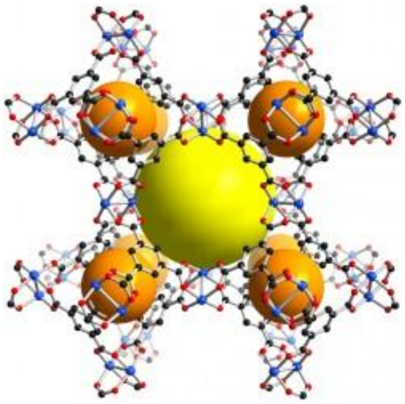
By careful selection of constituents, MOFs can also exhibit large pore volume and excellent chemical stability along with very high surface area. Research on synthesis, structures and property of various MOFs has shown that they are promising materials for many applications such as energy storage, gas storage, heterogenous catalysis and sensing. Apart from direct use, MOFs have also been used as support substrates for nanomaterials or as sacrificial templates/ precursors for preparation of various nanostructures.

Although still scarce, there are several reasons which justify the continuous effort for developing new porous high valence MOFs. One of the most significant problems is the low chemical stability of this class of materials. The often poor water stability of most limits their use in real applications, while recent studies have shown that for a given linker, increasing the charge of the metal usually leads to an enhancement of the hydrothermal stability of the MOF. Other important perspectives concern the possibility of enlarging the range of MOF chemistries to develop new architectures of interest associated with specific properties arising from the intrinsic properties of these highly charged cations (redox or photo-activity, catalysis...).

Direct preparation of MOFs by using high valence metal ions (Zr^{4+}, Cr^{3+}, Al^{3+}, etc.) has attracted great research interests. The outstanding stability of these high valence MOFs toward moisture is attributed to the strong interactions between metal ions and carboxylate linkers according to the hard/soft acid−base principle. Particularly, Al-MOFs have gained great attention because of their abundant metal source, light porous density, as well as robust thermal and chemical stability e.g. assembled by unique 8-ring clusters $\{Al_8(OH)_4(OCH_3)_8\}^{12+}$ and 2-aminoterephthalic acid, is a typical Al-MOF.

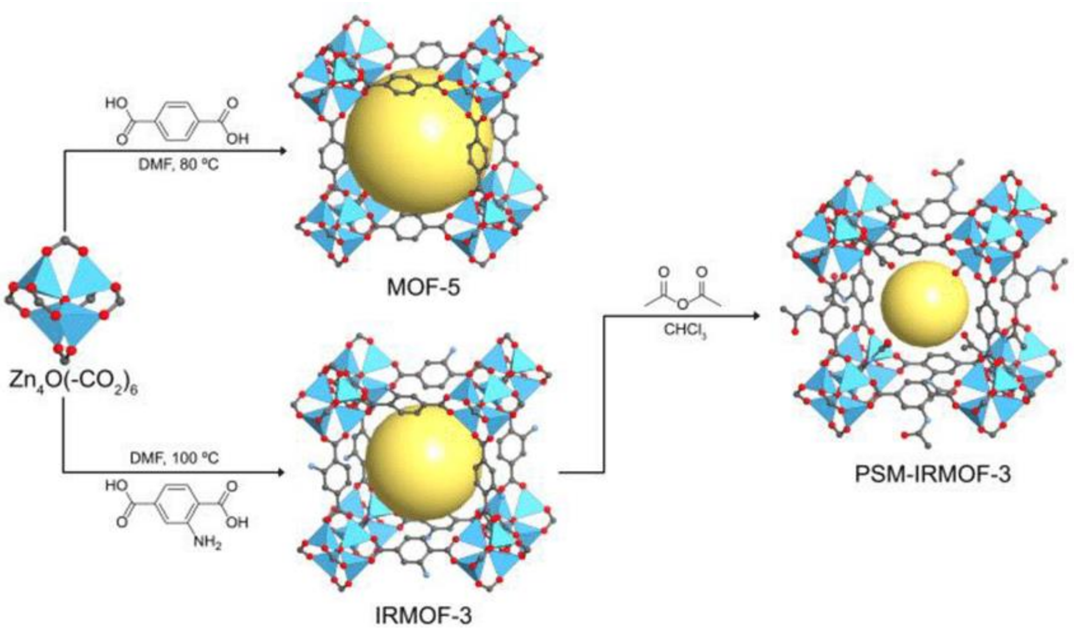
2. SOME MOFs BASED ON METAL / METAL CLUSTERS USED

(2a) HKUST-1 (Hong Kong University of Science and Technology)



It is a Copper-based metal organic framework. HKUST-1 was first reported in 1999 by Chui et al and is composed of Benzene-1,3,5-tricarboxylate(BTC) ligands coordinating Copper in a cubic lattice. In the framework of HKUST-1, Cu(II) ions form paddlewheel dimers, where each Copper atom is coordinated by 4 oxygens from BTC linkers and water molecules. The capture and storage properties of hydrogen are strongly dependent on the structure of the resulting organic and inorganic 3-dimentional bridging linking. Hydrogen adsorption studies show that this material can store 0.47 wt% of hydrogen at 303K and 35 bar pressure. This occurs at low temperatures. HKUST-1 has been shown to be capable of adsorbing significant amounts of hydrogen at 77K. At room temperature or above, adsorption is not of any commercial significance. Nitrogen adsorption isotherms show that HKUST-1 MOF has approximately type-1 isotherm BET specific surface area of 1055 m^2g^{-1}. Porous HKUST-1 MOF was prepared using a novel hydrothermal method based on the reported procedures. Cupric nitrate hemi-pentahydrate (6.0g) was dissolved in deionised water. It was followed by the addition of Benzene-1,3,5-tricarboxylic acid (4.0g) in a 250mL of solvent consisting of equal parts of ethanol and deionised water and mixed thoroughly until it was completely dissolved. The resultant solution was transferred into a 250mL Teflon-lined stainless steel autoclave. It was kept at 110^{o}C for 18h in oven to yield small crystals. Then after cooling, the blue crystals were isolated. The dimensionality of the MOFs was strongly affected by the solvent used for synthesis. Also, lack of specific interaction sites limits the applicability of these materials as catalysts. HKUST-1 has been called by several different names such as MOF-199 and Cu-BTC. (*Reference 3).*

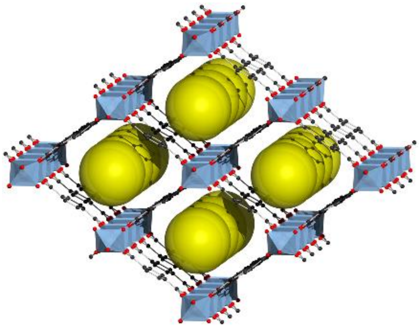
(2b) MOF-5



MOF-5 described in 1999, consists of Zn_4O units connected by linear 1,4-benzenedicarboxylate struts to form a cubic network. MOF-5 was prepared using room temperature synthesis, wherein separate N,N-dimethylformamide(DMF) solutions of terephthalic acid with triethylamine and zinc acetate dihydrate were prepared, then the zinc salt solution was added to the organic solution with rapid stirring at ambient temperature. Almost immediately a white precipitate was observed and the reaction was allowed to proceed for 2.5h.

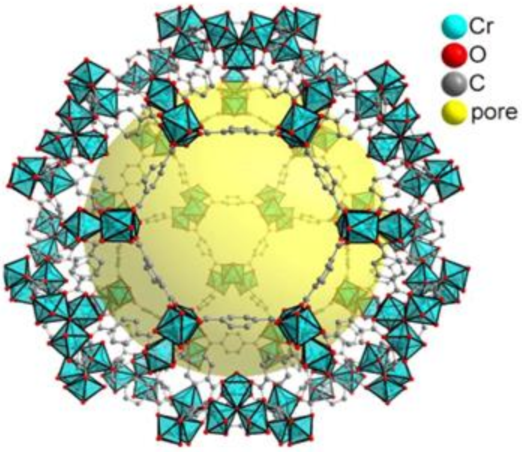
MOF-5 synthesis was repeated without addition of a base, using zinc acetate dihydrate, and the mixture was stirred for only 45mins, again yielding pure MOF-5 .This demonstrates that the addition of triethylamine as a base is unnecessary when zinc acetate is used as a source of Zn(II)in the MOF-5 synthesis. Langmuir surface area for MOF-5 was found to be 3909m^2/g. (*Reference 4.)*

(2c) MIL-53(Al) (Materials of Institute Lavoisier)



Metal-organic framework MIL-53(Al) was synthesized by a solvothermal method using Aluminum nitrate as the aluminium source and 1,4-benzenedicarboxylic acid (H_2BDC) as the organic ligand. The metal-organic framework (MIL-53(Al)), which is built up by the interconnection of infinite trans chains of corner-sharing (via OH groups) $AlO_4(OH)_2$ octahedra with BDC ligands, has a 3D skeleton structure composed of 1D rhombus channels. MIL-53(Al) has Lewis acid sites (Al^{3+}) of uniform distribution, specific surface area, and remarkable thermal and chemical stability and has been used as heterogeneous catalyst. MIL-53(Al) was synthesized by a solvothermal method. First, 13 g (35 mmol) aliquot of aluminum nitrate ($Al(NO3)_3 \cdot 9H_2O$) and 2.88 g (17.5 mmol) 1,4-benzenedicarboxylic acid (H_2BDC) were mixed with 50 mL deionized water in a 100 mL Teflon-lined stainless steel autoclave, then placed in an oven at 220 °C for 72 h. After completion of the reaction, the autoclave was cooled down to room temperature. The product was filtered, and washed four times with deionized water. It was then purified by a solvent extraction method using N, N-dimethylformamide (DMF) to remove uncoordinated H_2BDC. The resultant white powder was washed with methanol three times to remove the DMF molecules trapped inside its cavities. Finally, the powder was dried in vacuum at 80 °C for 2 h. MIL-53(Al) was obtained in a yield of 82. *(Reference 2.)*

(2d) MIL-101(Cr)



MIL-101 is a member of the large family of MOFs with the largest Langmuir surface area ($4500m^2g^{-1}$), pore size (29–34Å), and cell volume (702.000Å). It was first reported by Férey et al. in 2005, who synthesized it from HF-Cr(NO3)$_3$-1,4-dicarboxylic acid- (H_2BDC-) H_2O. Since the discovery of large-pore MIL-101, several groups have tried to synthesize MIL-101 for gas adsorption. However, it is hard to obtain crystalline MIL-101 with a high BET surface of more than $3200m^2 \cdot g^{-1}$. MIL-101 was synthesized according to an earlier report with some modifications. The mixture of reactants including H_2BDC, Cr(NO3)$_3$, HF, and H_2O was heated in a Teflon-lined stainless steel autoclave at 200°C for 8h. The resulting green solid material was filtered using a 0.2µm membrane and then extracted in ethanol with Soxhlet equipment for 12h to remove residual amount of H_2BDC still present in the product. The effects of the molar ratio of chromium nitrate and water to H_2BDC on the formation of MIL-101 were also monitored. MIL-101 is constituted from the trimer units (Cr_3O_{16}), which are made up of CrO_6 clusters, wherein a central chromium atom is surrounded by 6 oxygen atoms. *(Ref.6)*

3. TECHNIQUES FOR SYNTHESIS OF MOFs

(3a) TRADITIONAL SYNTHESIS

This can be divided into two categories; Solvothermal and non-solvothermal. The term solvothermal implies use of any solvent and is a more general term (hydrothermal incase of water). Solvothermal synthesis is carried out at the boiling temperature of the solvent or above its boiling point in special closed chemical reactors at elevated pressures caused by solvent vapours or produced by a pump. The heating of solvent above its boiling point enhances the solubility of salts and promotes reaction. The product yields are always higher and the products are of better crystallinity. Also slow crystallisation from the solution leads to the formation of regular large crystals with a high internal surface area. Solvothermal synthesis requires special equipment (autoclaves or sealed containers) that can withstand increased pressures. Examples of MOFs synthesised solvothermally are MIL and Zn based MOFs.

On the other hand, non-solvothermal synthesis does not require complex equipment. It can be done both at room temperature and via heating. The major aspects of such synthesis involves choice of salt (metal source), organic linker and solvent as well as the adjustment of pH and temperature to provide maximal yield of target MOF. The precipitate formation is promoted by increasing temperature and evaporating solvent. Reported MOFs such as MOF-5, MOF-74, MOF-177, ZIF-8 have been synthesised by this method. *(Ref. 7)*

(3b) MICROWAVE SYNTHESIS

Micowaves are electromagnetic radiations with frequencies between 300 to 3,00,000 MHz. Only the electrical component of microwaves has an effect on synthesis of compounds. There are two types of MW impact on a substance that lead to heating: the action on polar molecules and on free ions. In both cases, polar molecules and ions try to align with the alternating field. In an electrolyte solution, electric current is generated and, hence, heating occurs due to resistance. In the case of polar molecules, for example, water, the resistance is caused by the presence of hydrogen bonds that prevent the dipoles from easily aligning with the variable field. Microwaves show strongest effect in liquid state. In vapour state its effect is weak due to lack of hydrogen bonding. In solids, MW radiation is inefficient since reorientation of molecules firmly bound in the crystal lattice of ice is impossible. Microwave treatment helps reduce the synthesis duration. This is because MW irradiation does not change the activation energy (which is a constant for each reaction) but provides energy to overcome the activation energy barrier. The solvent used must be suitable for synthesis of MOFs and should absorb microwave energy and be able to convert electromagnetic energy into heat. Another specific feature of microwave heating is some increase in the boiling point of a solvent as compared with conventional heating; i.e., as the boiling point is achieved and, usually, even above this temperature, the solvent does not boil, being in the metastable state. This phenomenon can be explained by the fact that a solution can boil only in contact with its vapour. Microwave radiation for synthesis of MOFs was used for the first time in 2005. This method made it possible to reduce the time of synthesis of the MIL-100 framework from 96h to 4 h. *(Ref. 7)*

(3c) ELECTROCHEMICAL SYNTHESIS

The key idea of the electrochemical synthesis of MOFs is that metal ions are introduced not from a solution of the corresponding salt or through the formation of these ions during the reaction of a metal with an acid, but as a result of electrochemical process. Namely, metal ions are supplied in the reaction mixture containing dissolved linker molecules and an electrolyte through the dissolution of anode. This makes it possible to avoid the formation of anions in the course of reaction and to initiate a continuous process, which is essential for going to the production of relatively large amounts of MOFs. To prevent metal cations from depositing on the cathode, protic solvents are used; however, in this case, hydrogen can be released in the course of electrochemical process. At the same time, some solvents, such as acrylonitrile, acrylates and maleates, are the first to be reduced, and with small amounts of these solvents the above problem is avoided. The electrochemical method was used for the first time to synthesize MOFs (HKUST-1) in 2005. It should be especially noted that this method affords both powders and films. For example, a thin layer of HKUST-1 was electrochemically deposited on copper mesh used as anode. *(Ref. 7)*

(3d) MECHANOCHEMICAL SYNTHESIS

Mechanochemistry studies reactions between solids usually initiated only by means of mechanical energy, for example, by milling in ball mills. Currently there is no general theory explaining physicochemical processes that occur in mechanochemical reactions. The most popular approaches are the hot-spot model and the magma ± plasma model. The former model considers the contact of two solid surfaces exposed to mechanochemical treatment. The magma ± plasma model focuses on the processes that occur directly at the contact spot of colliding particles. According to this model, the local temperature at such spots can exceed 1048C owing to the instantaneous formation of plasma and large energy release, including emission of free electrons. It seems like that these theories are inapplicable to the mechanochemical synthesis of MOFs since such high temperatures would lead to the decomposition of the initial organic components and the product. However, a strictly local character of such temperature bursts and their extremely short duration can initiate reactions between milled components rather than lead to their degradation. For the synthesis of MOFs, this method was used for the first time in 2006. The authors mixed copper acetate and isonicotinic acid (HINA) in a ball mill for a few minutes. This procedure led to a rather well-crystallized product with the formula $Cu(INA)_2.xH_2O.yAcOH$. *(Ref. 7)*

(3e) IONOTHERMAL SYNTHESIS

Ionothermal synthesis, the use of ionic liquids as both solvent and template (structure directing agent), has been used to prepare zeolites and inorganic-organic hybrids such as metal organic frameworks. Ionic liquids are a class of organic solvents with high polarity and a preorganised solvent structure. Room temperature or near room temperature ionic liquids are classically defined as liquids at ambient temperatures (or <100°C) that consists only of ions. They have excellent solvating properties, little measurable vapor pressure and high thermal stability. Many ionic liquid cations are chemically very similar to species that are already known as good templates (alkyl imidazolium-based, pyridinium-based ionic liquids). Many are relatively polar solvents, making them suitable for the dissolution of the inorganic components required for the synthesis. One of the defining properties of ionic liquids is their lack of a detectable vapor pressure which effectively results in the elimination of the safety concerns associated with high hydrothermal pressures and has also led to their use in microwave synthesis. In ionothermal synthesis, the addition of water or fluoride seems to be important in determining the phase selectivity of the reaction. The ability to add either of these two important additives to the synthesis allows a level of control in ionothermal synthesis that is often absent in other methods. *(Ref. 8)*

4. APPLICATIONS OF MOFs

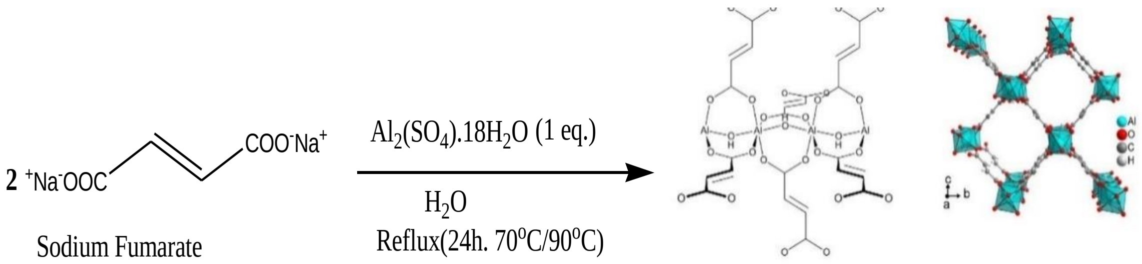
MOFs, due to their large surface areas, adjustable pore sizes and controllable properties form promising candidates as adsorbents for toxic ions, gases and other materials. Hazardous anions are a group of pollutants in drinking waters in addition to metal ions and organics which are known to be toxic and carcinogenic. The presence of these anions in ground and surface waters has resulted in severe contamination and has caused adverse health effects. Among the toxic anions, Chromate, Fluoride, Arsenate, etc. have shown concern in treatment of wastewaters and drinking waters. Infact, in humans, oral exposure to Cr(VI) compounds, may result in hematological toxicity. Also ingestion of a lethal dose of Chromate leads to Cardiovascular collapse. The recently discovered MOFs, have represented a new addition to the area of capturing various types of hazardous ions. They show highly efficient adsorption of various substances in comparison to other conventionally available adsorbing materials such as zeolites. With the growing number of health issues and growing demand to curb environmental pollution, there is a lot of scope to fabricate newer MOFs with improved adsorption capacity, due to their excellent properties. Also, these find a wide range of applications in toxic Gas adsorption in industries and heavy metal adsorption from industrial waste waters. *(Ref. 9)*

5. EXPERIMENTAL METHODS AND CHARACTERISATION

(5a) Synthesis of Al-Fum

Al-Fum was synthesised according to the patented approach. For solution 1, Sodium fumarate salt (0.320g, 2 eq.) was dissolved in 6mL of d/w. For solution 2, aluminium sulphate octahydrate (0.666g,1eq) was dissolved in approximately 5mL of d/w. Solution 2 was added to Solution 1, dropwise, under reflux conditions and stirring (60°C, 2h). The white precipitate obtained was filtered and washed with d/w 2-3 times followed by stirring(10min) and then centrifuged(30 min) and dried overnight (80°C). This MOF is already reported in the literature.

Reported BET surface area =1156 m^2/g *(Ref. 10)*

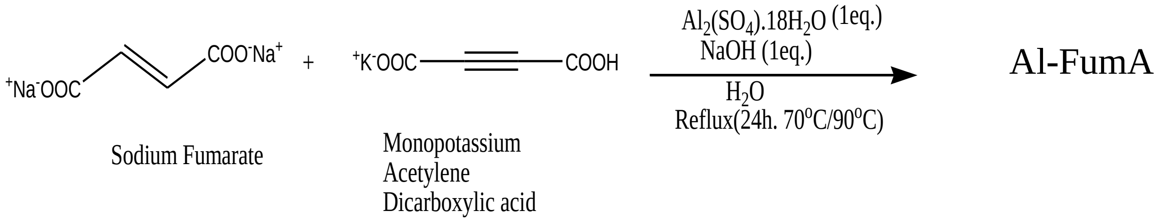


Aluminium fumarate (Al-fum)

(5b) Synthesis of Al-FumA

Al-FumA was synthesised via the same approach as Al-fum. For solution 1, Sodium hydroxide (0.04g, 1eq), disodium fumarate (0.116g, 1eq) and mono-potassium acetylene dicarboxylic acid salt (0.152, 1eq) was dissolved in around 6mL water. For solution 2, Aluminium sulfate octahydrate (0.666g,1eq) was dissolved in approximately 5mL of d/w. Solution 2 was added to solution 1 under similar conditions. Precipitation was observed only after refluxing the mixture overnight. The white precipitate obtained was washed, centrifuged(30min) and dried overnight to obtain pure compound. The above product was synthesised at 70°C and 90°C. The product yield obtained at 90°C was slightly higher than that obtained at 70°C.

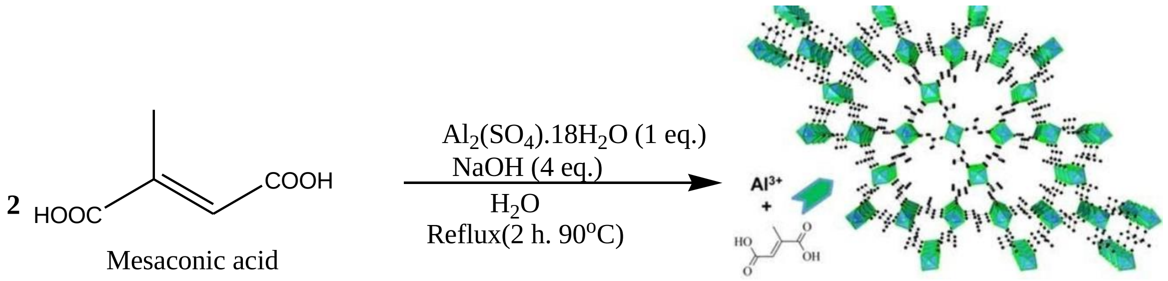
Measured BET surface area= 212.08m^2/g



(5c) Synthesis of Al-Mes

Al-Mes was synthesised according to the patented approach. For solution 1, Sodium hydroxide (0.16g,4eq) Mesaconic acid (0.260g, 2 eq.) was dissolved in 6mL of d/w. For solution 2, aluminium sulphate octahydrate (0.666g,1eq) was dissolved in approximately 5mL of d/w. Solution 2 was added to Solution 1, dropwise, under reflux conditions and stirring (90°C, 2h).The white precipitate obtained was filtered and washed with d/w 2-3 times followed by stirring(10 min) and then centrifuged(30min) and dried overnight (80°C). This MOF is alredy reported in the literature.

Reported BET surface area = 1040m^2/g *(Ref.11)*

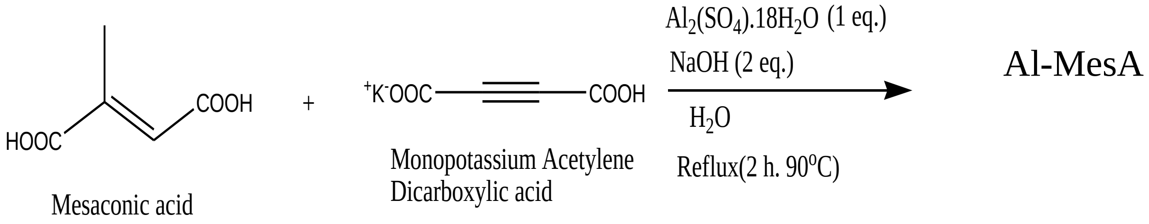


Al-Mesaconate(Al-Mes)

(5d) Synthesis of Al-MesA

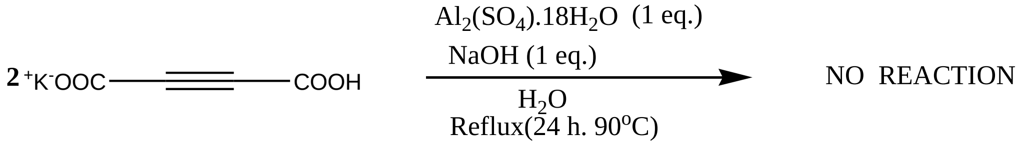
Al-MesA was synthesised via the same approach as Al-mes. For solution 1, Sodium hydroxide (0.08g, 2eq), Mesaconic acid (2-methyl fumarate) (0.130g, 1eq) and mono-potassium acetylene dicarboxylic acid salt (0.152, 1eq) was dissolved in around 6mL water. For solution 2, Aluminium sulfate octahydrate (0.666g,1eq) was dissolved in approximately 5mL of d/w. Upon addition of Solution 2 to solution 1 under reflux (90°C, 2h) conditions and stirring immediate precipitation was observed. The white precipitate obtained was washed(d/w), centrifuged(30min) and dried overnight to obtain the pure compound.

Measured BET surface area = 670m^2/g



(5e) Synthesis of Al-ADA

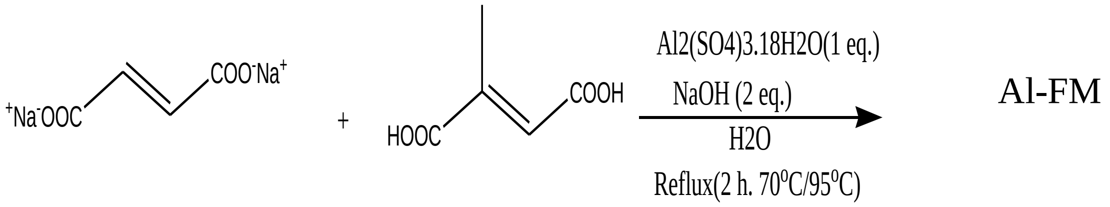
For solution 1, Sodium hydroxide (0.08g,1eq) Mono potassium dicarboxylic acid (0.304g, 2 eq.) was dissolved in 6mL of d/w. For solution 2, aluminium sulphate octahydrate (0.666g, 1eq) was dissolved in approximately 5mL of d/w. Solution 2 was added to Solution 1, dropwise, under reflux conditions and stirring (90^{o}C, 24h). No product was obtained. This shows that acetylene dicarboxylic acid doesn't bind to metal.



(5f) Synthesis of Al-FM

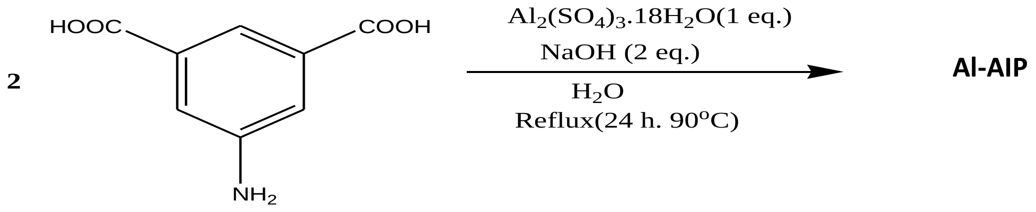
For solution 1, Sodium hydroxide (0.08g, 2eq), Mesaconic acid (2-methyl fumarate) (0.130g, 1eq) and Sodium fumarate salt (0.160g, 1eq) was dissolved in around 6mL water. For solution 2, Aluminium sulfate octahydrate (0.666g,1eq) was dissolved in approximately 5mL of d/w. Upon addition of Solution 2 to solution 1 under reflux (2h) conditions and stirring immediate precipitation was observed. The white precipitate obtained was washed(d/w), centrifuged(30min) and dried overnight to obtain the pure compound. The above product was synthesised at 70^{o}C and 95^{o}C. The product yield obtained at 95^{o}C was slightly higher than that obtained at 70^{o}C.

Measured BET surface area = 235m^2/g



(5g) Synthesis of Al-AIP

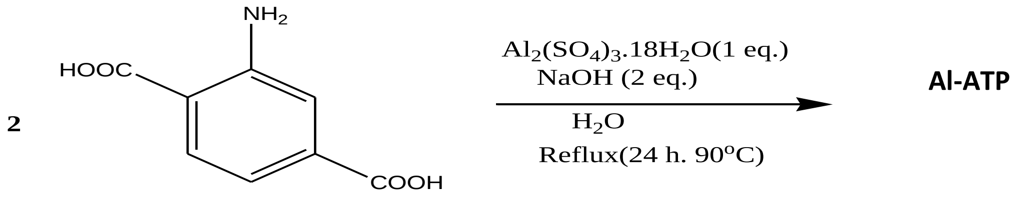
For solution 1, Sodium hydroxide (0.16g, 2eq), 2-Amino isophtallic acid (0.181g, 2eq) was dissolved in around 6mL water in a 250mL round bottom flask. For solution 2, Aluminium sulfate octahydrate (0.666g,1eq) was dissolved in approximately 5mL of d/w, separately. Upon addition of Solution 2 to solution 1 immediate precipitation was observed. The above assembly was refluxed overnight at 90°C and stirred. The white precipitate obtained was washed(d/w), centrifuged(30min) and dried overnight to obtain the pure compound.



5-Amino isophthalic acid

(5h) Synthesis of Al-ATP

For solution 1, Sodium hydroxide (0.16g, 2eq), 5-Amino terephthallic acid (0.181g, 2eq) was dissolved in around 6mL water in a 250mL round bottom flask. For solution 2, Aluminium sulfate octahydrate (0.666g,1eq) was dissolved in approximately 5mL of d/w, separately. Upon addition of solution 2 to solution 1 immediate precipitation was observed. The above assembly was refluxed overnight at 90°C and stirred. The precipitate (yellow) obtained was washed(d/w), centrifuged(30min) and dried overnight to obtain the pure compound.



2-Amino terephthalic acid

Characterisation of Al-FumA

Al-FumA synthesised using the patented procedure was characterised using the Powder X-ray diffraction (PXRD) technique. It was observed that the plot of Intensity v/s 2ϴ obtained coincided with the plot of Al-fum, which is already reported in literature.

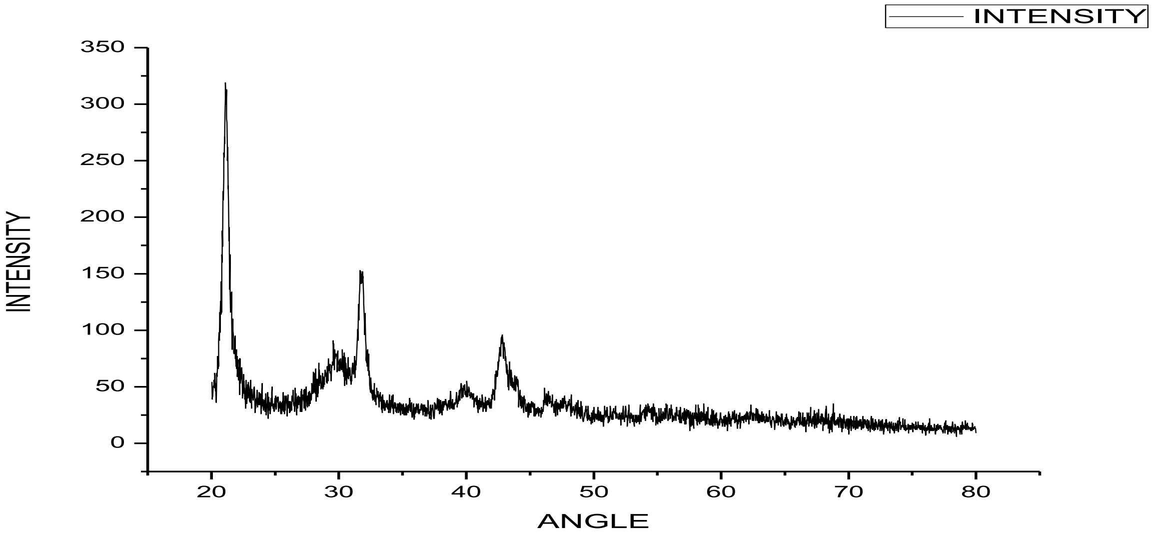


Figure 1: PXRD plot for Aluminium Fumarate (Al-fum)

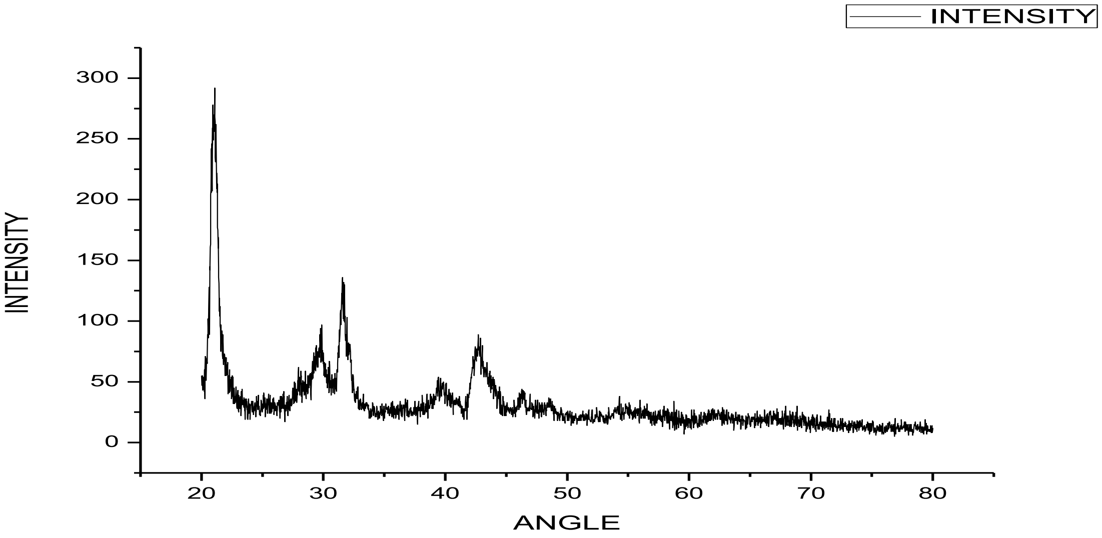


Figure 2: PXRD plot for Al-FumA

The above analysis confirmed that Acetylene dicarboxylic acid must have not coordinated in the process.

Characterisation of Al-MesA

Similar results as in case of Al-FumA were observed incase of Aluminium-MesA, wherein the PXRD data again revealed no change between Aluminium Mesaconate and Al-MesA plots, indicating almost no coordination from Acetylene dicarboxylic acid as shown below,

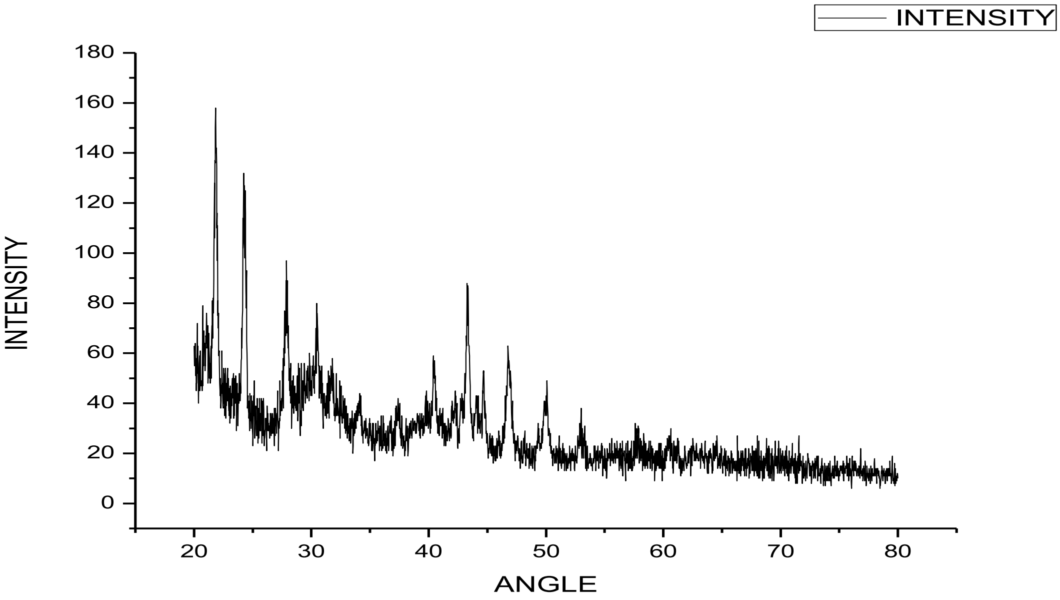


Figure 3: PXRD plot for Aluminium Mesaconate(Al-mes)

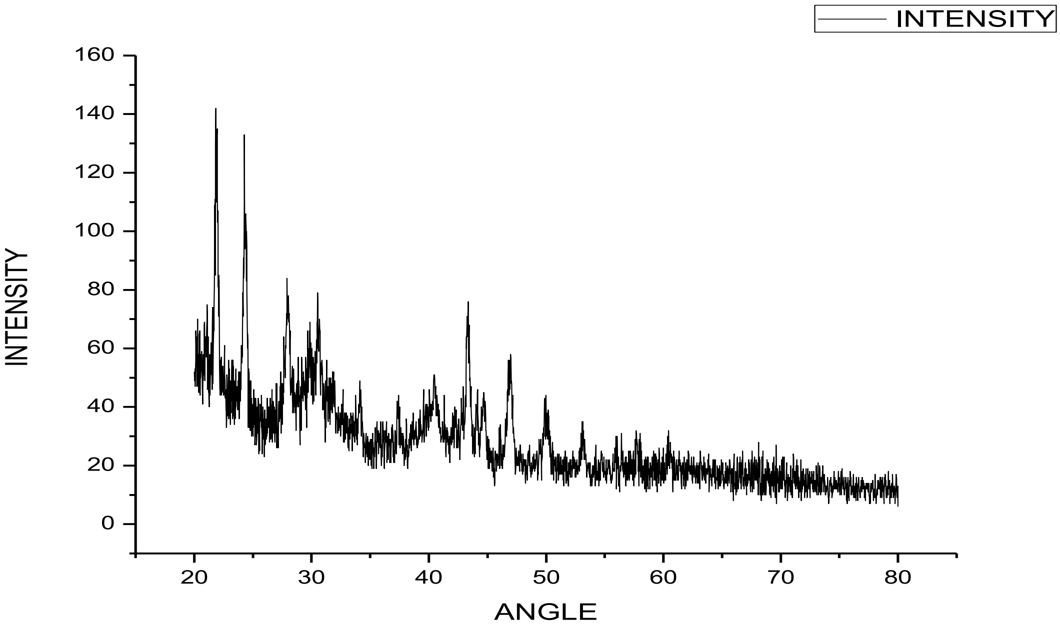


Figure 4: PXRD plot for Al-MesA

Characterisation of Al-FM

In case of Aluminium-FM, which is not reported so far, the PXRD data obtained, showed some contrast, indicating some coordination from both Fumaric acid as well as Mesaconic acid.

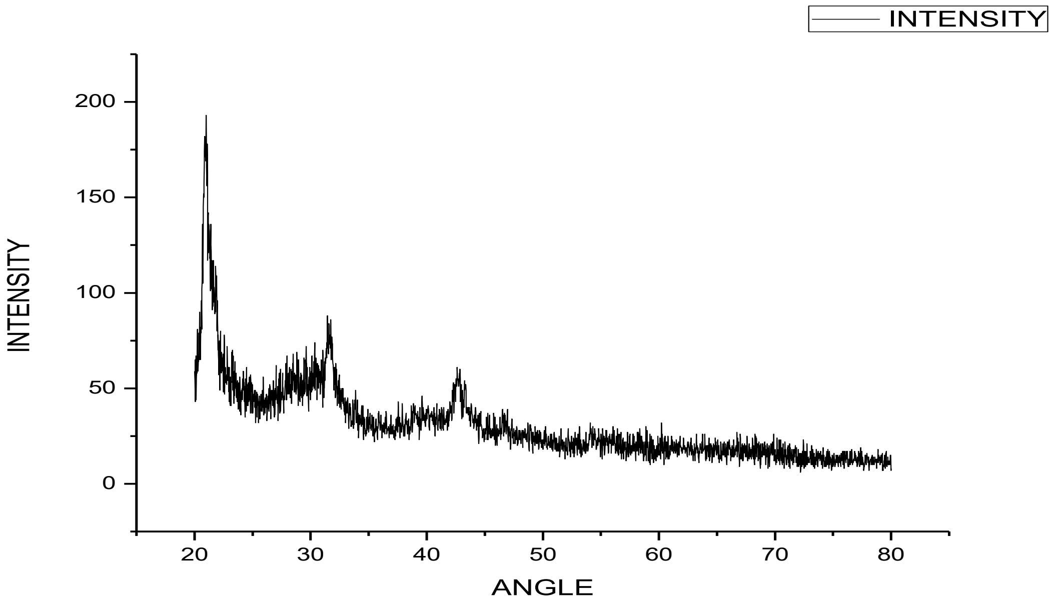


Figure 5: PXRD plot for Al-FM at 70ºC

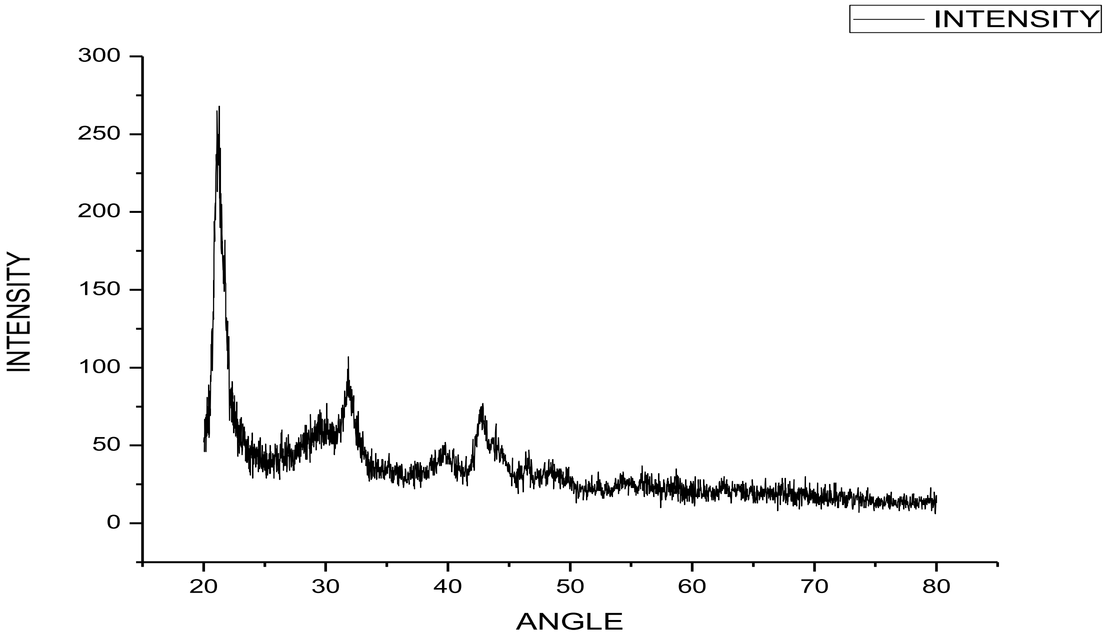


Figure 6: PXRD plot for Al-MA

6. Chromate and dichromate adsorption studies by UV-visible spectroscopy:

(6a) Adsorption studies of Al-FM

Aluminium-FM was used to investigate its chromate and dichromate adsorption capacity using UV-Visible Spectroscopy. The results obtained were not satisfactory, as expected, due to the lower surface area (235m^2/g).

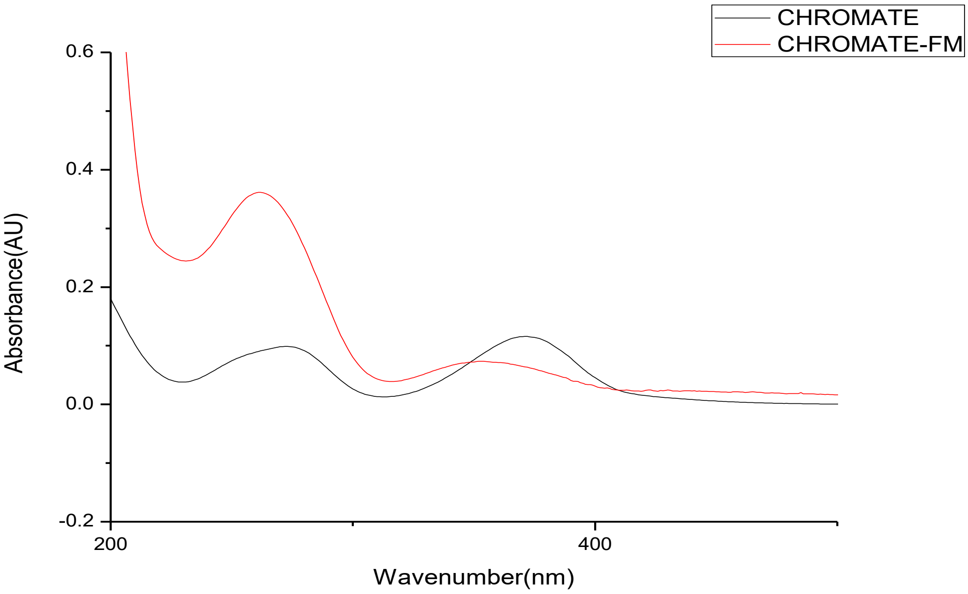


Figure 7: Curves for Chromate Adsorption by Al-FM

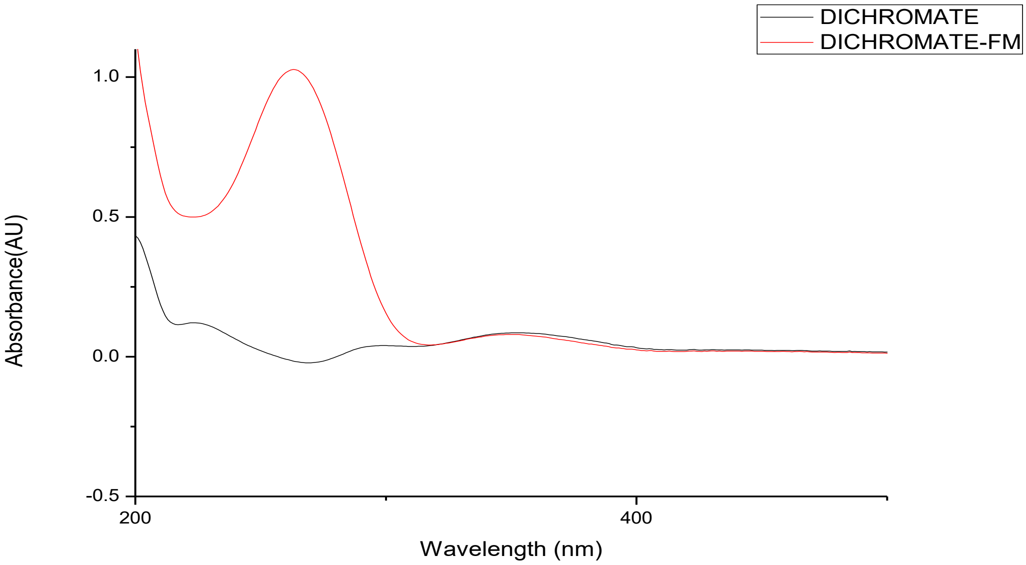


Figure 8: Curves for Dichromate Adsorption by Al-FM

Chromate and Dichromate show a strong Charge Transfer band at ~380nm wavelength in visible region of Electromagnetic Spectra. 25mL(10^{-3}M) of each of the Chromate and Dichromate salt solutions were prepared in 25mL standard volumetric flasks. 10^{-5}M (30µL in 3mL) of this solution was subjected to UV-visible analysis. 100mg of Al-FM was stirred in the same above solution(10^{-3}M) for 1h. and the filterate obtained was similarly made into 10^{-5}M solution and spectra was obtained as shown above.

Chromate shows two peaks, one at 272nm and other at 370nm. Upon addition of Al-FM, the intensity of the first band increased and that of the Charge Transfer Band(~370nm) slightly decreased. The decrease in the Charge Transfer Band indicates the amount of adsorption. The UV-visible analysis revealed 38.4% adsorption of toxic Chromate anion by Al-FM. However, there was no change observed in the Charge Transfer Band (~354nm) incase of dichromate ion, indicating zero adsorption.

(6b) Adsorption studies of Al-AIP

Ligands having amino group show better linkage capacity than other simple dicarboxylic acid ligands discussed so far. One of the above two, MOFs consisting of organic linkers with amino group, showed significant amount of chromate adsorption but zero dichromate adsorption.

The MOF synthesised using Amino Iso-thallic acid and Aluminium was studied for chromate and dichromate adsorption using UV-visible Spectroscopy following the same procedure as that discussed for Al-FM above.

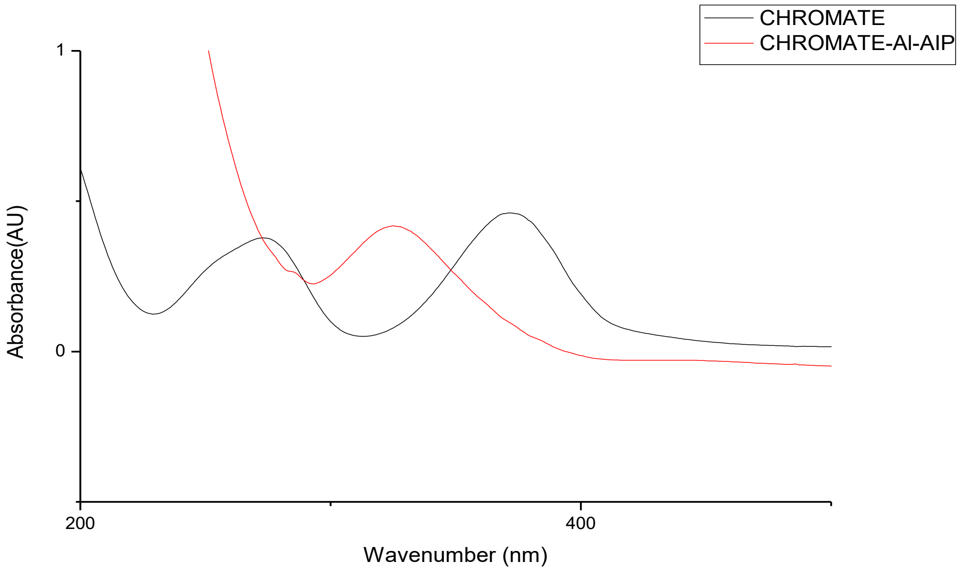


Figure 9: Curves for chromate adsorption by Al-AIP.

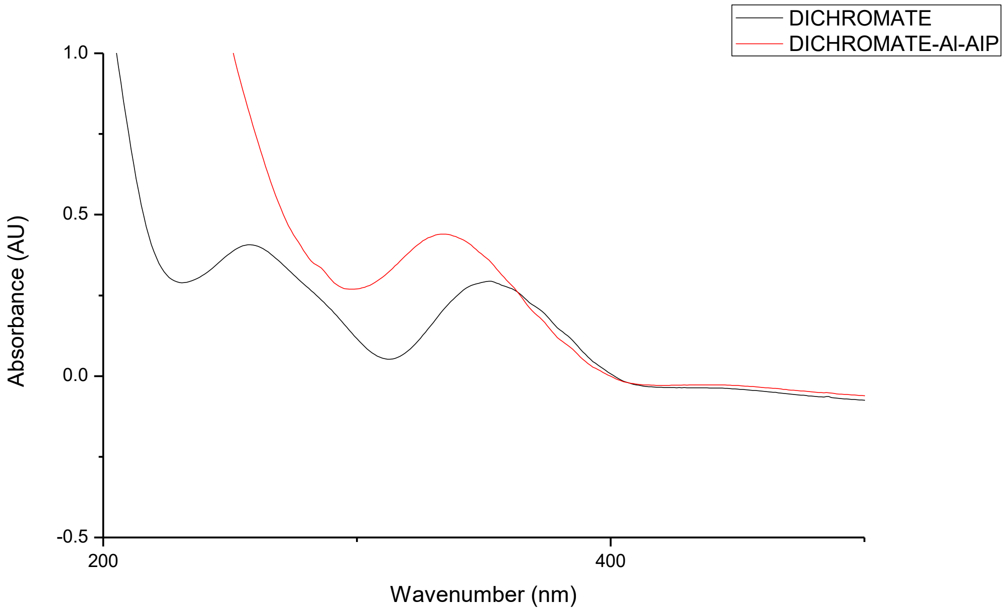


Figure 10: Curves for dichromate adsorption by Al-AIP

The above spectra for chromate adsorption show a significant hypsochromic shift in the Charge Transfer band at 370nm to 324nm after stirring the Chromate solution with Al-AmIso-NH_2 MOF. However, there was no change in intensity of the peak which indicates no significant chromate adsorption. Similar results were obtained for dichromate adsorption studies with comparatively smaller shift in Charge Transfer Band (353nm to 332nm).

(6c) Adsorption studies of Al-ATP

The second amino group based MOF synthesised using Amino Terephthallic acid and Aluminium salt showed significant amount of chromate adsorption which is of commercial importance. The chromate and dichromate adsorbed by the above MOF was successfully studied using UV-visible Spectroscopy, in a way, similar to that done in previous cases.

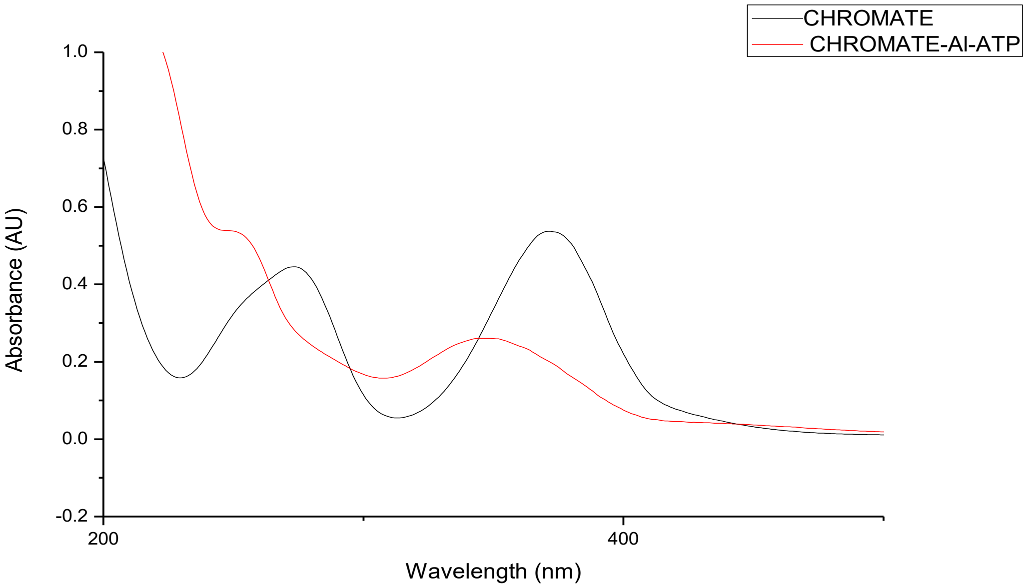


Figure 11: Curves for Chromate Adsorption by Al-ATP.

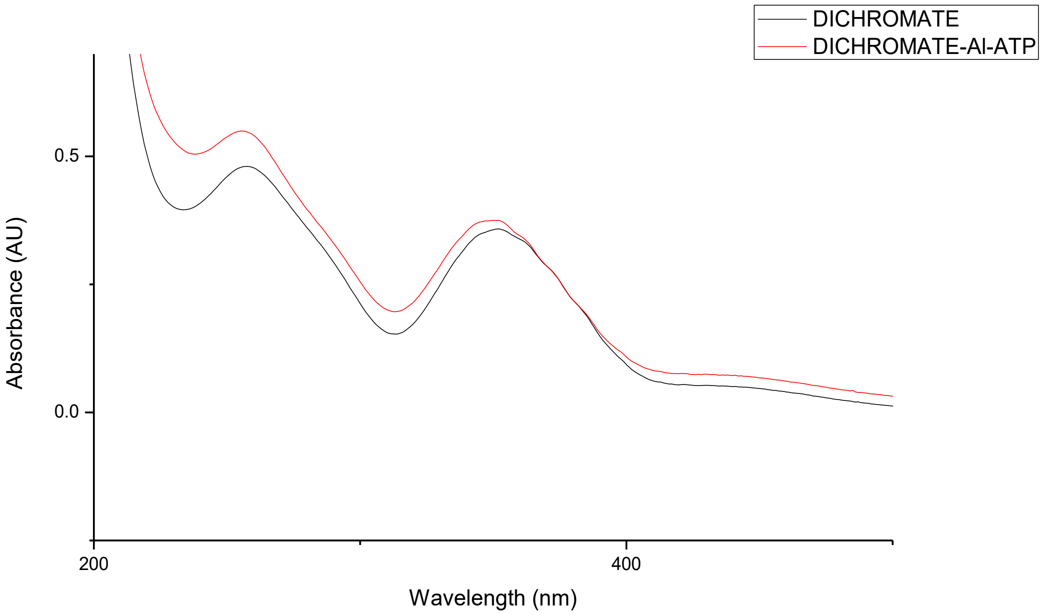


Figure 12: Curves for Dichromate Adsorption by Al-ATP.

The Spectra for chromate adsorption showed a slight shift (373nm to 347nm) and significant decrease in the intensity of Charge Transfer Band indicating 51.4% of chromate adsorption. However, it did not show any dichromate adsorption as revealed by the spectra above.

7. Conclusion

The Amino functionalised MOF, Al-ATP was found to be an effective adsorber of toxic Chromate anion in comparison to other non-functionalised MOFs. Its Adsorption Capacity was calculated to be 51.4%. This can be due to the formation of Hydrogen bonding interactions between Amine hydrogens and the Chromate Oxygens. Also, Chromate being comparatively smaller in size than Dichromate ion readily got adsorbed. Dichromate being bigger in size did not get adsorbed significantly. This indicates that the MOF (Al-ATP) comprises of pores with moderate pore size and is suitable for adsorption of smaller and medium sized anions. Pore size and surface area of MOFs influence Chromate Adsorption significantly. In general, higher the surface area, better the extent of adsorption.

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