

# Boronic Acid Functionalized Zirconium based MOF for the Complete Adsorptive Removal of Alizarin Dye

S. G. Prasannakumar, K. S. Asha\* and S. P. Smrithi

Department of Chemistry, M.S. Ramaiah College of Arts, Science and Commerce, MSRIT Post, MSR Nagar, Bengaluru - 560054, Karnataka, India; [asha.nair.ks@gmail.com](mailto:asha.nair.ks@gmail.com)

## Abstract

Nowadays, one of the severe problems that threaten the survival of human beings is water pollution. Water pollution caused by diverse poisonous compounds, specifically hydroxyl aromatic compounds and their derivatives have been evident and prominent environmental issue. In this work, an adsorptive method to remove the hydroxyl aromatic compounds particularly catechol based Alizarin red S dye by the activated metal organic framework have been attempted. The nano scale Zr-UiO-66 was synthesized using terephthalic acid as ligand, 4-carboxy phenyl boronic acid as coordination modulator and the morphology of the nano crystals was octahedral. The as-synthesized new metal organic framework Zr-UiO-66 after adsorption confirms the existence of boronic acid and structural stability after the incorporation of the boronic acid group using adsorption studies such as  $^{11}\text{B}$  NMR, PXRD, UV, IR and TGA. The zirconium based MOFs are very important in terms of their stability in water. These MOFs are largely used for gas separation, storage, sensing and degradation of chemical warfare agents, etc. The control of size of these MOFs to nano regime can be achieved using the monocarboxylic acids like acetic acid, benzoic acid. A mixed-ligand approach was implemented in this work.

**Keywords:**  $^{11}\text{B}$  NMR, Metal-Organic Framework, Mixed-Ligand, Organic Pollutants, Solvothermal.

## 1.0 Introduction

Water pollution is one among the severe problems that adversely affect the existence and progress of the society worldwide. Hence it is imperative to find answers effectively to remove pollutants from water sources<sup>1-3</sup>. The presence of non-biodegradable organic moieties/molecules such as dyes used in various industries in the water resources has become a serious threat. Conventional water purification technologies like flocculation, coagulation, chemical precipitation etc. have a lot of disadvantages. Compared to such conventional water treatment techniques, advanced techniques such as photocatalysis and adsorption stand out as the most advantageous ones owing to their

energy and economic benefits. A variety of natural, artificial, macro and nanosized adsorbents are available for waste water treatment. As a rapidly emerging branch of co-ordination chemistry, inorganic-organic hybrid materials with alterable porous structures and multitudinous active sites can also be employed as adsorbents and photocatalysts for water sanctification<sup>4-6</sup>. Additionally MOFs find immense application in the separation of methane gas from coal mines.

A class of porous co-ordination polymer known as metal organic framework which are highly porous in nature shows unparalleled degree of tunability, high surface areas and chemical properties, structural diversity and physical properties. Metal organic frameworks are crystalline porous accoutrements constructed from

\*Author for correspondence

a combination of co-ordinatively clicked Secondary Building Units (SBUs), organic linkers and metal or metal cluster nodes or bumps and multifunctional organic linkers that generate a plethora of crystals with topologically different open network type structures through tone assembly at molecular level<sup>7-9</sup>. The two elements are linked together by covalent bonds to obtain extended 3-D infinite horizonless network structure. The combination of internal porosity, acceptable adequate thermal stability makes the metal organic frameworks to have attracted tremendous attraction in gas storage/separation, catalysis, drug delivery, electrochemical operation, captivation, carriers for nano accoutrements, it isn't surprising that MOF's have photo luminescent property too<sup>10</sup>. Due to their intriguing properties and facile synthesis, MOF's have been widely applied for different applications such as gas, store house, catalysis, detectors, separation, captivation, super-capacitors and drug delivery. Infinite extended polymeric structures can be formed or separate closed oligomeric structures can be formed upon synthesis and utmost detailed structural information is obtained from X-ray crystallographic studies.

Ligand used in the synthesis plays a vital role hence the ligand can sustain the open pore structure. Due to this reason organic ligands with aromatic rings are widely used than flexible long chain molecules. At present over 90,000 MOF's have been synthesized and over 50,000 predicted. The extended pi delocalization and the pore size of UiO-66 gave rise to the structure determination and functionality of MOFs. There are several types of ligands like anionic, cationic and neutral. There are several common characters of diverse type of ligands. After removing the guest notes in the pores, there will be firm host-guest interaction that further improves both the adsorption ability and separation selectivity at minimal concentrations<sup>11-13</sup>.

A variety of metal centers and functionalized organic ligands are used in the synthesis of MOF's under diverse synthetic conditions. Transition metals of the first row are frequently chosen because of their well-known collaboration properties with carboxylate groups under hydro and solvo-thermal conditions. Then we have transition metal zirconium as the metal centre for the preparation of MOF, isostructural zirconium incorporated metal organic framework (Zr-MOF's) have drawn the attention of researchers owing to their remarkable

stability at elevated temperature, high pressure and their chemical stabilities against bases and acids. The water stable zirconium MOF's have been tested as adsorbents that can remove adulterants from polluted water<sup>14-16</sup>. However, the low adsorption capacity of Zr-MOF can be used with an exceptional ion exchange capability by directly introducing Zr-MOF to pyridinium salt as ligand.

## 2.0 Materials and Methods

### 2.1 Chemicals

Zirconium oxychloride, terephthalic acid, 4-carboxyphenylcarbonic acid, acetic acid, dimethyl formamide and concentrated hydrochloric acid are procured from sisco research laboratories private limited. Distilled water has been used for the synthesis of MOF.

### 2.2 Synthesis of UiO-66

45.11 mg (0.14 mmol) of  $ZrOCl_2 \cdot 8H_2O$  was weighed into a glass beaker and dissolved in 5mL of DMF and stirred for 15 minutes, to this 0.7 mL of acetic acid was added and continued to stir for another ten minutes. This mixture was kept aside and then 24.88 mg of Terephthalic acid was weighed to another glass beaker and dissolved it in 5 mL of DMF solvent and stirred the mixture for five minutes. Both the mixtures are then mixed well and taken in a 25 mL Teflon lined Autoclave. It was heated at 120 °C in a hot air oven for 24 hrs. The MOF was formed in the form of white colored gel. This latter was washed with DMF two times and Ethanol three times and dried in oven at 200 °C for overnight. The as-synthesized MOF was used for analysis.

### 2.3 Synthesis of B-UiO-66

45.11 mg (0.14 mmol) of  $ZrOCl_2 \cdot 8H_2O$  was weighed into a glass beaker and dissolved in 5mL of DMF and stirred for 15 minutes, to this 0.7 mL of acetic acid and 24.88 mg (0.15 mmol) of 4-Carboxyphenylboronic acid were mixed and continued to stir for another ten minutes. This mixture was kept aside and then 24.88 mg (0.15 mmol) of Terephthalic acid was weighed to another glass beaker and dissolved it in 5 mL of DMF solvent and stirred the mixture for five minutes. Both the mixtures are then mixed well and taken in a 25 mL Teflon lined Autoclave. It was heated at 120 °C in a hot air oven for 24 hrs. The MOF was formed in the form of white colored gel. This

latter was washed with DMF two times and Ethanol three times and dried in oven at 200 °C for overnight. The as-synthesized MOF was used for analysis.

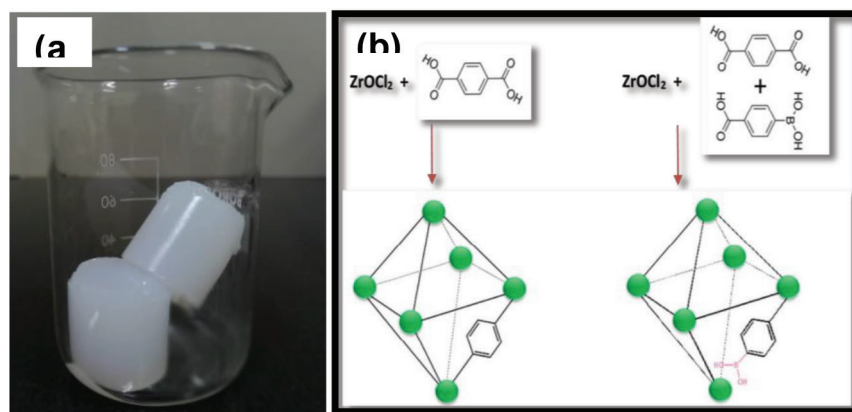
### 3.0 Results and Discussions

Zirconium MOF obtained as per the synthesis protocol is shown in Figure 1 (a) and the scheme is as shown in Figure 1 (b).

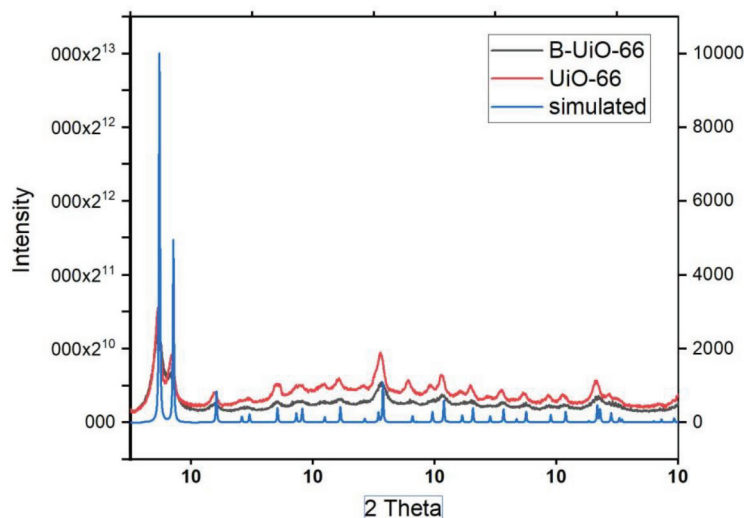
The X-Ray Diffraction pattern analysis of as-synthesized MOFs was done for checking their purity. It was evidenced that the X-ray diffraction patterns of both UiO-66 and B-UiO-66 are exactly matching with simulated pattern extracted from their crystallographic information file<sup>17</sup>.

The infrared spectrum of UiO-66 indicates that the peak around wavenumber 1500 $\text{cm}^{-1}$  shows vibration of carbon-carbon double bond on the benzene ring and the peak at wavenumber 1390 $\text{cm}^{-1}$  is due to stretching of O-C-O from the ligand. The peaks around 950 and 660 $\text{cm}^{-1}$  indicates presence of C-H vibrations<sup>18</sup>. It gives the evidence that IR bands of both UiO-66 and B-UiO-66 is very much similar.

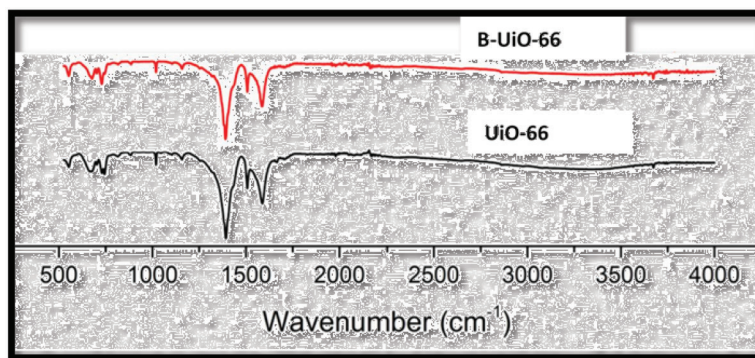
The existence of groups of free boronic acid in the MOFs was affirmed and the quantitative determination was carried out by the <sup>11</sup>B-NMR spectroscopic technique. It can be inferred that the peak at -4.4 belongs to the Boron atoms of boronic acid and the reference NaBF<sub>4</sub> respectively. The known quantity of boronic acid is taken as the theoretical value and is compared with that of the values obtained from NMR spectrum.



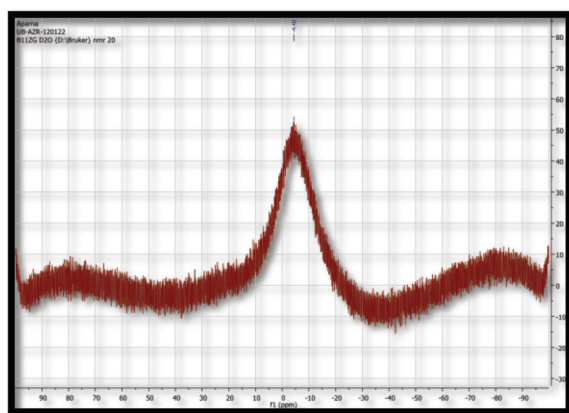
**Figure 1.** (a) Image of the as synthesized MOF gel (b) Schematic of synthesis route of UiO-66 and Boronic acid grafted UiO-66 MOFs.



**Figure 2.** PXRD Analysis of UiO-66 and Boronic acid grafted UiO-66 MOFs.



**Figure 3.** FT- IR Spectra of UiO-66 and Boronic acid grafted UiO-66 MOFs.



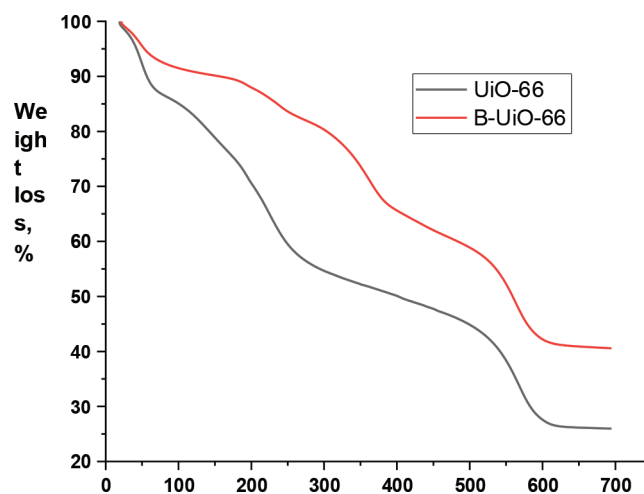
**Figure 4.**  $^{11}\text{B}$  NMR spectrum of B-UiO-66.

The structural stability of the MOF before and after boronic acid incorporation was once again confirmed by doing thermogravimetric analysis. It clearly shows that the weight loss pattern both the MOFs are well matching and the framework stability is also confirmed.

The BET surface area of UiO-66 and B-UiO-66 were studied to check the porosity of MOFs after boronic acid incorporation into the framework. It was found that there is loss of surface area after boronic acid incorporation and this must be due to the replacement of the main ligand in the framework by boronic acid and it might block pore space available in the framework<sup>19</sup>. The BET specific surface area of B-UiO-66 is 231.0182 m<sup>2</sup>/g. The surface area is reduced to almost half of the original after ligand replacement.

Adsorption of catechol based dye by the Activated MOFs:

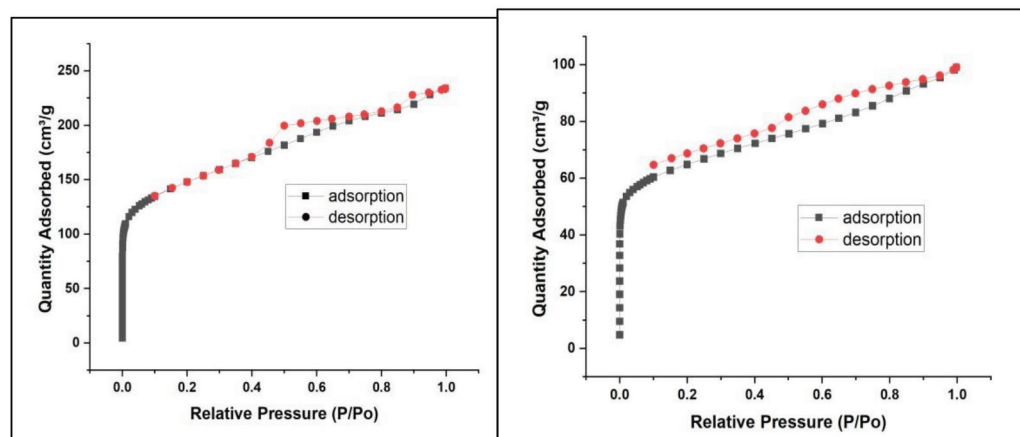
The as synthesized MOFs were activated by eliminating the water molecules inside the pores by heating at 100 °C for a period of 12 hours under vacuum conditions. The MOF samples were stored in a desiccator



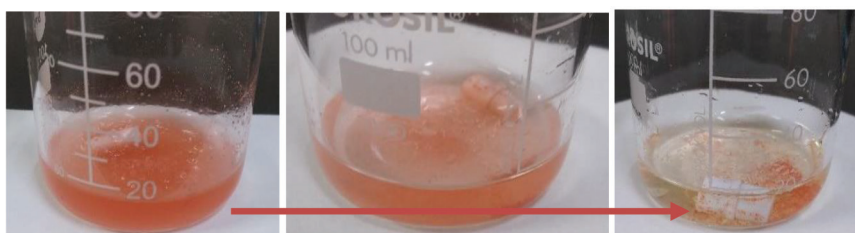
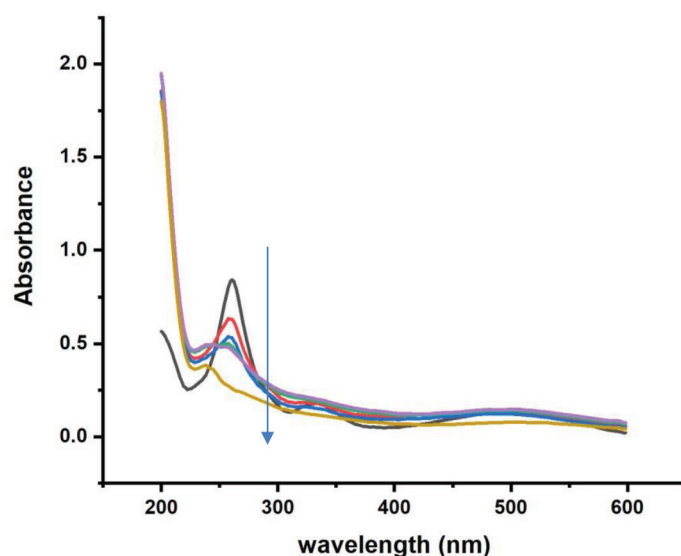
**Figure 5.** Thermogravimetric analysis of UiO-66 and B-UiO-66.

before carrying out the adsorptive removal experiments. The adsorption capability of the activated B-UiO-66 MOF towards Alizarin red dye from aqueous solution was carried out. Stock solutions (2 g/L) concentration were prepared in distilled water and stored in a cool, dry place. The working solutions were prepared by the dilution the stock solutions using distilled water.

The adsorption experiments for the removal of Alizarin dye was done at room temperature. Initially, 30 mL of 200 mg/L concentration pollutant was taken in 100 mL beaker. To this solution, 20 mg of the synthesized, adsorbent was added. The suspensions were shaken at 100 rpm in an orbital shaker. 3 mL of resultant solutions were withdrawn at particular time interval and the supernatant was centrifuged at 10000 rpm for 10 minutes and then filtered to remove any residues of MOFs. Then the concentration of the pollutant dye was analysed by checking the absorption spectrum of alizarin red using



**Figure 6.**  $N_2$  adsorption-desorption curve for (a) UiO-66 and (b) B-UiO-66.



**Figure 7.** (a) Absorption spectrum collected for aliquots of Alizarin dye at different time intervals during dye adsorption on MOF; (b) The photo of MOF suspension in dye solution taken at different time intervals.

UV-visible spectrometer. It was observed that the dye was completely adsorbed on MOF within less than one hour.

## 4.0 Conclusion

Boronic acid grafted into framework MOF was synthesized by taking UiO-66 as parent compound and

it was successfully employed for the effective adsorption of catechol dyes (Alizarin red S was selected in this case) from the aqueous solution owing to the increased affinity of the boronic acid groups with the cis-diols.  $^{11}B$  NMR data affirmed the presence of free boronic acid groups. The PXRD, BET surface area calculation through  $N_2$  adsorption studies, IR, and TGA confirmed the structural

stability of the MOF after boronic acid incorporation whereas the UV-Vis spectroscopic study was done for the quantification of dye adsorption. The dye absorbs in UV region at around 270 nm as absorption maximum. The complete dye adsorption could be attained by this MOF within short period of time with greater affinity of catechol group in the dye towards boronic acid groups.

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