An Approachable Solvothermal Synthesis of Uio-66 for Carbon Dioxide Capture from Automobile Emissions

A. P. Pandhare[1] Suyog Lokhande[2] Mahesh Mengale[3] Ashish Kohad[4] Nikhil Jumnake[5]
[1,2,3,4,5]Department of Mechanical Engineering
[1,2,3,4,5]Savitribai Phule Pune University, Sinhgad College of Engineering Vadgaon BK, Pune, India

Abstract— Metal-organic frameworks (MOFs) are a class of porous material which is made by strong bonds between metal ions and organic linkers. Zirconium-based MOFs are subclass of MOFs known for their high surface area, large pore volume and excellent stability especially in the presence of water. In this study, the Zr-MOF (UiO-66) was fabricated by the solvothermalsynthesis method, with the addition of HCl to reaction mixture. A mixed-ligand Zr-MOF material has been synthesized for CO2 capture at room temperature. This Zr-MOF (UiO-66) was tested using XRD and BET surface area test. The Study also tells about surface area increment of defective UiO-66 and gives an idea about the selection of the proper grade of chemical material required in the synthesis of UiO-66.

Keywords: Metal-Organic Frameworks, Zr-MOF, Uio-66, Adsorption, Carbon Dioxide, Emission

I. INTRODUCTION

Carbon dioxide (CO2) and Methane (CH4) are major greenhouse gases [1]. Plenty amount of greenhouse gases emitting into the atmosphere hassled to major environmental issues, the substantial harm to the natural environment has caused widespread concern around the world. Among them, CO2 is the largest contributor. So far, CO2 capture is important to face the challenge of climate change [2]-[3].

Metal-organic frameworks (MOFs) are new kinds of porous adsorbents. MOFs have been generated that exhibit the highest known surface area, high porosity, the lowest crystal densities, high hydrogen storage capacity and also CO2 capture capacity [4]-[7]. MOFs are widely used in adsorption, separation, catalysis process. So far, MOF materials have been synthesized and used in CO2 capture [2]. Among the MOFs zirconium-based organic frameworks (Zr-MOFs) Uio-66 is one who attracted more attention recently. For their remarkable stability, especially in the presence of water [8]-

Depending on final structures and properties, MOFs may be prepared using several distinct synthetic methods such as: slow diffusion, hydrothermal, solvothermal, electrochemical, mechanochemical, microwave-assisted heating, and ultrasound [3], [10]-[11]. The synthesis of Uio-66 using a solvothermal process change activation process to enhance the porous structure and its application in H2 and CO2adsorption [1], [12].

Post synthetic defect exchange (PSDE) reduces the porosity of defective Uio-66 but improves both CO2 uptake and CO2 selectivity. Whereas PSE (Post Synthetic Exchange) does not affect the porosity of non-defective Uio-66 [8]. In this paper, we are presenting the Uio-66 synthesis process for the application to capture CO2. The general requirement of Uio-66 to capture CO2 is as follows [13]:

1) The average surface area must be ≥ 850 m2/g.
2) Pore size: 8.5Å to 11.5Å.

In the following synthesis processes, the first two processes give fewer values than required. So that they are No-Go type of process but synthesis 3 process gives the more surface area and required pore size. Other than that, this paper gives an idea about the proper selection of chemical grade as required in the process. Also tells the importance of concentrated HCL (Hydrochloric acid) in the synthesis process.

II. EXPERIMENTAL

A. Reagents and Chemicals

Essential information about the required chemicals given in Table 1. These given chemicals are sufficient for the synthesis of Uio-66.

Sr. No.	Name	Grade/Purity	Case no.	Company Name
1	Zirconium (IV) Chloride anhydrous: (ZrCl4)	99.5%	10026-11-6	Merck Life Science Pvt. Ltd.
2	Terephthalic (H2BDC) Acid	98%	100-21-0	LobaChemie Pvt. Ltd.
3	N.N-Dimethylformamide purisss[DMF] (C3H7NO)	HPLC & AR	68-12-2	Spectrochem Pvt. Ltd. Mumbai. (INDIA)
4	Methanol Anhydrous (especially dried) (CH4O)	AR	67-56-1	Spectrochem Pvt. Ltd. Mumbai. (INDIA)
5	Hydrochloric Acid (HCL)	LR	7647-01-0	Research Lab Fine Chem Industries
6	Ethanol (C2H5OH)	LR	64-17-5	Changshu Hongsheng Fine Chemical Co., Ltd

Table 1: Information about the Required Chemicals

B. Synthesis of Zr-MOFs (UiO-66)

1) Synthesis 1:

UiO-66 synthesis was performed by first dissolving equimolar amounts of ZrCl4 (3.5 mmol, 0.82 g) and H2BDC (3.5 mmol, 0.58 g) [14] in 50 ml DMF and stirring for 15 minutes [1]. This clear solution was transfer into a

Teflon-lined stainless steel autoclave reactor. The reaction took place at 120o C for 24 hours [14]-[15]. The resulting product wash means centrifuged thrice with DMF (commercial grade) and once with Ethanol (LR) [16]. The final product Uio-66 crystals where hot air oven-dried at 120o C for 24 hours [1]. This is how we got the final product of UiO-66. But this process gives very less surface area because of the use of low-grade chemicals.

2) Synthesis 2:

For performing UiO-66 synthesis first dissolve equimolar amounts of ZrCl4 (3.5 mmol, 0.82 g) and H2BDC (3.5 mmol, 0.58 g) [14] in 50 ml DMF and stirring for 15 minutes [1]. This clear solution was transfer into a Teflon-lined stainless steel autoclave reactor, and to remove moisture from the above surface of the solution we flush Nitrogen (N2) gas in it. The reaction took place at 120o C for 24 hours [14]. The resulting product was centrifuged for 10 minutes at 4000 RPM, and wash thrice with DMF (AR) and one time with Methanol (LR). The final product crystal was vacuum dried at 105o C overnight. This is how we got the final product of UiO-66 having more surface area than synthesis 1.

3) Synthesis 3:

The synthesis of UiO-66 had been carried out by dissolving ZrCl4 and H2BDC in DMF (HPLC). The weight ratio of ZrCl4 and H2BDC must be 1.0162 [13].

Therefore we took 1 g of ZrCl4, 0.984 g H2BDC and 120 ml DMF (HPLC) for our synthesis process. The solubility of ZrCl4 in DMF is enhanced by HCL, also HCL speeds product formation [13]. Surface area measurement of the material demonstrates that the higher HCL concentration leads to larger surface areas [13]. Here we used 8 ml HCL (35-38%) for the above-mentioned quantities of DMF and ZrCl4. Stirred the above solution for 2 hours [13]. This solution was transferred into a Teflon-lined stainless steel autoclave reactor, to remove the moisture contain from surface of the solution we flush N2 gas in it. The reaction took place at 150o C for 12 hours in a hot air oven [13]-[18]. The resulting product then centrifuged three times with DMF (AR) and one time with Methanol (AR). Centrifuging done for 25minutes at 2500 RPM for every wash. The final product crystal was vacuum dried at 120o C for 18 hours in a vacuum dryer. By following the above-said process we got maximum surface area (1051.827 m2/g) which is sufficient to capture carbon dioxide. CO2 adsorption in zirconium MOF UiO-66 almost doubles with post-synthetic exchange of Zr by Ti (Titanium) [17].

4) Synthesis 4:

Synthesis of Uio-66 to enhancing CO2 capturing the performance of defective Uio-66 [8]. In this process, we increase the surface area of the material to capture CO2. The result of synthesis 1 gives only 65.366 m2/g surface area which was insufficient to capture CO2. To overcome this defect we used the following method. First, we took the UiO-66 in a beaker and mixed with DMF (HPLC). Then centrifuged this solution three times with DMF (HPLC) and one time with Methanol (AR). Then put it in vacuum dryer for 18 hours at 120o C. By doing this process we got new Uio-66 having results similar to the synthesis 3.

III. RESULTS AND DISCUSSION

A. XRD Analysis

X-Ray Diffraction is frequently abbreviated as XRD. It is a non-destructive test method used to analyze the structure of crystalline materials. It also used to identify the crystalline phases present in a material [19].

XRD pattern was drawn by using origin software. The XRD pattern in Figure 1 showed typical UiO-66 2-Theta peak positions (~7.4, 8.5 and 25) as reported in previous studies [1]-[2], [18], and [20]. As observed in Figure 1 there were very similarities in the XRD pattern as compared to previous observations [1]. This suggests that the addition of HCL and weight ration of ZrCl4 to H2BDC shall not harm the crystallite structure of Zr-MOF (UiO-66), so it proved that weight ratio and HCL concentration is correct. In Figure 2 the XRD pattern not showed the 2-Theta peak position as reported in previous studies of UiO-66. From this, we proved that quality, grade and weight ratio of materials effects crystalline phases present in the material.

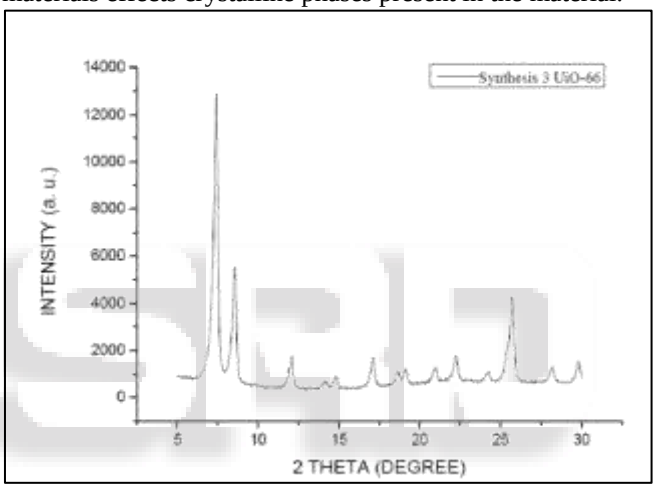

Fig. 1: XRD pattern of synthesis 3of UiO-66

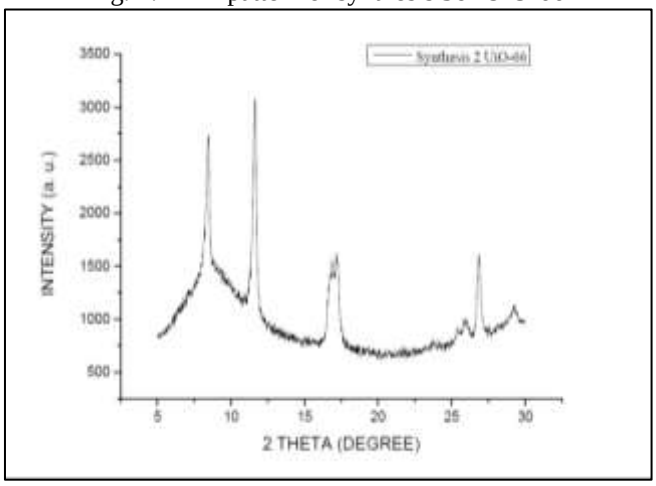

Fig. 2: XRD pattern of synthesis 2 of UiO-66.

Figure 3 shows both the XRD pattern of UiO-66 made by synthesis 3 and synthesis 2 processes. It gave a clear idea about the deviation of pattern and peak values of two different synthesis methods of UiO-66.

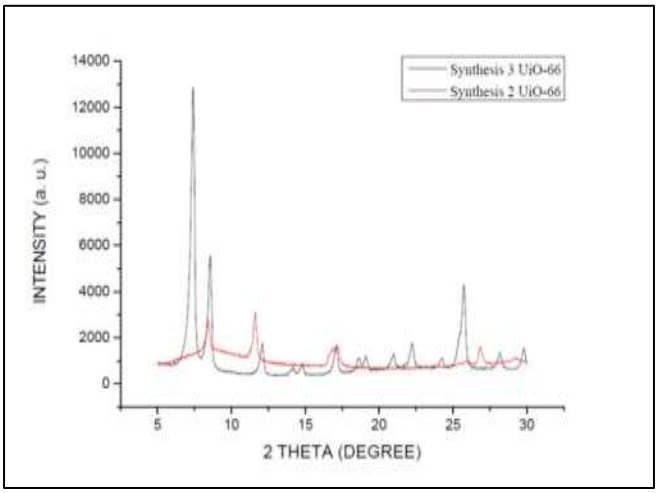

Fig. 3: XRD patterns

B. BET Analysis

Brunet-Emmett-Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as a basis for an important analysis technique for the measurement of the specific surface area of materials.

1) CO2 Adsorption-Desorption Isotherms (Synthesis 1 Results):

Carbon dioxide adsorption and desorption isotherms are used to get the structural information about the synthesized 1 Uio-66 as shown in Figure 4 the isotherm shows linear properties. A linear increment between the relative pressures from 0 to 0.8 revealed that there were microspores inside. The parameters of the porous structure calculated from these isotherms and pore size distributions where presented in Table 2. The calculated surface area and pore size of Uio-66 by synthesis 1 where 66.366 m2/g and 17.8 Å respectively.

Compared to Uio- 66 reported in synthesis 3, the sample shows a lower crystallinity. That may be due to synthesis conditions and low grade of synthesis material. Also, this happened due to not use of vacuum dryer.

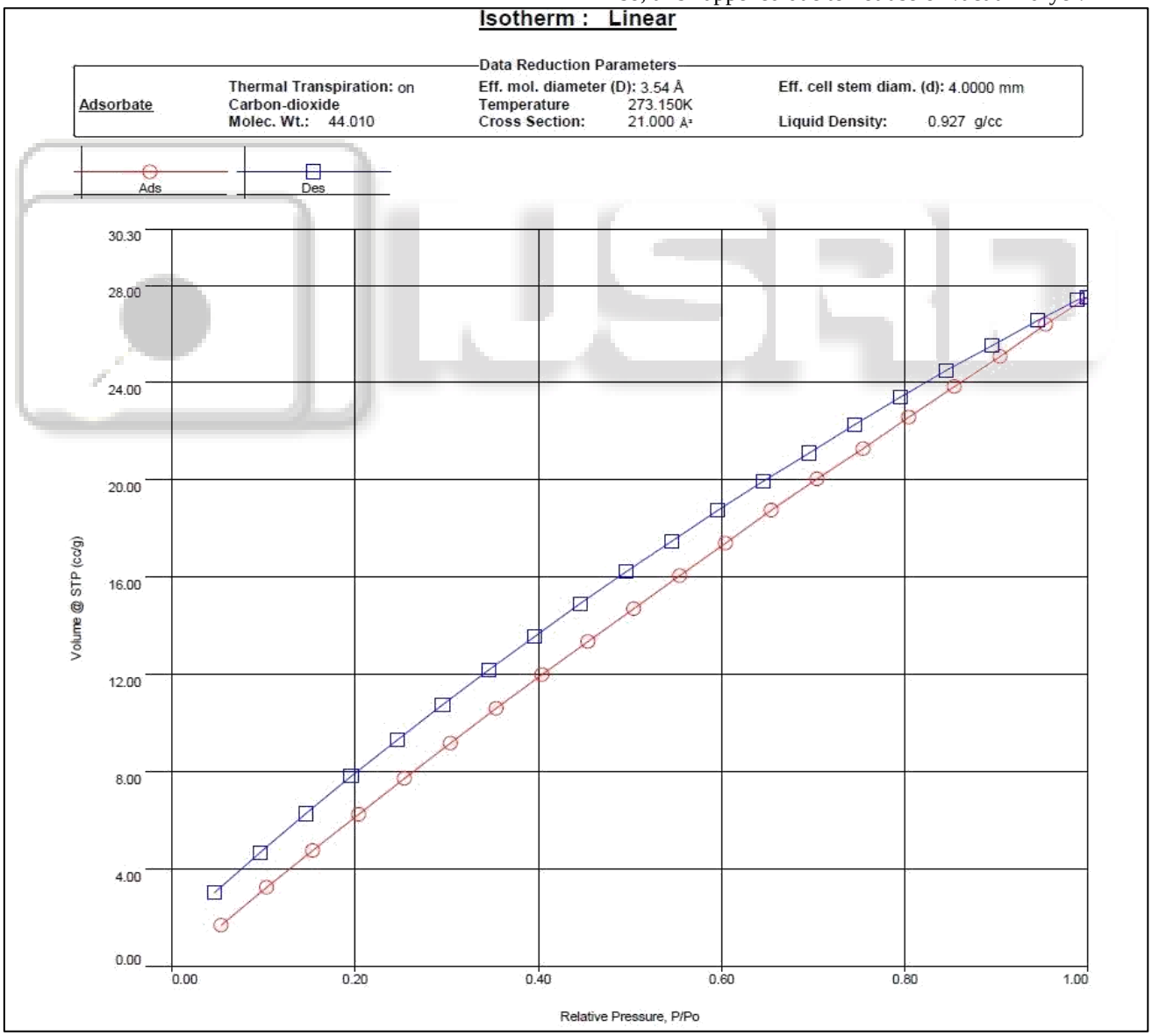

Fig. 4: CO2 Adsorption desorption isotherms of sorbents of synthesis 1

2) N2 Adsorption-Desorption Isotherms (Synthesis 2 Results):

Nitrogen adsorption and desorption isotherms are used to get the structural information about the synthesized 2 Uio-66 as shown in Figure 5 that exhibited permanent micro porosity, it gives linear nature of isotherms. The parameters of the porous structure calculated from these isotherms and pore size distributions were presented in Table 2. The calculated surface area and pore size of synthesis 2 Uio-66 were 464.743 m2/g and 26.2 Å respectively. Compared to Uio-66 reported in synthesis 3, the sample shows a lower crystallinity, it is because of the use of low-grade chemicals.

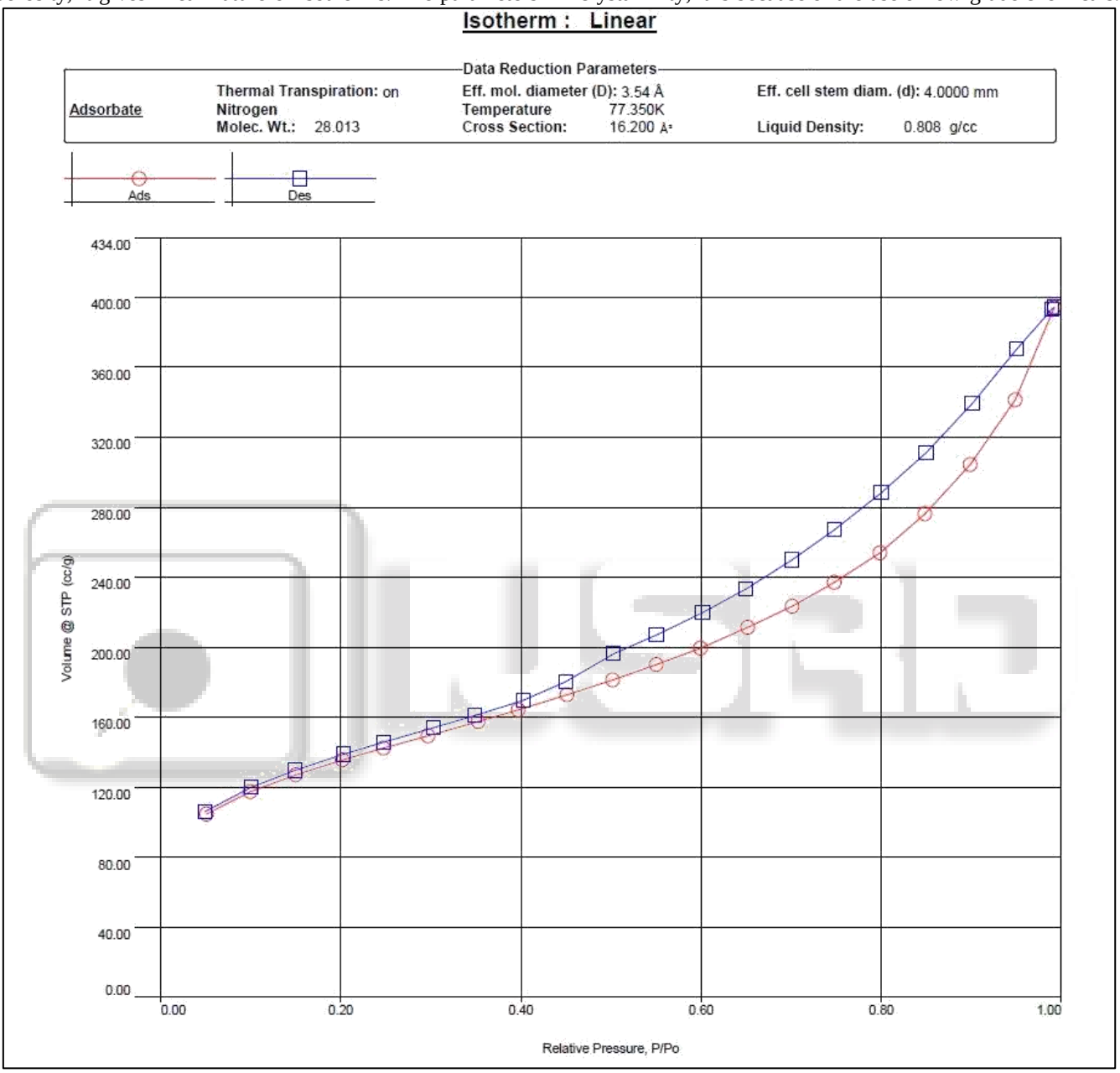

Fig. 5: N2 Adsorption-desorption isotherms of sorbents of synthesis 2

3) N2 Adsorption-Desorption Isotherms (Synthesis 3 Results):

Synthesized 3 Uio-66 is the sample which is having sufficient surface area and pore size to capture carbon dioxide. The isotherm in Figure 6 shows a sharp increase between the relative pressures of 0.05 to 0.2 revealed that there were plenty of micropores inside. The parameter of the porous structure calculated from these isotherms and pore size distributions were presented in Table 2. The calculated surface area and pore size of synthesized 3 Uio-66 where 1051.827 m2/g and 11.38 Å respectively. Compared to Uio-66 reported in the literature [13] and [2], the sample shows a lower crystallinity. But the results are sufficient to capture carbon dioxide.

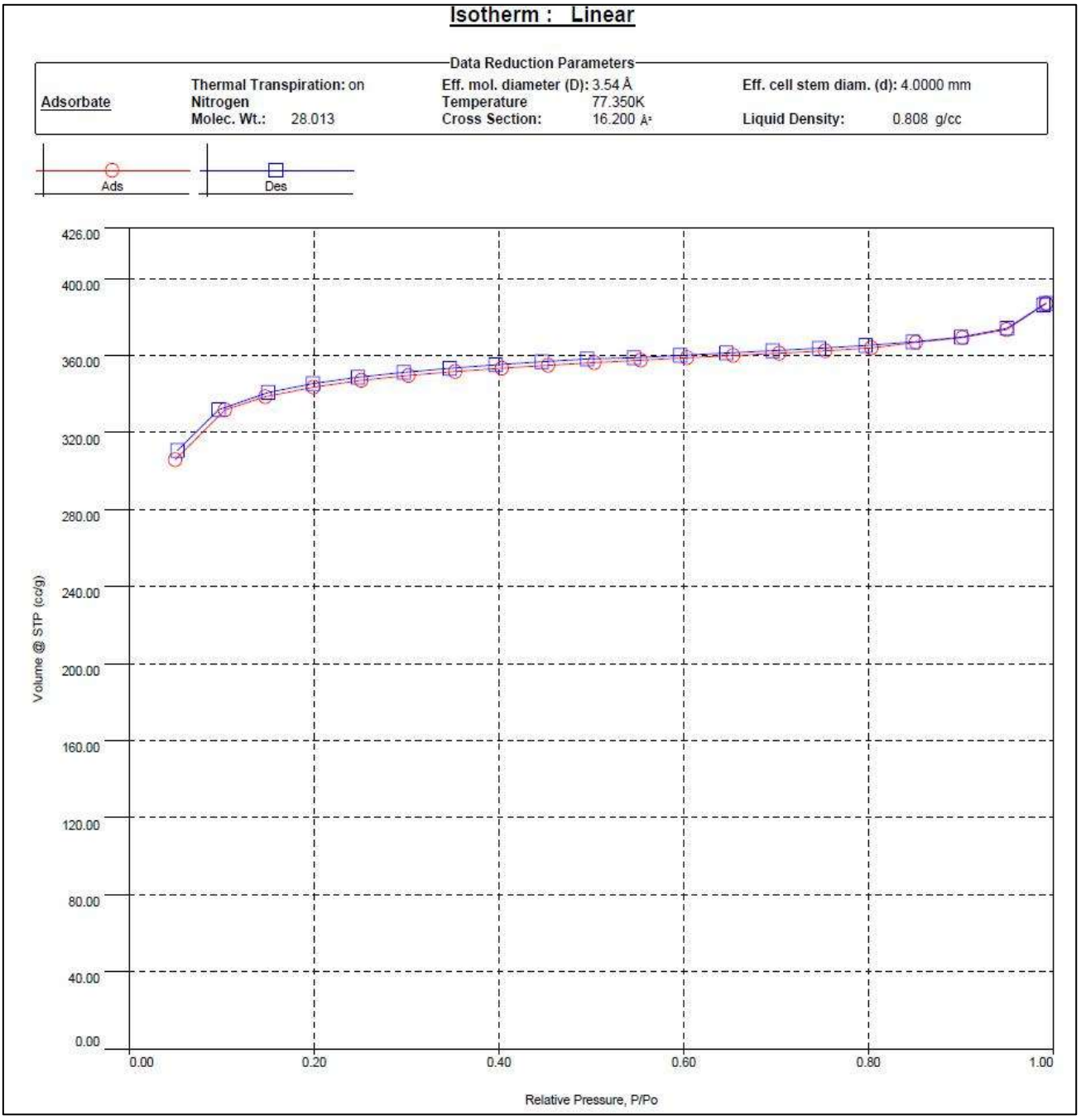

Fig. 6: N2 Adsorption-desorption isotherms of sorbents of synthesis 3

Compound	Adsorbent	Surface Area BET (m^2/g)	Liquid Density (g/cc)	Average pore radius (Å)
Uio-66[13]	N2	1580	-	-
Uio-66[2]	N2	1250	-	2.6
Synthesis 3	N2	1051.827	0.808	11.38
Synthesis 2	N2	464.743	0.808	26.2
Synthesis 1	CO2	65.366	0.927	17.8

Table 2: Structural Properties of Uio-66 by Different Synthesis Methods

IV. CONCLUSION

In our study, the selection of proper weight ratio (1.0162) of ZrCl4 to H2BDC in the synthesis process of Zr-MOF (UiO- will produce an effect on structure and properties as shown in Figure 3 The addition of HCl and high HCl concentration leads to a larger surface area. Time and temperature in the synthesis process plays an important role in the perfect synthesis. The defective UiO-66 (less surface area) is treated by re-washing the material using 3 wash of HPLC grade DMF and last wash by AR grade methanol then uses a vacuum dryer for drying. This results in increment in surface area.

ACKNOWLEDGMENTS

This work was supported by the Mechanical Department of Sinhgad College of Engineering Pune, Sinhgad Dental College Pune, and Sinhgad Pharmacy College Pune. All the authors would like to thank all of them.

REFERENCES

[1] Hussein Rasool Abid, Gia Hung Pham, Ha-Ming Ang, Moses O. Tade, Shaobin Wang, Adsorption of CH4 and CO2 on Zr- metal organic frameworks, Journal of Colloid and Interface Science, 366 (2012) 120-124.
[2] Qiheng Huang Jing Ding, Xiang Huang, Xiaolan Wei, Weilong Wang, Experimental and computational investigation of CO2 capture on mix-ligand metal-organic framework UiO-66, Energy Procedia 105 (2017) 4395 – 4401.
[3] Tyler G. Grissom, Darren M. Driscoll, Diego Troya, Nicholas S. Sapienza, Pavel M. Usov, Amanda J. Morris, and John R. Morris Molecular-Level Insight into CO2 Adsorption on the ZirconiumBased Metal−Organic Framework, UiO-66: A Combined Spectroscopic and Computational Approach, J. Phys. Chem. C 2019, 123, 13731−13738.
[4] Jesse L.C. Rowsell, Omar M. Yaghi, Metal-organic frameworks: a new class of porous materials, Microporous andMesoporous Materials 73 (2004) 3–14.
[5] Jeffrey R. Longa and Omar M. Yaghib, The pervasive chemistry of metal-organic frameworks, Chem. Soc. Rev., 2009, 38, 1213– 1214.
[6] Sunyoung Bae, NabilahZaini, Khairul Sozana Nor Kamarudin, Kye Sang Yoo, Jinsoo Kim, and MohdRoslee Othman, Rapid solvothermal synthesis of microporous UiO-66 particles for carbon dioxide capture, Korean J. Chem. EngpISSN: 0256-1115 eISSN: 1975- 7220.
[7] Ye-Wang Peng, Rui-Juan Wu, Meng Liu, Shuang Yao, Ai-Fang Geng and Zhi-Ming Zhang, Nitrogen Coordination to Dramatically Enhance the Stability of ln-MOF for Selectively Capturing CO2 from CO2/N2 mixture, Cryst. Growth Des. DOI: 10.1021/acs.cgd.8b01709.
[8] Athanasios Koutsianos, EwaKazimierska, Andrew R. Barron, Marco Taddei, and Enrico Andreoli, A new approach to enhancing the CO2 capture performance of defective UiO- 66 via post- synthetic defect exchange, J. Name., 2013, 00, 1- 3.
[9] Dr. Marco Taddei, UiO-66: Case Study Metal-Organic Framework, PSI, Catalysis Class 529-0502-00L
[10] Min Hui Yap, Kam Loon Fow, George Zheng Chen, Synthesis and applications of MOF-derived porous nanostructures, Green Energy & Environment 2 (2017) 218e245
[11] Junjie Zhu, Linbo Wu, Zhiyang Bu, SuyunJie, and Bo-Geng Li, Polyethyleneimine- Modified UiO-66-NH2(Zr) Metal−Organic Frameworks: Preparation and Enhanced CO2 Selective Adsorption, ACS Omega 2019, 4, 3188−3197
[12] Christopher A. Trickett, AasifHelal, Bassem A. Al-Maythalony, Zain H. Yamani, Kyle E. Cordova1, and Omar M. Yaghi, The chemistry of metal-organic frameworks for CO2 capture, regeneration and conversion, Nature reviews materials volume 2 article number 17045.
[13] Michael J. Katz, Zachary J. Brown, Yamil J. Colo, Paul W. Siu, Karl A. Scheidt, Randall Q. Snurr, Joseph T. Hupp and Omar K. Farha, A facile synthesis of UiO-66, UiO-67 and their derivatives, Chem. Commun., 2013, 49, 9449.
[14] JeewanPokhrel, NidhikaBhoria, Chao Wu, K. Suresh Kumar Reddy, HarisMargetis, StavroulaAnastasiou, Gigi George, Vikas Mittal, George Romanos, DimitriosKaronis, Georgios N. Karanikolos, Cu- and Zr-based Metal-Organic Frameworks and their Composites with Graphene Oxide for Capture of Acid Gases at Ambient Temperature, Journal of Solid State Chemistry, https://doi.org/10.1016/j.jssc.2018.07.022.
[15] Yan Cao 1, Hongmei Zhang, Fujiao Song, Tao Huang, Jiayu Ji, Qin Zhong, Wei Chu, and Qi Xu, UiO-66-NH2/GO Composite: Synthesis, Characterization and CO2 Adsorption Performance, Materials 2018, 11, 589.
[16] Xinlei Liu, NilayKeser Demir, Zhentao Wu, and Kang Li, Highly Water-Stable Zirconium Metal−Organic Framework UiO-66 Membranes Supported on Alumina Hollow Fibers for Desalination, J. Am. Chem. Soc. 2015, 137, 22, 6999-7002.
[17] Cher Hon Lau, RavichandarBabarao and Matthew R. Hill, A route to drastic increase of CO2 uptake in Zr metal-organic frame work UiO-66, Chem. Commun., 2013, 49, 3634-3636.
[18] IkaDiahRahmawati, RatnaEdiati, DidikPrasetyoko, Synthesis of UiO-66 Using Solvothermal Method at High Temperature, IPTEK, Journal of proceeding series, Vol. 1, 2014, ISSN: 2354-6026.
[19] Sonwabo E. Bambalaza, Henrietta W. Langmi, Robert Mokaya,Nicholas M. Musyoka, JianweiRenad and Lindiwe E. Khotseng,Compaction of a zirconium metalorganic framework (UiO-66) for high-density hydrogen storage applications, J. Mater. Chem. A, 2018, 6, 23569.
[20] Ramanathan Vaidhyanathan, Metal-Organic Framework: Crystalline Stacked Molecular Containers, General Article Volume 19 Issue 12 December 2014 pp 1147-1157.

