ISSN NO. 2320-5407

Journal Homepage: -www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI:10.21474/IJAR01/1225
DOI URL: http://dx.doi.org/10.21474/IJAR01/1225

RESEARCH ARTICLE

A COMPARISON OF GAS ADSORPTION ON METALORGANIC FRAMEWORKS USING A STICKING FACTOR CONCEPT.

Esosa Mark Iriowen and*Andrew Goudy.
Delaware State University, Department of Chemistry, 1200 N Dupont Highway.

……………………………………………………………………………………………….....

Manuscript Info

Manuscript History

Received: 13 June 2016
Final Accepted: 19 July 2016
Published: August 2016

Key words:-
Metal organic framework, BET Isotherms, Gas adsorption, Sticking Factor.

Abstract

A study was done to determine how a new parameter denoted sticking factor would correlate with gas adsorption by MOFs. The adsorptions of hydrogen, carbon dioxide and methanegaseson a variety of MOFs werecompared at low and high pressures. It was found that, at low pressures, sticking factorcorrelated better with gas adsorption capacity than did surface area. At higher pressures, surface area correlated better with the gas adsorption capacity than did sticking factor for the adsorption of hydrogen and carbon dioxide on MOFs. However, the sticking factor correlated better with methane gas uptake at both low and higher pressures than did surface area. The most likely reason for this is that, under the conditions used,the isotherms for methane did not show saturation at higher pressures whereas those for hydrogen and carbon dioxide did. This demonstrates that it is saturation not pressure that determines whether a correlation will exist between sticking factor and gas uptake. So in general it can be stated that, when saturation has occurred, gas adsorption capacity will be proportional to the surface area, but prior to saturationthe adsorption capacity will be proportional to the sticking factor.Since MOFs are relatively complex materials with various functional groups, open coordination sites, etc., it is truly remarkable that a simple parameter such as the sticking factor is able to correlate so well with gas uptake prior to saturation.

Copy Right, IJAR, 2016,. All rights reserved.

……………………………………………………………………………………………….....

Introduction:-

Metal organic frameworks (MOFs) have attracted considerable attention because many of them have large surface areas with the ability to adsorb large amounts of gases such as hydrogen, carbon dioxideand methane(Zhao et al., 2008), (Yaghi et al., 2003), (Murray et al., 2009).It has long been established that hydrogen gas uptake in carbonaceous materials is proportional to the surface area. There have been recent reports of MOFs that have surface areas in excess of 4000 m^2/g(Furukawa et al., 2010), (Wilmer et al., 2013) .Chahine's rule states that a 500 m^2 increase in surface area will result in an increase in 1 wt% H_2 (Poirier et al., 2001).However, there are other factors that may also affect gas uptake by MOFs.(Frost et al., 2006)did Grand canonical Monte Carlo simulations to predict the adsorption isotherms for hydrogen on MOFs . Their results showed that at low pressures, hydrogen uptake correlated well with adsorption enthalpy but at higher pressures uptake correlated with surface area. At the highest pressures, uptake correlated with free volume(Wang et al., 2007) did a systematic Monte Carlo simulation

Corresponding Author:-Andrew Goudy.
Address:-Delaware State University,Department of Chemistry, 1200 N Dupont Highway. Dover, DE19901. USA

on the adsorption of methane in a series of 10 MOFs to confirm the desirable characteristics of an optimal adsorbent for methane storage. One of the characteristics included large accessible surface area. However, at low loading (pressure) materials with the strongest enthalpy interactions with the adsorbed molecules showed the highest levels of adsorption capacity.Based on the simulation, it was concluded that the accessible surface area and free volume play a main role in determining methane uptake at 298 K and 3.5 MPa.(Yang, et al., 2008)performed a systematic computational study to investigate the effects of several parameters on the adsorption behavior of carbon dioxide on MOFs. It was found that the suitable pore size is between 1.0 and 2.0 nm. For MOFs with pore sizes in this range, it was found that, at pressures up to 7.0 MPa, the larger the accessible surface area and free volume, the higher the CO_2 storage capacity. Thus it seems as though high surface area is an important factor in determining gas adsorption capacity of MOFs at higher pressures. However, at low pressure high isosteric heat of adsorption may be more important.

(Iriowen et al., 2015)demonstrated that a new parameter denoted sticking factor(Θ) correlated well with gas adsorption enthalpy at 77 K and pressures up to 1 bar.This term is a measure of the sticking efficiency of gas adsorption on MOFs. It had been initially introduced by (Orefuwa et al., 2013**)**to discuss the effect of nitrofunctionalization on the hydrogen uptake by IRMOF-8. The sticking factor can be calculated from equation 1

$$\theta = \frac{Q_{ads}}{S_{SA}} \times \frac{N_A}{M_{mm}} \qquad (1)$$

Where Q_{ads} is the weight percentage of gas adsorbed, S_{SA} is the surface area of the MOF in m^2/g, N_A is Advogadro's number and M_{mm} is the molar mass of the adsorbed gas. Since the sticking factor is the fraction of hydrogen gas adsorbed per unit area of surface, it actually represents the efficiency in which the molecules are able to bind to the surface. It is also evident that since the sticking factor is directly proportional to the enthalpy of hydrogen adsorption it is a direct measure of the binding strength of hydrogen on the surface. Enthalpy measurements are not available for many MOFs and in those cases the sticking factor concept is another way of predicting the tendency of those MOFs to adsorb gases. One of the limitations of the study done by (Iriowen et al., 2015)is that it was limited to the adsorption of hydrogen gas on MOF surfaces at low pressures (less than 1 bar). Thus it is uncertain that the sticking factor will correlate with adsorption enthalpy at higher pressures. The study was also limited to the adsorption of hydrogen gas. There is a need to determine if sticking factor will correlate with adsorption enthalpy for heavier gases which may display stronger interactions between the molecules and the MOF surfaces. The aim of this work is toexpand on the previous study done by (Iriowen et al., 2015) to include studies on the adsorption of methane and carbon dioxide gases on MOFs at both low and higher pressures.

Materials and Methods:-

The Fe-BTC and Zn-Mim used in this study were obtained commercially from Sigma Aldrich U.S.A. and were used without further purification. The Zn-BDC and Zn-NDC were prepared by a rapid solvothermal process developed by (Orefuwa et al., 2012), (Orefuwa et al., 2013)and theCu-BTC by a mechanochemical synthesis method described by (Yang et al., 2011).BET surface areas and pore volumes were determined using a Micromeritics ASAP 2020 sorptometer.High pressure gas adsorption capacities were determined using a High Pressure Volumetric Analyzer (HPVA-100) and low pressure adsorptions were done using the ASAP 2020.Before analysis, the samples were degassed under vacuum at room temperature for 1 hour at 200 °C.Prior to degassing, the thermal stability of the samples was determined using a Perkin Elmer-Diamond TG/DTA thermogravimetric Analyzer (TGA). The synthesis and characterization procedures are described in greater detail elsewhere (Iriowen et al., 2015), (Orefuwa et al., 2012), (Orefuwa et al., 2013)**.**

Results and Discussion:-

The gas adsorptions of H_2, CH_4 and CO_2 were compared ona variety of MOFs under several conditions. The adsorption data for five of the MOFs:Zn-BDC, Zn-NDC, Cu-BTC, Fe-BTC and Zn-Mim), were collected in this lab while data for several other MOFs were obtained from the various literature sources shown in Tables 1 - 3. The surface areas for these five MOFs were determined volumetrically from N_2 adsorption-desorption isotherms at 77 K. The BET isotherms for these determinations have been reported in an earlier publication(Iriowen et al., 2015). The values for the BET surface areas that were obtained from these isotherms are listed in Tables 1 - 3 along with other data.

Previous Results for Hydrogen Adsorption at 77 K and Low Pressure:-

In an earlier study done in this lab, an effort was made to determine the H_2 gas adsorption capacity on the five MOFs mentioned above at 77 K and at pressures less than 1 bar [10], and to determine if a correlation existed between H_2 uptake and the sticking factor. In order to do this, H_2 adsorption isotherms were determined in which H_2 weight percent was plotted as a function of pressure in bar. These isotherms have been published (Iriowen et al., 2015). They showed that the hydrogen uptake increased with pressure in the range up to 1 bar. The weight percentages obtained from these isotherms at 1 bar are given in Table 1 along with weight percentagesobtained from the literature for several other MOFs. These weight percentages were used in equation 1 to determine sticking factors (ϴ) for the MOFs. The values of ϴ are also listed in Table 1. Plots of wt.% versus surface area were constructed and compared to plots of wt.% versus ϴ. These have also been published (Iriowen et al., 2015).It was found that, under these conditions,a better correlation existed between ϴ and wt.% than between surface area and wt.%.

Hydrogen Adsorption at 77 K and high pressure:-

In the present study, the five MOFs used in the earlier work were studied at higher pressures. Based on the Grand Canonical Monte Carlo simulations done by (Frost et al., 2006), it is expected that the gas adsorption behavior will be different at higher pressures than at low pressures. Their results showed that at low pressures, hydrogen uptake correlated well with adsorption enthalpy but at higher pressures uptake correlated with surface area. If sticking factor is truly a measure of adsorption enthalpy, we should observe a change in the behavior of the sticking factor at low and higher pressures. Therefore it was decided that the same type of measurements done at low pressures should be done at higher pressures. To accomplish this,H_2 adsorption isotherms were determined at 77 K and at pressures ranging up to 100 bar. The adsorption isotherms obtained under these conditions are shown in Fig. 1. These isotherms were used to determine weight percentages when saturation had occurred. These weight percentages are listed in Table 1 just below the corresponding values at low pressures. The weight percentages for several other MOFs obtained from literature sources have been included as well. Values for ϴ were computed from equation 1 as was done in the low pressure case. Plots of surface area versus wt.% and ϴ versus wt.% were constructed and are shown in Figs.2a and 2b, respectively. In order to compare the data in the two graphs, a linear regression line was constructed and the correlation coefficient (R^2) was determined for each set of data. The values of R^2 ranged from 0 to 1 with $R^2 = 1$ being the best and 0 being the worst. The equation for the straight line is also displayed in each graph. The results show that $R^2 = 0.3968$ for the graph of surface area versus wt.%(Fig. 2a) whereas a value of 0.0004 was obtained for the graph of ϴ versus wt.% (Fig. 2b). The linear regression line for the graph of ϴ versus wt.% displayed a negative slope while the line for the plot of surface area vs. wt.% showed a positive slope. This indicates that in the high pressure case a better correlation exists between surface area and wt.% than between ϴ and wt.%. This is the expected result based on the simulations done by (Frost et al., 2006).

Carbon Dioxide Adsorption at 298 K and at Low/High Pressures:-

It was also of interest to see how a gas such as CO_2 would adsorb onto MOFs. This gas has 22 electrons and thus its van der Waals attractions are much stronger than those of H_2 with only 2 electrons. Adsorption isotherms for CO_2 were constructed at 298 K, at low and high pressures, for the five MOFs used in this study as well as for several others from literature sources. The plots done at low pressure are shown in Fig. 3a and those at high pressure are in Fig. 3b. It was of interest to determine if the same type of behavior observed for H_2 adsorption at low and high pressures would be seen here. The weight percentages obtained from the isotherms at low and high pressures are given in Table 2. These were used in equation 1, along with surface areas, to determine sticking efficiencies. They are also included in Table 2. Figs. 4a and 4b contain plots of wt.% versus surface area and wt.% versus ϴ at low pressure, respectively. We see that, at low pressure, there is a slight negative slope to the linear regression line in Fig. 4a with $R^2 = 0.021$. This shows that there is no correlation between surface area and wt.% at low pressure. In Fig. 4b the line has a positive slope with $R^2 = 0.6798$. This shows that there is a much better correlation between ϴ and wt.% than between surface area and wt.% at low pressure. Figs. 5a and 5b contain corresponding plots at high pressure. In the surface area vs. wt.% plot (Fig. 5a) there is a positive slope to the regression line with ($R^2 = 0.6742$) and in the sticking efficiency vs. wt.% plot(Fig. 5b) there is a negative slope to the line with ($R^2 = 0.2121$). This shows that there is a much better correlation at high pressure between surface area and wt.% than between ϴ and wt.%. This is similar to the behavior that was observed for H_2 adsorption at high pressure.So again this agrees with the results expected based on the simulations done by (Frost et al., 2006).

Methane Adsorption at 298 K and at Low/High Pressures:-

Based on the results obtained with H_2 and CO_2 it seems clear that ϴ correlates better with wt.% at low pressure and surface area correlates better with wt.% at high pressure. In order to further confirm these findings a third gas, CH_4, was studied. This gas has only 10 electrons and thus the van der Waals interactions with the surfaces should be weaker than those in CO_2 and stronger than those in H_2 under the same conditions. As was done in the case of CO_2, adsorption isotherms for this gas were determined at 298 K and at low and high pressures. The graphs for these are shown in Figs. 6a and 6b. The weight percentages obtained from these graphs are given in Table 3. These weight percentages were used along with surface areas to calculate sticking efficiencies from equation 1. The values are also included in Table 3. Figs. 7a and 7b contain plots of wt.% versus surface area and wt.% versus ϴ respectively at low pressure. As in the two previous cases, ϴ correlates better with wt.%($R^2 = 0.7528$) than does surface area ($R^2 = 0.0145$) at low pressure. This is again the result that is expected. It should be noted that only five data points were included in each of these graphs. This is because there was a lack of available literature data to include. Regardless of this, the data at low pressure was sufficient to show that the same trendsexist that were seen with the other gases. Figs. 8a and 8b contain corresponding plots at high pressure. In this case, it was expected that the opposite behavior would be observed and that surface area would correlate better with wt.% than would ϴ. Surprisingly it was found that ϴ also correlated better with wt.% than does surface area, even at high pressure.

The most likely reason for the unexpected and apparently different behavior, in the case of CH_4 at high pressure, can be seen if we examine the high pressure isotherms for the three gases. The isotherms for H_2 at 77 K (Fig. 1) and CO_2 at 298 K (Fig. 3b)show that saturation has occurred. However, the high pressure isotherms for CH_4 in Fig. 7b show that saturation has not yet occurred at 298 K. In the H_2 case, thevan der Waals attractions are strong enough at the low temperature of 77 K for saturation to occur.In the CO_2 case, saturation occurs at 298 K because the relatively large number of electrons in this molecule (22 in this case) enhances the strength of the van der Waals interactions. Apparently, in the case of CH_4, the interactions of 10 electrons with the MOF surfaces do not produce sufficiently strong van der Waals interactions at 298 K for saturation to occur. Thus we see that, in all these cases, surface area correlates better with wt.% when saturation has occurred. Before saturation has occurred, it is ϴ that correlates better with wt.%.

Conclusions:-

A comparison of the adsorption capacities of various MOFs for H_2, CO_2 and CH_4gases were made at high and low pressures. Theresults showed that, at low pressure, a better correlation exists between adsorption capacity and sticking factor (ϴ) than between adsorption capacity and surface area. Since ϴ is known to be proportional to adsorption enthalpy, which is a measure of the binding energy, this indicates that the strength of interactions between the MOFs and the adsorbed gases is a very important factor in determining gas adsorption capacity at low pressure. The results also showed that at higher pressures the surface area correlated better with adsorption capacity than did ϴ, in the cases of H_2 and CO_2. This is what would be expected based on published Grand Canonical Monte Carlo simulations (Frost et al., 2006) However it was a surprise to find that ϴ correlated better with methane gas uptake at both low and higher pressures than did surface area. The most likely reason for this is that, under the conditions used, the isotherms for CH_4 did not show saturation at higher pressures whereas those for H_2 and CO_2 did. When saturation has occurred, the surfaces are fully covered and MOFs with the greatest surface areas would be expected to adsorb the most. So in general it can be concluded that when MOF surfaces are fully saturated, gas adsorption capacity will be proportional to the surface area but when saturation hasn't been achieved, adsorption capacity will be proportional to the sticking factor. Based on this, the sticking factor should be a convenient way of predicting gas uptake, prior to saturation, when enthalpy data is not available. Since adsorption enthalpy, surface area and pore volume are the parameters which influence and describe the adsorption behavior of MOFs, it is truly remarkable that a simple parameter such as sticking factor has been able to correlate so well with gas adsorption uptake of these complex materials.

Acknowledgement:-

This research was financially supported by the U.S. Department of Energy Grant Number DE-FC36-06GO86046 and the U.S. Department of Transportation Grant Number DTOS59-07-G-00056.

Table 1:-Hydrogen Gas Adsorption.

Low Pressure (LP) and High Pressure (HP) quantities for hydrogen gas adsorption on selected MOFs at 77 K

MOFs *(Metal + Linker)*	**BET** **(m^2/g)**	**Wt. %** ***(@ 77 K)***	**P (bar)**	**Stick. Eff. x10^{20}** ***(@ 77 K)***	**Ref.**
Zn-*BDC*	2163	1.40*(LP)* 3.72*(HP)*	1 21.3	1.93*(LP)* 5.13*(HP)*	This Work
Zn-*NDC*	1599	1.74*(LP)* 3.16*(HP)*	1 49.8	3.24*(LP)* *5.89(HP)*	This Work
Zn-*Mim*	1581	1.26*(LP)* 3.39*(HP)*	1 63.8	2.37*(LP)* *6.32(HP)*	This Work
Fe-*BTC*	1031	0.89*(LP)* 3.15*(HP)*	1 49.2	2.57*(LP)* *9.10(HP)*	This Work
Cu-*BTC*	1398	2.00*(LP)* 3.56*(HP)*	1 22.2	4.26*(LP)* *7.59(HP)*	This Work
CUK-1	630	1.60*(LP)*-	1	1.23*(LP)*-	(Humphreyet al., 2007)
CUK-2	420	0.66*(LP)*-	1	1.21*(LP)*-	(Humphrey et al., 2007)
TUDMOF-1	1280	1.75*(LP)*-	1	4.08*(LP)*-	(Kramer et al., 2006)
PCN-10	1407	2.34*(LP)*-	1	4.96*(LP)*-	(Wang, et al., 2008)
PCN-11	1931	2.55*(LP)*-	1	3.94*(LP)*-	(Wang et al., 2008)
PCN-12	1943	3.05*(LP)*	1	4.68*(LP)*	(Wang, et al., 2008)
PCN-12’	1577	2.4*(LP)*	1	4.54*(LP)*	(Wang et al., 2008)
PCN-17	820	0.94*(LP)*-	1	3.42*(LP)*-	(Ma, et al., 2008)
IRMOF-18	1501	0.88*(LP)*-	1	1.75*(LP)*-	(Rowsell et al., 2004)
UMCM-150	2300	2.1*(LP)*-	1	2.72*(LP)*-	(Wong et al., 2007)
Cu-BTT	1710	2.42*(LP)*-	1.2	4.22*(LP)*-	(Dincă et al., 2007)
MOF-74	783	1.75*(LP)*-	1	6.66*(LP)*-	(Rowsell and Yaghi 2006)
MIL-53 (Cr)	1100	3.1*(HP)*	16	8.4*(HP)*	(Férey et al., 2003)
Fe-pbpc	1200	3.05*(HP)*	20	7.5*(HP)*	(Wang, et al., 2007)
Ni-OH-pbpc	1553	4.15*(HP)*	20	7.9*(HP)*	(Jia et al., 2007)
MOF-505	1670	4.02*(HP)*	20	7.2*(HP)*	(Lin et al., 2006)
Cu-tpb	1120	2.8*(HP)*	30	7.5*(HP)*	(Dinca et al., 2008)
Cu-BDC	1300	2.7*(HP)*	33.7	6.2*(HP)*	(Takei et al., 2008)

Table 2:-Carbon Dioxide Gas Adsorption.

Low Pressure (LP) and High Pressure (HP) quantities for carbon dioxide gas adsorption on selected MOFs at 298 K

MOFs	**BET (m^2/g)**	**CO_2*(Wt.%)* 298 K**	**P (bar)**	**Sticking Eff.*($\times 10^{20}$)* 298 K**	**Ref.**
Zn-BDC	2163	7.47*(LP)* 39.5*(HP)*	1 26.3	0.47*(LP)* 2.50*(HP)*	*This Work*
Zn-NDC	1599	7.80*(LP)* 49.8*(HP)*	1 26	0.67*(LP)* 4.26*(HP)*	*This Work*
Zn-Mim	1581	2.89*(LP)* 32.6*(HP)*	1 26.3	0.25*(LP)* 2.82*(HP)*	*This Work*
Cu-BTC	1398	18.3*(LP)* 55.3*(HP)*	1 30.6	1.80*(LP)* 5.41*(HP)*	*This Work*
Fe_BTC	1031	5.81*(LP)* 45.4*(HP)*	1 31.1	0.77*(LP)* 6.03*(HP)*	*This Work*
Cu-EBTC	1852	-		-	(Hu et al., 2009)
CAU-1	1268	-		-	(Si et al., 2011)
MOF-23	760	-		-	(Furukawa et al., 2008)
SNU-15	356	-		-	(Cheon and Suh 2009)
BIF-9-Li	1523	-		-	(Wu et al., 2009)
BIF-9-Cu	1287	-		-	(Wu et al., 2009)
PCN-6	3811	15.9*(LP)*	1	0.57*(LP)*	(Kim et al., 2011)
MOF-177	5400 4500	3.6*(LP)* 60.8*(HP)*	1 50	0.15*(LP)* 1.85*(HP)*	(Mason et al., 2011) (Sumida et al., 2011)
IRMOF-3	2160	5.1*(LP)*	1	0.32*(LP)*	(Sumida et al., 2011)
MOF-253	2160	6.2*(LP)*	1	0.39*(LP)*	(Bloch et al., 2010)
CPL-2	633	6.6*(LP)*	1	1.43*(LP)*	(Sumida et al., 2011)
Fe-BTT	2010	13.5*(LP)*	1	0.92*(LP)*	(Sumida et al., 2010)
SNU-50	2300	13.7*(LP)*	1	0.82*(LP)*	(Prasad et al., 2010)
ZIF-78	620	9.1*(LP)*	1	2.01*(LP)*	(Sumida et al., 2011), (Das and D'Alessandro 2015)
Mg-MOF-74	1174	27.5*(LP)*	1	3.21*(LP)*	(Bao et al., 2011), (Dietzel et al., 2009)
Co-MOF-74	957	24.5*(LP)*	1	3.5*(LP)*	(Yazaydın et al., 2009)
Ni-MOF-74	1218	-	-	-	(Dietzel et al., 2009)
MOF-210	6240	74.2*(HP)*	50	1.63*(HP)*	(Furukawa et al., 2010)
MOF-200	4530	73.9*(HP)*	50	2.23*(HP)*	(Furukawa et al., 2010)
NU-100	6143	69.8*(HP)*	40	1.56*(HP)*	(Farha et al., 2010)
MOF-205	4460	62.6*(HP)*	50	1.92*(HP)*	(Furukawa et al., 2010)
PCN-68	5109	57.2*(HP)*	35	1.53*(HP)*	(Yuan et al., 2010)
IMOF-3	802	8.6*(LP)*	1	1.47*(LP)*	(Debatin et al., 2010)
IRMOF-11	2096	7.3*(LP)*	1	0.48*(LP)*	(Millward and Yaghi 2005)

Table 3:-Methane Gas Adsorption.

Low Pressure (LP) and High Pressure (HP) quantities for methane gas adsorption on selected MOFs at 298 K

MOFs *(Metal + Linker)*	**BET** (m^2/g)	**Wt. %** *(@ 298K)*	**P** (bar)	**Stick. Eff.x10^{20}** *(@ 298K)*	**Ref.**
Zn-*BDC*	2163	0.84*(LP)* *10.56(HP)*	1 36	0.15*(LP)* *1.84(HP)*	This Work
Zn-*NDC*	1599	0.81*(LP)* *12.44(HP)*	1 36	0.19*(LP)* *2.93(HP)*	This Work
Zn-*Mim*	1581	0.42*(LP)* *6.71(HP)*	1 36	0.09*(LP)* *1.60(HP)*	This Work
Fe-*BTC*	1031	0.55*(LP)* *10.29(HP)*	1 36	0.20*(LP)* *3.75(HP)*	This Work
Cu-*BTC*	1398	1.31*(LP)* *13.70(HP)*	1 36	0.35*(LP)* *3.69(HP)*	This Work
MIL-100(Cr)	1900	- 12.1*(HP)*	- 35	- 2.39*(HP)*	(Llewellyn et al., 2008)
$Co_2(BDC)_2$(dabco)	1600	- 12.2*(HP)*	- 35	- 2.87*(HP)*	(Llewellyn et al., 2008)
PCN-11	1931	- 16.3*(HP)*	- 35	- 3.17*(HP)*	(Wang et al., 2008)
PCN-14’	1753	- 18.9*(HP)*	- 35	- 4.05*(HP)*	(Ma et al., 2008)
COF-8	1350	- 8*(HP)*	- 35	- 2.23*(HP)*	(Makal et al., 2012)
HCP-1	1904	- 6.6*(HP)*	- 15	- 1.3*(HP)*	(Makal et al., 2012)
HCP-4	1366	- 6.5*(HP)*	- 15	- 1.79*(HP)*	(Makal et al., 2012)
PPN-1	1249	- 7.6*(HP)*	- 35	- 2.29*(HP)*	(Makal et al., 2012)
PPN-2	1764	- 9.8*(HP)*	- 35	- 2.09*(HP)*	(Makal et al., 2012)

Figure 1:-Hydrogen adsorption isotherms for various MOFs at 77 K and high pressure.

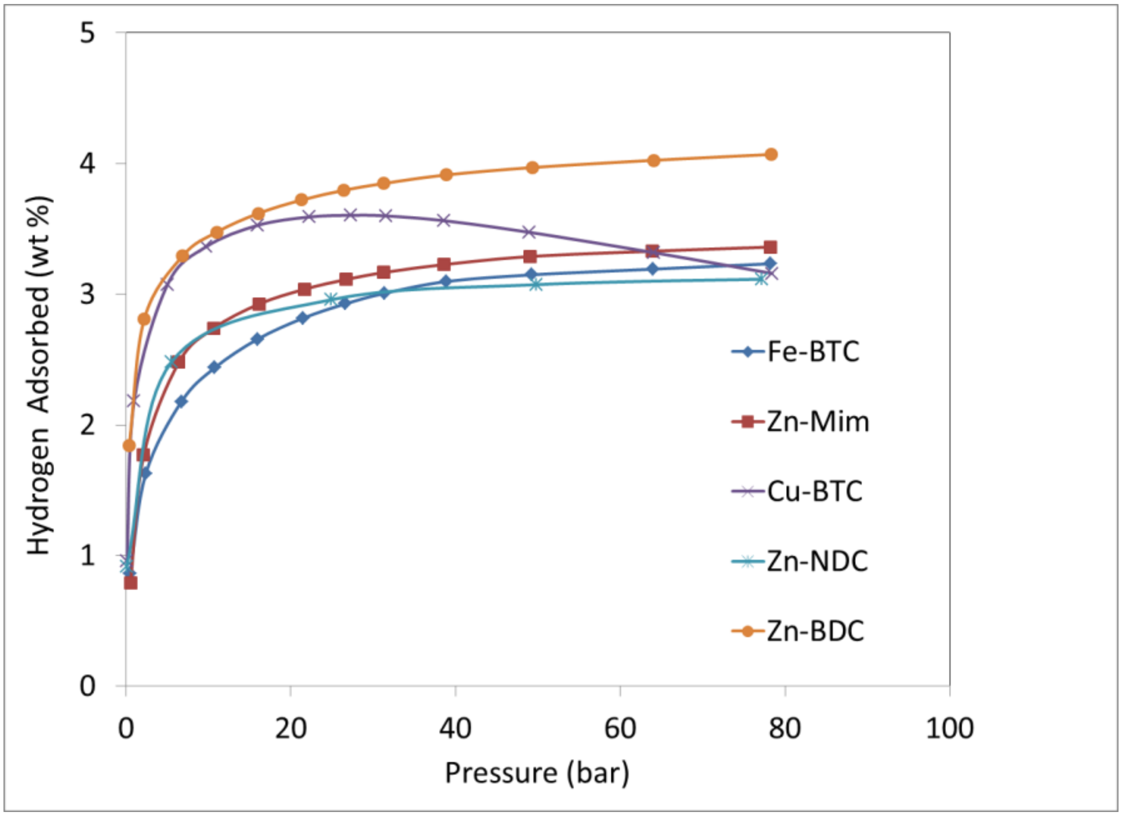


Figure 2a:-Weight percent hydrogen adsorbed versus surface area at 77 K and high pressure.

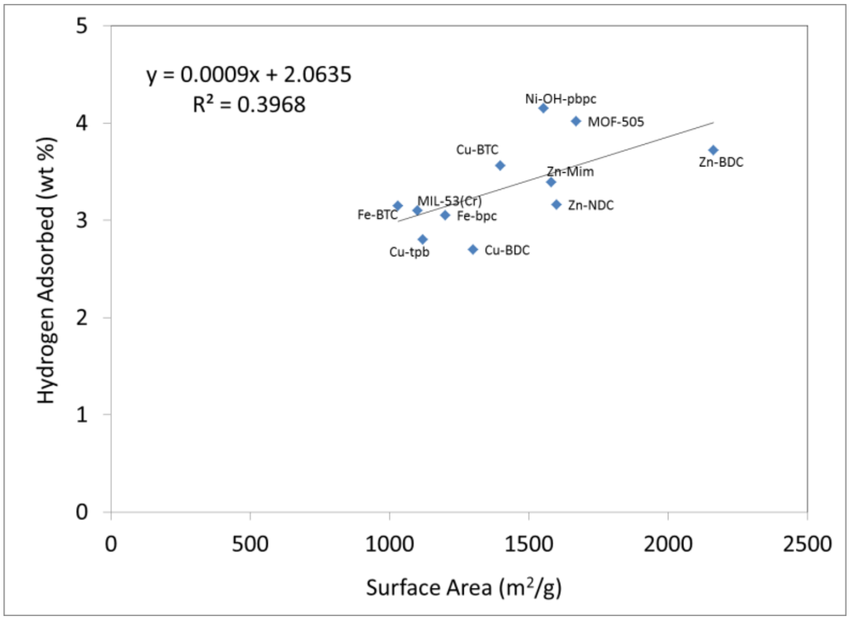


Figure 2b:-Weight percent hydrogen adsorbed versus sticking factor at 77 K and high pressure.

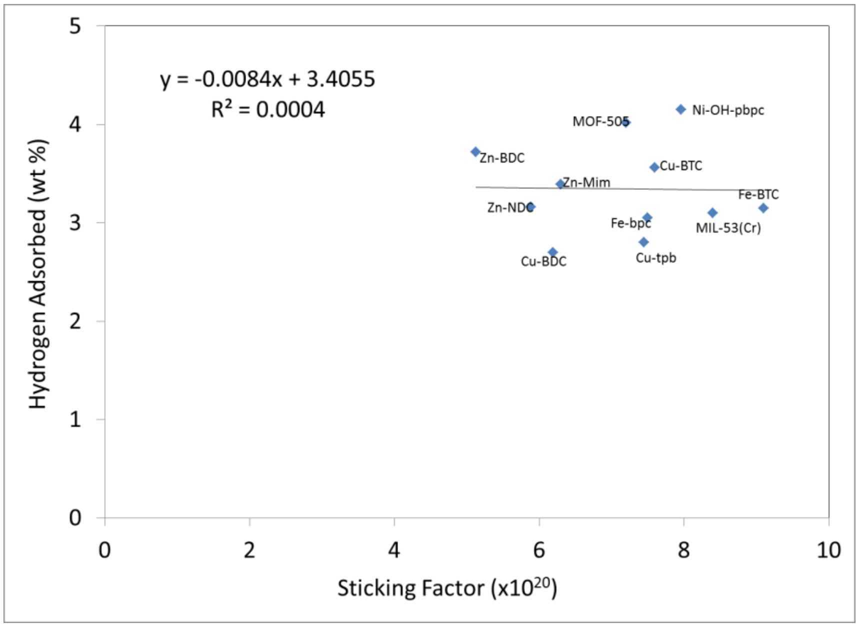


Figure 3a:-Carbon dioxide adsorption isotherms for various MOFs at 298 K and low pressure.

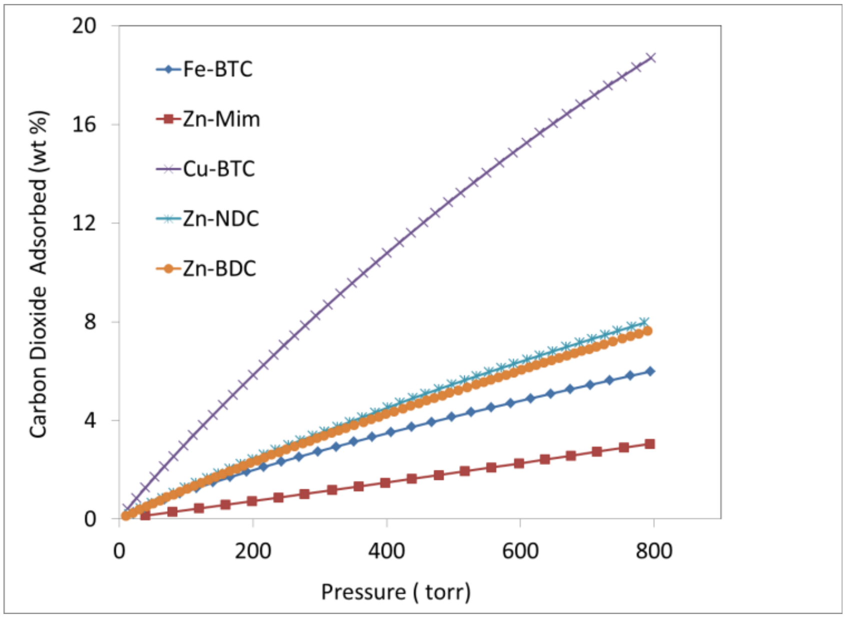


Figure 3b:-Carbon dioxide adsorption isotherms for various MOFs at 298 K and high pressure.

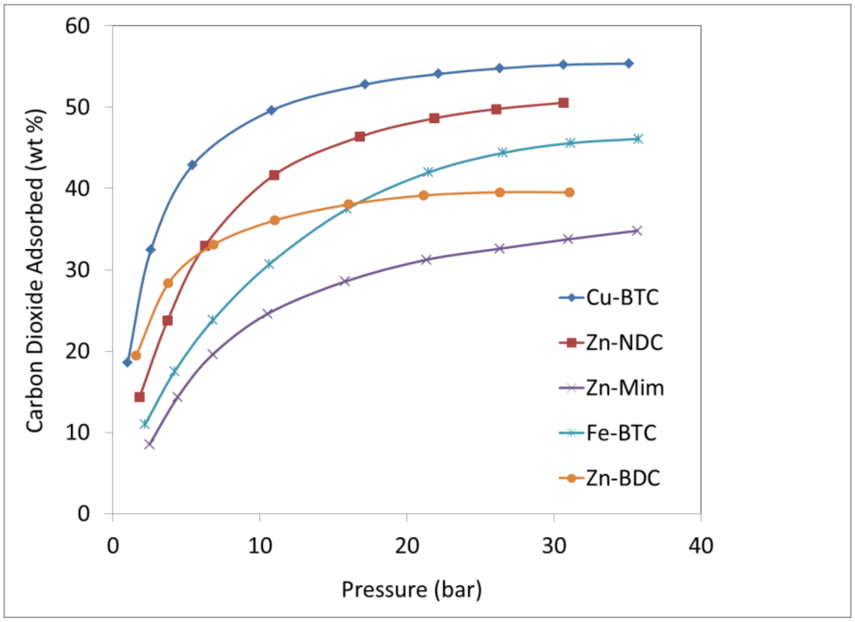


Figure 4a:-Weight percent carbon dioxideadsorbed versus surface area at 298 K and low pressure.

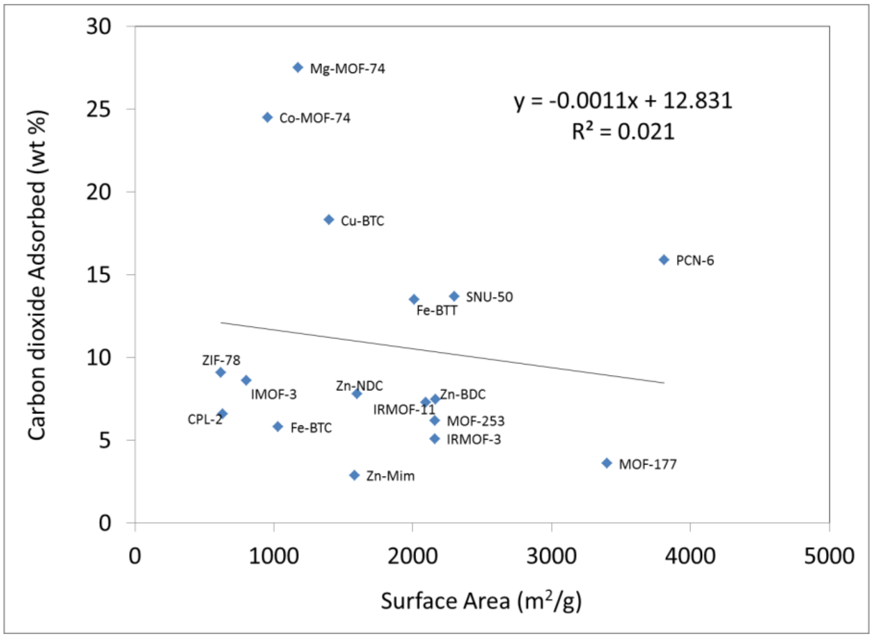


Figure 4b:-Weight percent carbon dioxideadsorbed versus sticking factor at 298 K and low pressure.

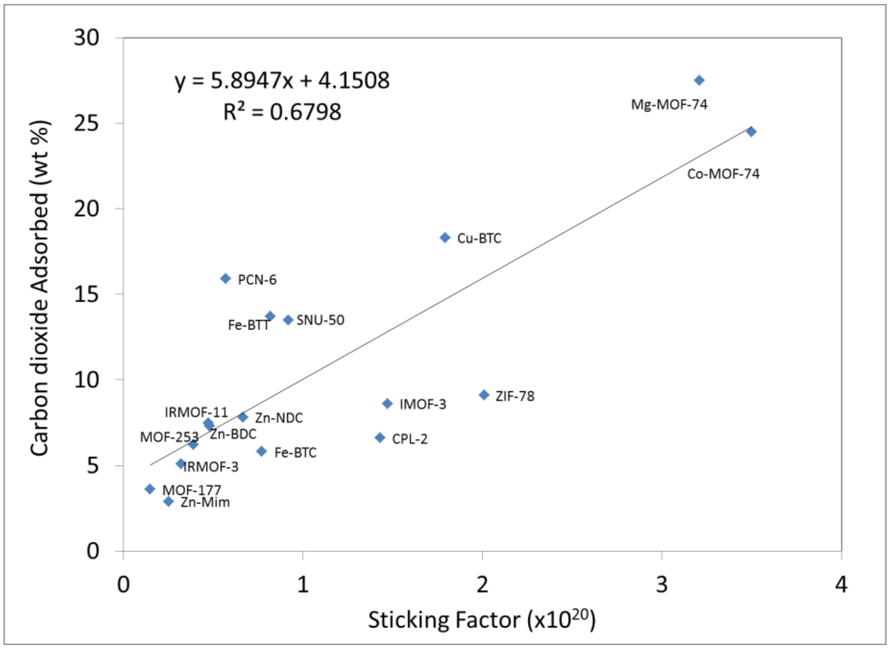


Figure 5a:-Weight percent carbon dioxideadsorbed versus surface area at 298 K and high pressure.

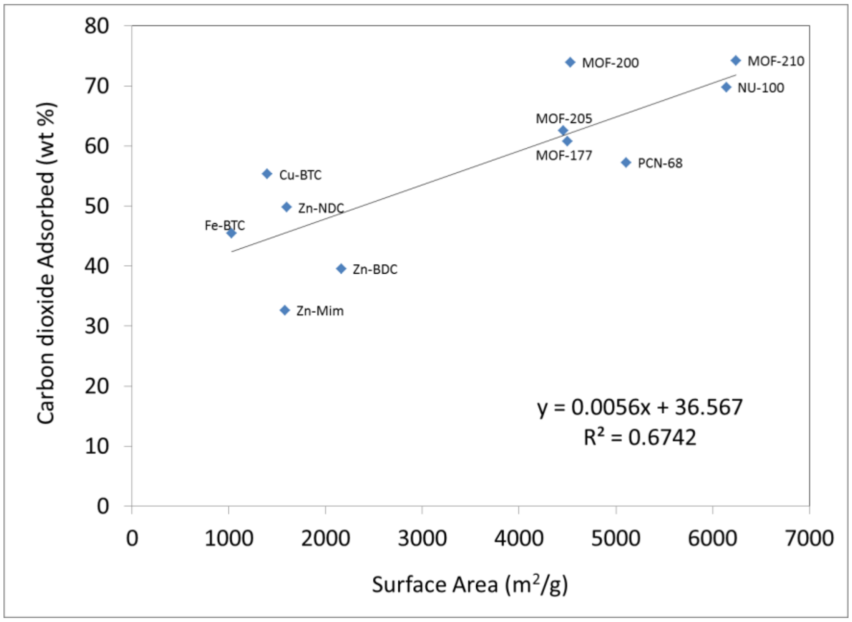


Figure 5b:-Weight percent carbon dioxideadsorbed versus sticking factor at 298 K and high pressure.

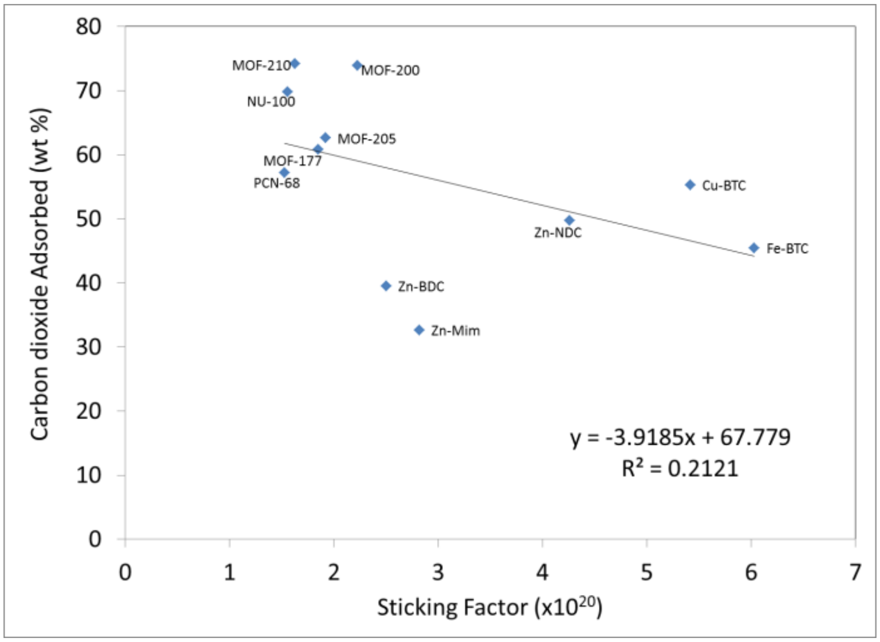


Figure 6a:-Methane adsorption isotherms for various MOFs at 298 K and low pressure.

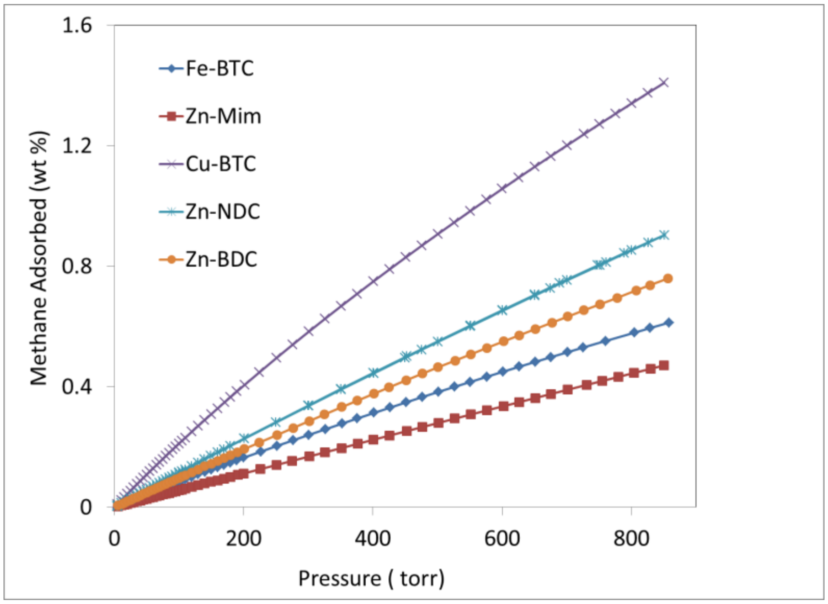


Figure 6b:-Methane adsorption isotherms for various MOFs at 298 K and high pressure.

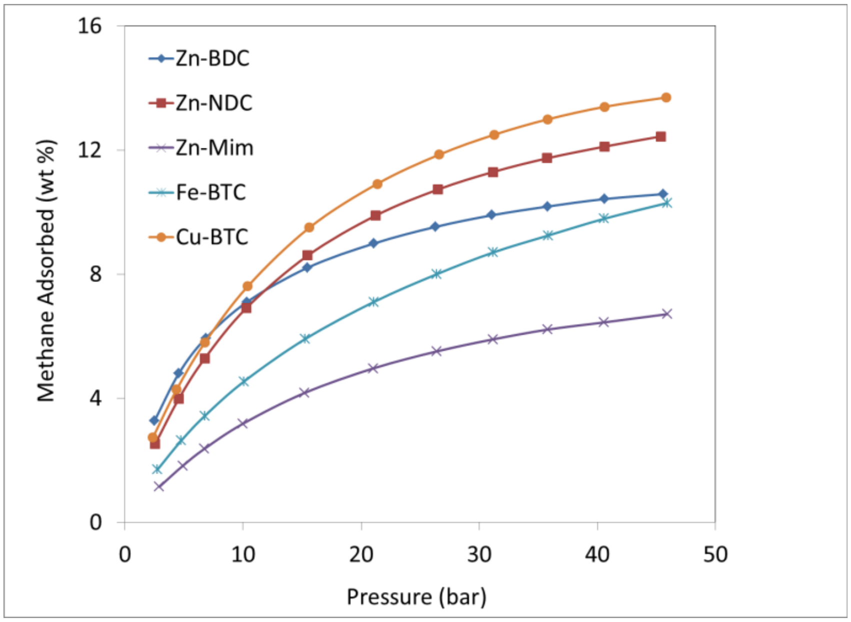


Figure 7a:-Weight percent methaneadsorbed versus surface area at 298 K and low pressure.

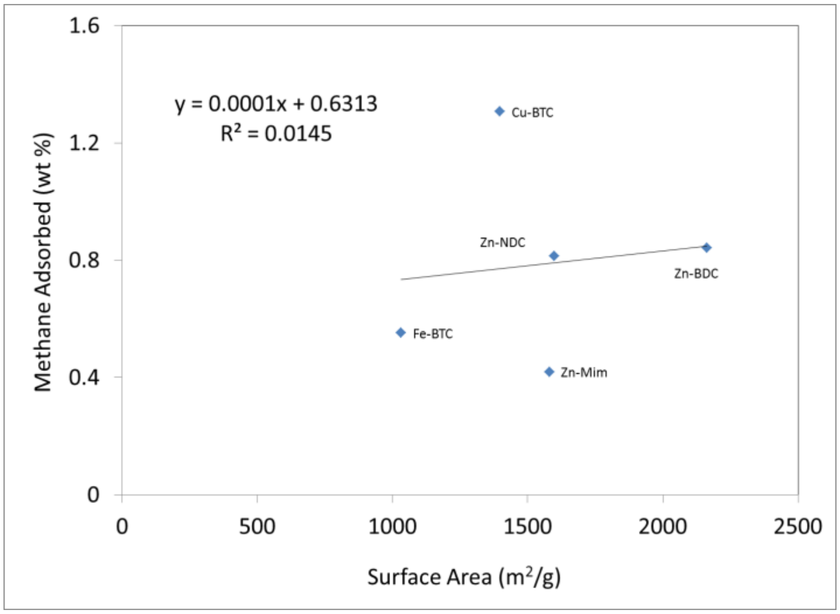


Figure 7b:-Weight percent methaneadsorbed versus sticking factor at 298 K and low pressure.

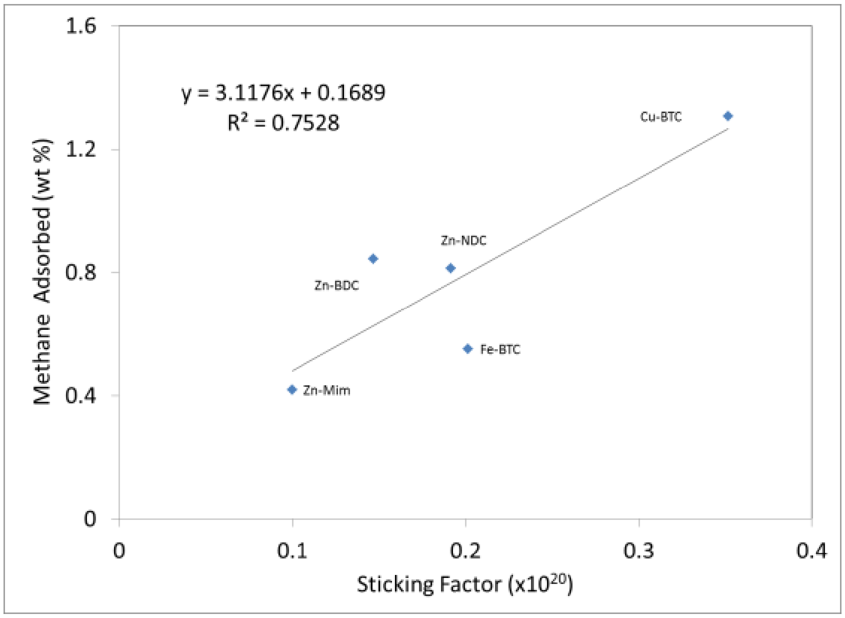


Figure 8a:-Weight percent methaneadsorbed versus surface area at 298 K and high pressure.

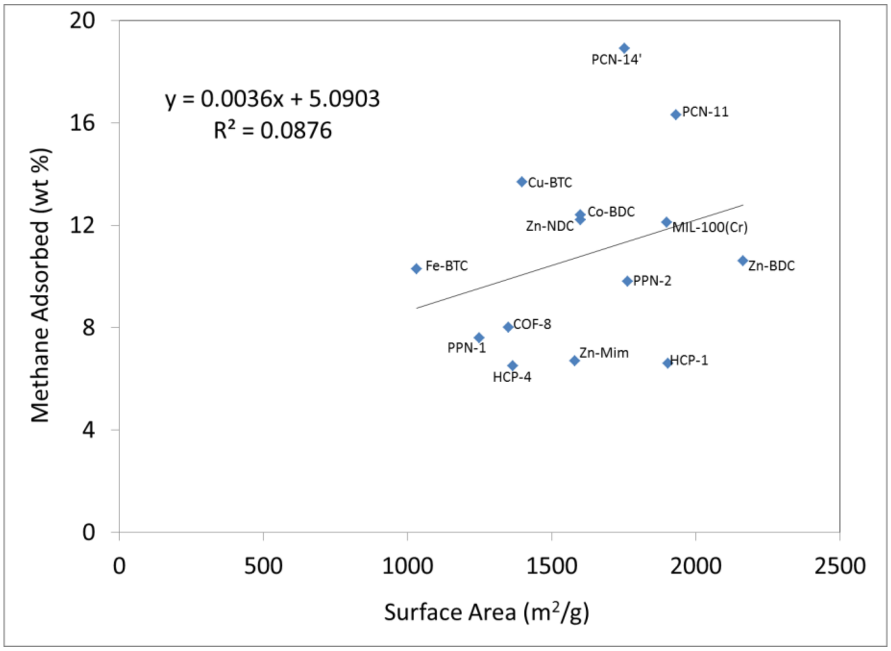
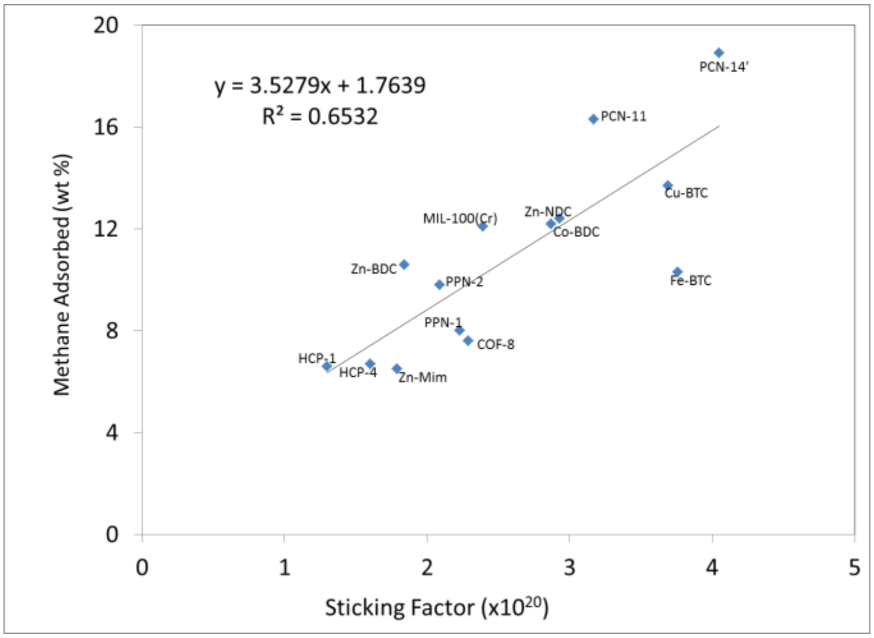


Figure 8b:-Weight percent methaneadsorbed versus sticking factor at 298 K and high pressure.



References:-

1. Bao, Z., Yu, L.. Ren, Q Lu X. and Deng, S. (2011). "Adsorption of CO_2 and CH_4 on a magnesium-based metal organic framework." Journal of colloid and interface science **353**(2): 549-556.
2. Bloch, E. D.,Britt, D.. LeeC, Doonan, C.J Uribe-Romo,F. J, Furukawa, F. J. H. Long, J. R.and Yaghi,O. M.. (2010). "Metal insertion in a microporous metal−organic framework lined with 2, 2′-bipyridine." Journal of the American Chemical Society**132**(41): 14382-14384.
3. Cheon, Y. E. and Suh,M. P. (2009). "Selective gas adsorption in a microporous metal–organic framework constructed of Co II 4 clusters." Chemical communications(17): 2296-2298.
4. Das, A. and D'Alessandro D. M. (2015). "Tuning the functional sites in metal–organic frameworks to modulate CO_2 heats of adsorption." CrystEngComm**17**(4): 706-718.
5. Debatin, F., Thomas, A. Kelling, A. Hedin, N. Bacsik, Z. Senkovska, I. Kaskel, S.. Junginger, M Müller H.and Schilde, U.. (2010). "In Situ Synthesis of an Imidazolate-4-amide-5-imidate Ligand and Formation of a Microporous Zinc–Organic Framework with H_2-and CO_2-Storage Ability." Angewandte Chemie International Edition**49**(7): 1258-1262.
6. Dietzel, P. D., Besikiotis V.and Blom. R.(2009). "Application of metal–organic frameworks with coordinatively unsaturated metal sites in storage and separation of methane and carbon dioxide." Journal of Materials Chemistry**19**(39): 7362-7370.
7. Dinca, M., Dailly, A. Tsay, C. and Long, J. R.(2008). "Expanded sodalite-type metal-organic frameworks: Increased stability and H_2 adsorption through ligand-directed catenation." Inorganic chemistry**47**(1): 11-13.
8. Dincă, M.,Han, W. S. Liu, Y. Dailly, A. Brown, C. M.and Long, J. R. (2007). "Observation of Cu^{2+}–H_2 Interactions in a Fully Desolvated Sodalite-Type Metal–Organic Framework." Angewandte Chemie International Edition**46**(9): 1419-1422.
9. Farha, O. K.,. Yazaydın, A. Ö Eryazici, I.. Malliakas, C. D Hauser, B. G.. Kanatzidis, M. G Nguyen, S. T. Snurr R. Q.and Hupp, J. T. (2010). "De novo synthesis of a metal–organic framework material featuring ultrahigh surface area and gas storage capacities." Nature chemistry**2**(11): 944-948.
10. Férey, G., Latroche, M. Serre, C. Millange, F. Loiseau T.and Percheron-Guégan,A., (2003). "Hydrogen adsorption in the nanoporous metal-benzenedicarboxylate M (OH)(O_2C–C_6H_4–CO_2) (M= Al^{3+}, Cr^{3+}), MIL-53." Chemical communications(24): 2976-2977.
11. Frost, H., Duren T. and Snurr, R. Q(2006). "Effects of surface area, free volume, and heat of adsorption on hydrogen uptake in metal-organic frameworks." The Journal of Physical Chemistry B**110**(19): 9565-9570.
12. Furukawa, H.,. Kim,, J Ockwig, N.W.'Keeffe M. O and YaghiO. M.(2008). "Control of Vertex Geometry, Structure Dimensionality, Functionality, and Pore Metrics in the Reticular Synthesis of Crystalline Metal−Organic Frameworks and Polyhedra." Journal of the American Chemical Society**130**(35): 11650-11661.
13. Furukawa, H., Ko, N.. Go, Y. B Aratani, N. Choi, S. B. Choi, E. Yazaydin, A. Ö. Snurr, R. Q. O'Keeffe M. and KimJ. (2010). "Ultrahigh porosity in metal-organic frameworks." Science**329**(5990): 424-428.
14. Hu, Y.,Xiang, S. Zhang, W. Zhang, Z. Wang, L. Bai J. and Chen,B. (2009). "A new MOF-505 analog exhibiting high acetylene storage." Chemical communications(48): 7551-7553.
15. Humphrey, S. M., Chang, J. S. Jhung, S. H. Yoon J. W.and Wood,P. T.(2007). "Porous Cobalt (II)–Organic Frameworks with Corrugated Walls: Structurally Robust Gas-Sorption Materials." Angewandte Chemie International Edition **46**(1-2): 272-275.
16. Iriowen, E., Orefuwa, S, and Goudy, A. (2015). "The role of sticking efficiencies in hydrogen gas adsorption on metal organic frameworks." Journal of Alloys and Compounds**645**: S242-S246.
17. Jia, J., Lin, X. Wilson, C. Blake, A. J. Champness, N. R Hubberstey, P. Walker, G. Cussen E. J.and Schröder,M.(2007). "Twelve-connected porous metal–organic frameworks with high H_2 adsorption." Chemical communications(8): 840-842.
18. Kim, J. Yang, S.-T. Choi, S. B. Sim, J. Kim J.and Ahn,W.-S.(2011). "Control of catenation in CuTATB-n metal–organic frameworks by sonochemical synthesis and its effect on CO_2 adsorption." Journal of Materials Chemistry **21**(9): 3070-3076.
19. Kramer, M.,. Schwarz, U and Kaskel, S. (2006). "Synthesis and properties of the metal-organic framework Mo 3 (BTC) 2 (TUDMOF-1)." Journal of Materials Chemistry **16**(23): 2245-2248.
20. Lin, X., Jia, J. Zhao, X. Thomas, K. M. Blake, A. J. Walker, G. S. Champness, N. R. Hubberstey P. and Schröder,M.(2006). "High H_2 Adsorption by Coordination-Framework Materials." Angewandte Chemie International Edition **45**(44): 7358-7364.
21. Llewellyn, P. L., Bourrelly, S. Serre, C. Vimont, A. Daturi, M. Hamon, L. De Weireld, G. Chang, J.-S. Hong D.-Y. and Kyu Hwang,Y.(2008). "High Uptakes of CO_2 and CH_4 in Mesoporous Metal Organic Frameworks MIL-100 and MIL-101." Langmuir**24**(14): 7245-7250.

22. Ma, S.,Sun, D. Simmons, J. M. Collier, C. D. Yuan D. and Zhou, H.-C. (2008). "Metal-organic framework from an anthracene derivative containing nanoscopic cages exhibiting high methane uptake." Journal of the American Chemical Society**130**(3): 1012-1016.
23. Ma, S., Wang, X. S. Yuan D. and Zhou, H. C.(2008). "A Coordinatively Linked Yb Metal–Organic Framework Demonstrates High Thermal Stability and Uncommon Gas-Adsorption Selectivity." Angewandte Chemie International Edition **47**(22): 4130-4133.
24. Makal, T. A., LiJ.-R., Lu W. and Zhou, H.-C.(2012). "Methane storage in advanced porous materials." Chemical Society Reviews**41**(23): 7761-7779.
25. Mason, J. A. Sumida, K. Herm, Z. R. Krishna R. and LongJ. R., (2011). "Evaluating metal–organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption." Energy & Environmental Science**4**(8): 3030-3040.
26. Millward, A. R. and Yaghi O. M. (2005). "Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature." Journal of the American Chemical Society **127**(51): 17998-17999.
27. Murray, L. J., Dinca M. and Long, J.R. (2009). "Hydrogen storage in metal–organic frameworks." Chemical Society Reviews**38**(5): 1294-1314.
28. Orefuwa, S., Iriowen, E. Yang, H. Wakefield, B. Goudy,. A.(2013). "Effects of nitro-functionalization on the gas adsorption properties of isoreticular metal-organic framework-eight (IRMOF-8)." Microporous and Mesoporous Materials**177**: 82-90.
29. Orefuwa, S. A., Yang, H. and Goudy. A.(2012). "Rapid solvothermal synthesis of an isoreticular metal–organic framework with permanent porosity for hydrogen storage." Microporous and Mesoporous Materials **153**: 88-93.
30. Prasad, T. K., Hong D. H. and Suh, M. P. (2010). "High Gas Sorption and Metal-Ion Exchange of Microporous Metal–Organic Frameworks with Incorporated Imide Groups." Chemistry–A European Journal **16**(47): 14043-14050.
31. Rowsell, J. L., Millward,A. R. Park K. S.and Yaghi, O. M. (2004). "Hydrogen sorption in functionalized metal-organic frameworks." Journal of the American Chemical Society**126**(18): 5666-5667.
32. Rowsell, J. L. andYaghi O. M. (2006). "Effects of functionalization, catenation, and variation of the metal oxide and organic linking units on the low-pressure hydrogen adsorption properties of metal-organic frameworks." Journal of the American Chemical Society **128**(4): 1304-1315.
33. Si, X., Jiao, C. Li, F. Zhang, J. Wang, S. Liu, S. Li, Z. Sun, L. Xu F.and Gabelica, Z.(2011). "High and selective CO_2 uptake, H_2 storage and methanol sensing on the amine-decorated 12-connected MOF CAU-1." Energy & Environmental Science**4**(11): 4522-4527.
34. Sumida, K., Horike, S.. Kaye, S. S Herm, Z. R. Queen, W. L. Brown, C. M. Grandjean, F. Long, G. J.. Dailly A and Long,J. R. (2010). "Hydrogen storage and carbon dioxide capture in an iron-based sodalite-type metal–organic framework (Fe-BTT) discovered via high-throughput methods." Chemical Science **1**(2): 184-191.
35. Sumida, K., Rogow, D. L. Mason, J. A. McDonald, T. M. Bloch, E. D. Herm, Z. R. Bae T.-H. and. Long,. J. R(2011). "Carbon dioxide capture in metal–organic frameworks." Chemical reviews **112**(2): 724-781.
36. Takei, T., Kawashima, J. Ii, T. Maeda, A. Hasegawa, M. Kitagawa, T. Ohmura, T. Ichikawa, M. Hosoe M.and Kanoya, I. (2008). "Hydrogen adsorption properties of lantern-Type dinuclear M (bdc)(dabco) 1/2." Bulletin of the Chemical Society of Japan**81**(7): 847-856.
37. Wang, S. (2007). "Comparative molecular simulation study of methane adsorption in metal-organic frameworks." Energy & fuels **21**(2): 953-956.
38. Wang, X.-S.,Ma, K. Rauch, J. M. Simmons, D. Yuan, X. Wang, T. Yildirim, W. C. Cole, J. J. López and A. d. Meijere, (2008). "Metal Organic Frameworks Based on Double-Bond-Coupled Di-Isophthalate Linkers with High Hydrogen and Methane Uptakes." Chemistry of Materials **20**(9): 3145-3152.
39. Wang, Y., ChengP., Chen, J. Liao D.-Z. and Yan,S.-P. (2007). "A heterometallic porous material for hydrogen adsorption." Inorganic chemistry **46**(11): 4530-4534.
40. Wilmer, C. E.,Farah, O. K. Yildirim,T.Eryazici, I. Krungleviciute, V. Sarjeant, A. A. Snurr, R. Q. Hupp,J. T. (2013). "Gram-scale, high-yield synthesis of a robust metal–organic framework for storing methane and other gases." Energy & Environmental Science **6**(4): 1158-1163.
41. Wong-Foy, A. G., Lebel O.and Matzger. A. J. (2007). "Porous crystal derived from a tricarboxylate linker with two distinct binding motifs." Journal of the American Chemical Society**129**(51): 15740-15741.
42. Wu, T., Zhang, J. Zhou, C. Wang, L. Bu X.and FengP.(2009). "Zeolite RHO-type net with the lightest elements." Journal of the American Chemical Society **131**(17): 6111-6113.
43. Yaghi, O. M.,O'Keeffe, M. Ockwig, N.W. Chae, H.K. Eddaoudi, M Kim.J.(2003). "Reticular synthesis and the design of new materials." Nature **423**(6941): 705-714.

44. Yang, H., Orefuwa, S. Goudy.A. (2011). "Study of mechanochemical synthesis in the formation of the metal–organic framework $Cu_3(BTC)_2$ for hydrogen storage." Microporous and Mesoporous Materials **143**(1): 37-45.
45. Yang, Q., Zhong C.and Chen,J. (2008). "Computational study of CO_2 storage in metal-organic frameworks." The Journal of Physical Chemistry C**112**(5): 1562-1569.
46. Yazaydın, A. O. Z. R., Snurr,R. Q.. Park, T.-H Koh, K. Liu, J.. LeVan, M. D Benin, A. I. Jakubczak, P.. Lanuza M and Galloway,D. B.(2009). "Screening of metal−organic frameworks for carbon dioxide capture from flue gas using a combined experimental and modeling approach." Journal of the American Chemical Society **131**(51): 18198-18199.
47. Yuan, D.,Zhao, D. Sun D. and ZhouH. C. (2010). "An Isoreticular Series of Metal–Organic Frameworks with Dendritic Hexacarboxylate Ligands and Exceptionally High Gas-Uptake Capacity." Angewandte Chemie International Edition**49**(31): 5357-5361.
48. Zhao, D., Yuan D. and Zhou,H.-C. (2008). "The current status of hydrogen storage in metal–organic frameworks." Energy & Environmental Science**1**(2): 222-235.