



# Investigation of Surface Absorption of Mercaptan from Gas by SBA-15 Supported ZnO Nano Particles

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**Abstract:** Sulfur in gases causes many problems associated with environmental pollution, and the loss of industrial equipment. Selective adsorption of sulfur compounds is one of the most widely used methods, the most important advantages of this method are the desulphurisation reaction at low temperature and pressure, which reduces the cost of refining operations. In this study, ZnO nanoparticles were made based on Silica mesoporous (SBA-15), different methods such as: ICP, BET, XRD were used to check the physical and chemical properties and the adsorbent action to remove gas-Iso-propyl-mercaptan (IPM). Various experiments were carried out to remove the mercaptan gas by adsorbent discontinuously. Then, the effect of effective absorption parameters such as temperature, loading rate, contact time, and initial gas concentration were studied. The maximum absorption was achieved in condition, contact time is 50 minutes, and temperature is 298 K. With a loading rate of 5% nanoparticles, initial concentration of 500 ppm. For determining the most suitable absorption isotherm, Temkin, Langmuir, Freundlich adsorption isotherm have been studied. The relationships between Langmuir Temkin, Langmuir isotherms for adsorbents were investigated. The result of this study showed that isotherm temperature with Freundlich is more consistent with experimental data ( $R^2 = 0.998$ ). The results showed that the adsorbents have a good ability to remove Iso-propyl mercaptan gas.

**Keywords:** Nano-Zinc Oxide- Removal of Iso Propyl Mercaptan- SBA-15(Santa Barbara Amorphous Type Material)- Adsorbent- Adsorption Isotherm

## INTRODUCTION

Gas liquids containing different sulfur compounds have high amount of mercaptan. Mercaptan is a poisonous material group which methyl and ethyl-mercaptan are abundant types from low molecular weight to heavy chained hydro-carbon type. Low weight mercaptan is poisonous, corrosive and odorous. In addition, they produce dangerous poisonous Sulfur dioxide by burning. Sulfur dioxide burning causes pollutant, acid raining, corrosion of equipment and facilities, refinery catalyst damage (Boniek, 2014). One of the ordinary methods for chemical de-sulfur is to use hydrogen. In this method, sulfur compounds transform to hydrogen sulfide and carbon under high pressure and temperature using non-homogeneous metal catalysts. Hydrogen sulfide is a gas type and will be separated easily from other products. But there are many problems in this method: 1- high cost for supply high temperature and pressure of hydrogen sources 2- heterocyclic aromatic compounds containing sulfur such as Thioufen and di-benzo Thioufen are resistant to this method. Therefore other methods should be found to remove sulfur (Bhasarkar, 2015; Martínez et al., 2015). Adsorption process is better in comparison with other methods due to low cost, high flexibility, easy design and construction, high sensitivity to poisonous material. It refines the gas for re-use without making poisonous material. (Zhu, 2013; Sarkar, 2014). Iso-propyl-mercaptan is a colorless liquid which smells like (2-propanethiol  $C_3H_8S$ ) causes

nausea, headache or vertigo. High concentration of vapor phase causes scald and eye pain, nose and respiratory canal pain. This is a high poisonous compound which is hazardous for environment. Also it is hazardous for industrial pipeline due to corrosion and should be separated from its carrier gas (Shin, 2011).

### Research Method

Plornic acid 99% from Sigma Aldrich as surfactant active material, HCl 32% Merc Co, Tetra ertho Silicat Merc Co as silicon source, Ethanol 99% Merc, Nitrate zinc 99% Merc were used.

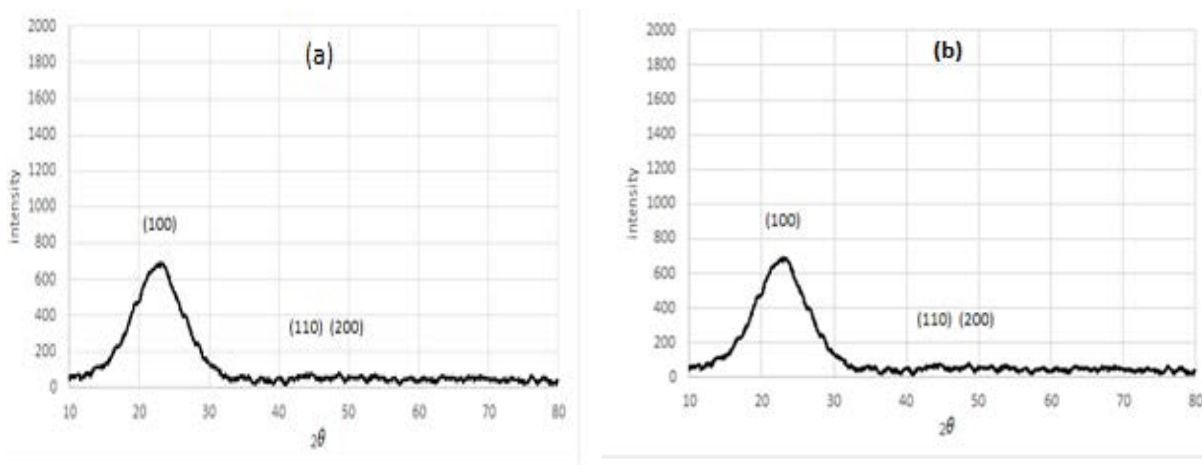
10 gr of Plornic acid (p123) is added to 250 mL of distillated water to be solved to change its color like milk. Then 2N hydrogen chloride (18.5 ml) is stirred and added to change the color from milky to limpid. Then 22.5 mL of Tetra ertho silicate is added to solution with sequence of drops. Produced suspension is stirred under 312 K (40° C) for 24 hours and under 373 K (100°C) for 20 hrs. Produced solid will be filtered under strainer paper and then it is washed by distillated water to be dried under room temperature. At last it will be calcified under 823 K (550 °C) for 5 hrs. (Issa M.E.I-Nahhal. et al. 2017)

### Addition of Nano-particles of zinc oxide

1 gr of SBA-15 is poured to 25 mL balloon under room temperature, then it is tried to load 5, 10 and 15% (0.187, 0.375 and 0.562 nitrate) to  $Zn(NO_3)_2 \cdot 6H_2O_2$  several times to reach 6 mL volume. They will be stirred for 45 minutes and then it will be placed under ultrasonic equipment for 20 minutes. Produced solid will be filtered by strainer paper. After washing, they will be placed in oven for 24 hours under 40°c to be dried and in furnace for 2 hours under 500 °C to be calcified.

### X ray diffraction

X-ray diffraction of SBA-15 (figure 1 part a) shows crystal faces (100), (110), (210) which represents high order hexagonal structure. Peak (100) shows a pore order in SBA-15. Fig b is related to x-ray diffraction of SBA-15-ZnO. Weakening of peak (100) is because of pore filling and decreasing of pore order in SBA-15 which proves entering of nano particles of oxide into mezo-pores.

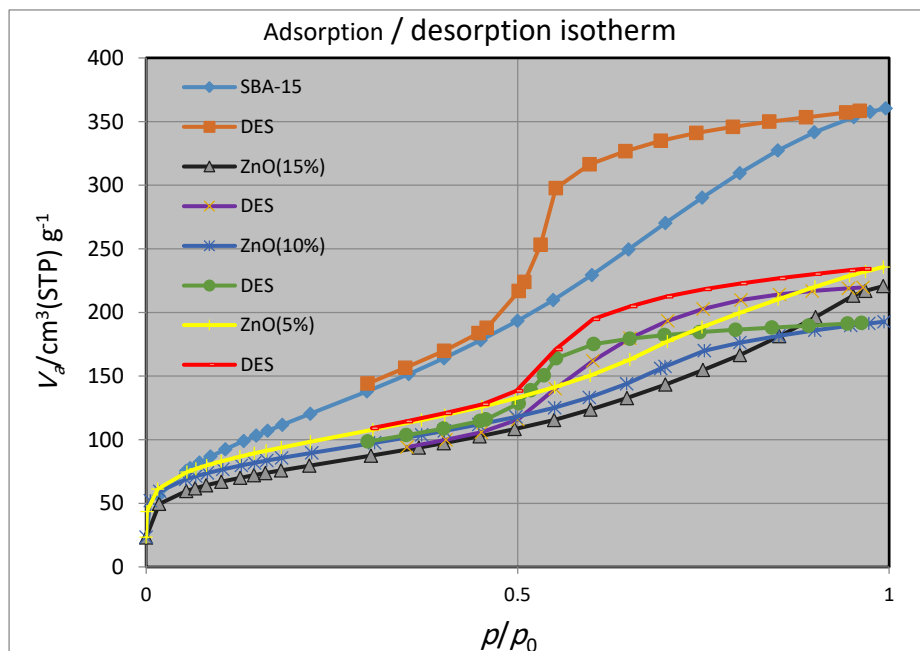


**Figure 1.** XRD pattern of SBA-15 (a) before and (b) X SBA-15 loaded by nano particles of zinc

### porosity diffraction

To study porosity type, specific surface area, diameter and volume of pores in SBA-15 in absorbent tool and de-absorbent nitrogen are used. Measurement was performed at 77 K temperature and sample was de-gassed at 300C temperature. Plot of absorb and de-absorb of SBA-15 nitrogen is isotherm plot of IV according to IUPAC classification which proves mezzo pore compound. Hysteresis loop existence between absorb and de-absorb branches is due to capillary liquids through the pores of mezzo porosities which are trapped due to liquefaction of gas among cylindrical pores. Delay is one of mezzo pore specifications during de-absorb.

(Evaporation happen in low pressure). Isothermal absorption plot IV is related to mezzo-pores. In addition, residual is H<sub>1</sub> type in this plot. Specific shape of each loop is due to its specific loop. H<sub>1</sub> loop is due to uniform pores with narrow distribution. Total volume and pore diameter average is calculated by BET curve. High percent shows that high are of absorbent is related to pores.



**Figure 2.** Adsorption / desorption isotherm SBA- 15 absorbent by ZnO nano particles

**Table 1.** Nitrogen Absorbent and de-absorbent specification.

sample	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>total</sub> (cm <sup>3</sup> g <sup>-1</sup> )	APD (nm)
SBA-15	438.24	0.55661	8.08
SBA-ZnO-5	333.45	0.3608	5.022
SBA-ZnO-10	309.47	0.3477	3.848
SBA-ZnO-15	271	0.2941	1.37

## Results and Analysis

To study and optimize effective parameters on mercaptan gas surface absorption by SBA-15 with help of nano particle zinc oxide to get highest amount of removing mercaptan isopropyl gas, proper results and repeatability, experimental parameters include following items (just one of them will be changed).

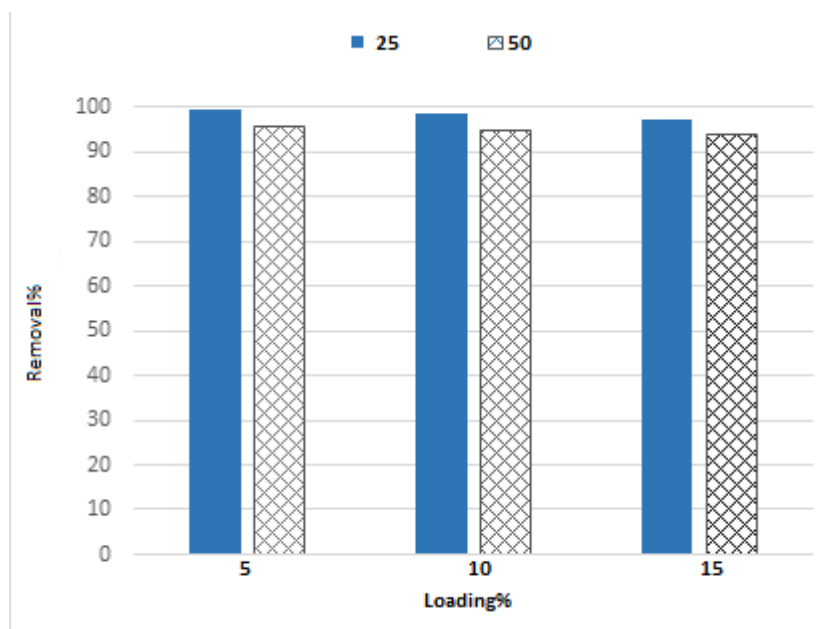
### Temperature effect:

Temperature of absorbent plays an important role, especially on surface absorption and its capacity. Temperature effect on type and its behavior for absorbent show pollutant gas absorbent extremely depends on temperature for all samples. 1 gram of absorbent is placed on specified tank. After activation, suitable temperature (25 and 50C) will be used and controlled by temperature controller. Therefore, temperature is the first parameter which is considered in study of surface absorption process.

### Load of nanoparticle effect

To specify load effect of nanoparticle on SBA-15 base, samples with 0, 5, 10 and 15% were studied. Results are shown in following plot. Figure shows percentage of mercaptan remove according to load amount for three absorbents. According to the plot, surface absorption is decreased by increasing available location of loading. Therefore, absorption performance is decreased. But absorption is increased in comparison with no loading

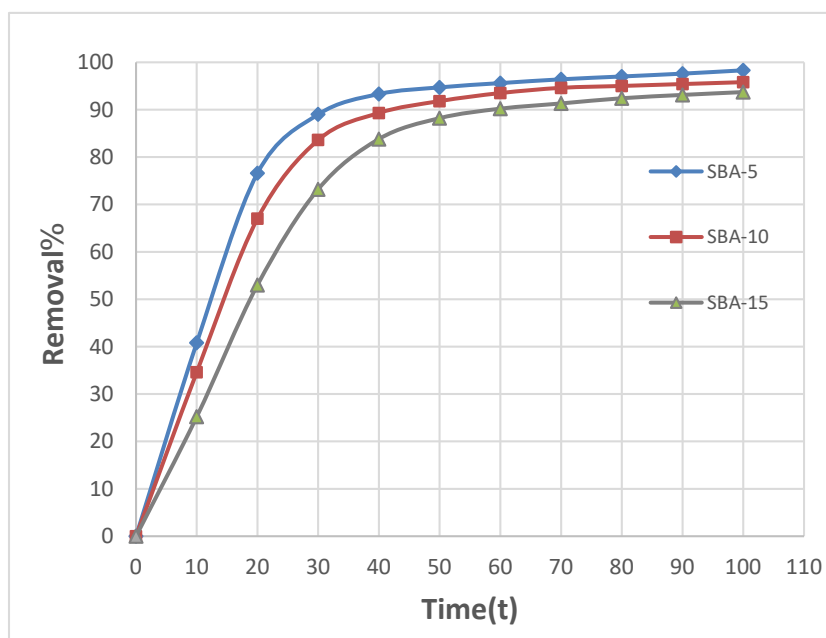
one. It shows that loading nano particle increase mercaptan gas absorption. Selectivity and high power of absorption cause incredible decrease of industrial process cost.



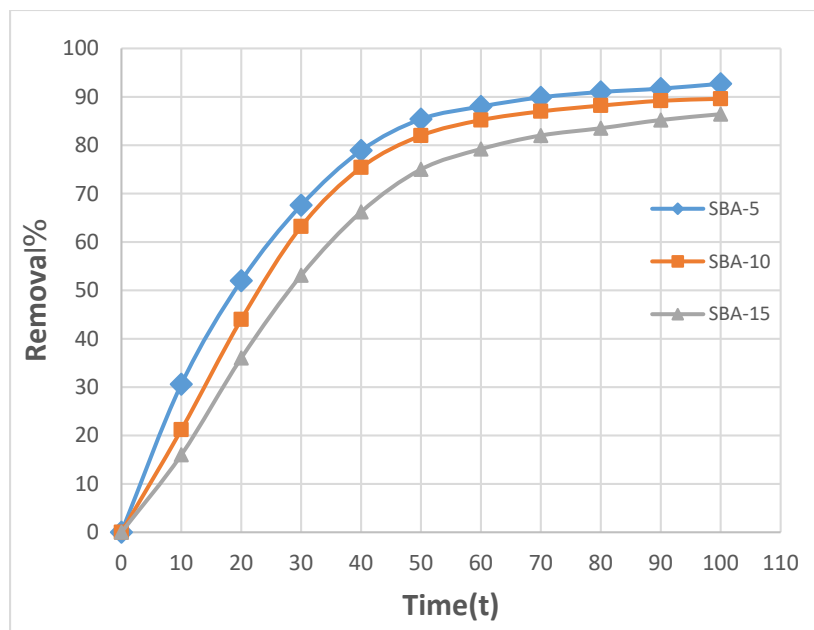
**Figure 3.** Plot of IPM remove percentage ratio for SBA-15 absorbent in different loading for two different temperature

**Time effect**

To study time effect, 1 gram of absorbent is poured on absorption tank and gas absorption from 0 to 100<sup>th</sup> minutes (25°) was studied. Maximum gas remove is for Mercaptan iso propyl. Results are shown in following plots.



**Figure 4.** Time to mercaptan iso propyl remove percent during the time at 25°C



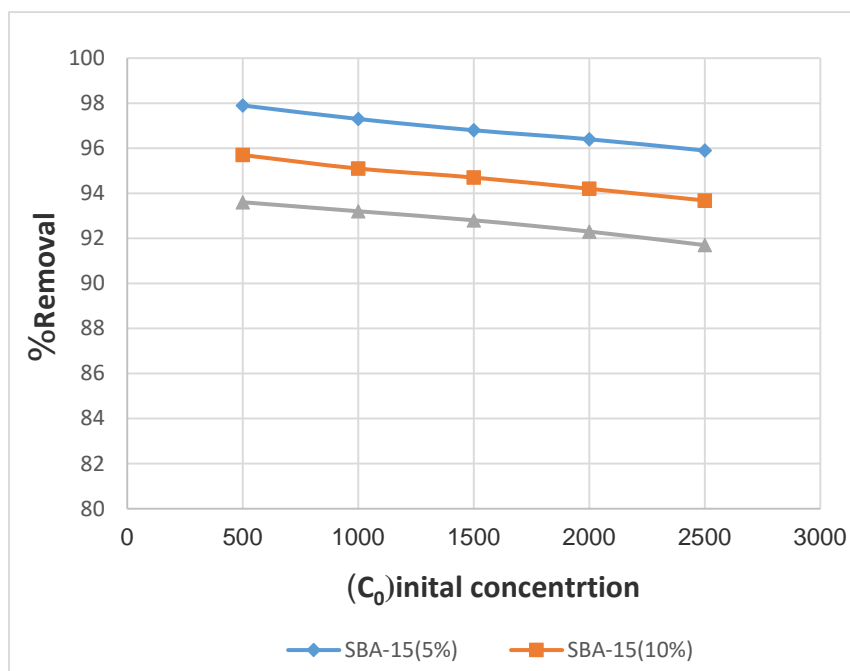
**Figure 5.** Time to mercaptan iso propyl remove percent during the time at 50°C

**Study of initial concentration of mercaptan isopropyl**

To study effect of initial concentration, injected gas to absorption tank according to input pressure are 500, 1000, 1500, 2000, 2500 respectively.

Absorption of mercaptan isopropyl was studied for two temperatures, 25 and 50C.

Increasing initial gas concentration increased production of isopropyl zinc compounds. Therefore, concentration of this compound is increased on the surface of absorbent which blocked absorption pores. Absorption is decreased and data results are shown as follows:



**Figure 6.** IPM gas removes percentage respect to initial concentration gas 25°C

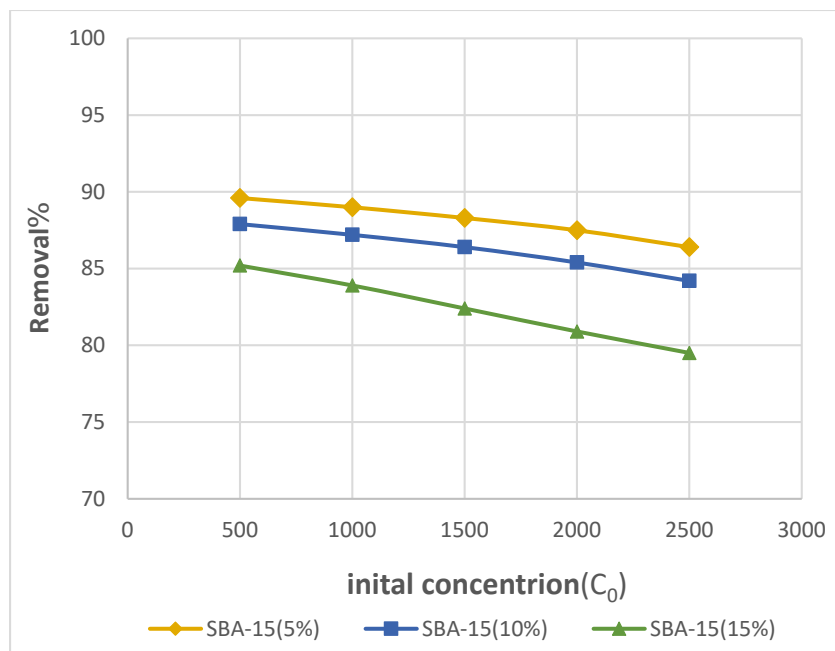


Figure 7. IPM gas removes percentage respect to initial concentration gas 50°C

#### Absorption Iso-therm plot.

To study absorption behavior on removing pollutant and plot of isotherm according to different articles and literature, different experiments were used.

Most of such methods include Batch type. One of these methods include application of initial concentration as constant and variable absorbent as m.

Other method is usage of constant absorbent (m) and initial concentration as variable. Therefore, since second method is more compatible to our condition, second method was used to plot isotherm. In this section, to study absorbent behavior of absorbent and determination prediction of absorbent, Temkin, Langmuir, Freundlich was used.

- **Langmuir**

Langmuir 1918 was the first person who presented organized theory kinetic-oriented for surface absorb on plat surface. In this theory, continuous process of molecule bombard on plate and molecule repelling on surface was occurred in so as molecule gathering rate to be zero on the equilibrium at the plate.

a) **Langmuir linearization**

$$\left(\frac{x}{m}\right) = q_{max} \left(\frac{b \cdot C_e}{1 + b \cdot C_e}\right)$$

To plot Langmuir iso thermo, two linear form of Langmuir isotherm line, mentioned in literature, was used.

**First method of linearization:**

$$\Rightarrow \frac{1}{x/m} = \frac{1}{q_e} = \left(\frac{1}{q_{max} \cdot b}\right) \left(\frac{1}{C_e}\right) + \frac{1}{q_{max}}$$

In first mode, Langmuir constants will be obtained after plotting  $(1/q_e)$  vs  $(1/C_e)$ , and specification of origin coordination, slope.

$(1/q_{max} \cdot b)$  as slope and  $1/q_{max}$  as origin.

**Second method of linearization:**

$$\Rightarrow \frac{C_e}{q_e} = \left( \frac{1}{q_{max}} \right) C_e + \frac{1}{q_{max} \cdot b}$$

For this type, after plotting  $C_e/q_e$  versus  $C_e$  and specification of origin and slope, Langmuir 2 isotherm will be obtained.

$(1/q_{max})$  : slope and  $1/q_{max} \cdot b$  : width of origin

In addition two parameters,  $q_{max}$  and  $b$ , other parameter, RL exist which determine adsorb isotherm.

RL=  $1/1+b \cdot C_0$

In this relation,  $C_0$  is maximum solved concentration in gas phase. RL is constant parameter and dimensionless which be determined by Eq.5-4.

- **Freundlich Isotherm:**

Freundlich isotherm is one of the first equation which is used to describe of equilibrium data. Isotherm equation is as follows:

$$\left( \frac{x}{m} \right) = K_f \cdot C_e^{1/n}$$

In which,  $(x/m)$  is partial absorption.  $K$  and  $n$  are Freundlich isotherm constants and dependent on temperature. Parameter  $n$  is usually greater than 1 and the bigger  $n$ , more non linearity obtained.

$K_f$  shows capacity of absorption by adsorbent.  $(1/n)$  shows absorption intensity.

**Freundlich linearization**

$$\left( \frac{x}{m} \right) = K_f \cdot C_e^{1/n}$$

**Linearization:**

$$\log \left( \frac{x}{m} \right) = \log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e)$$

Therefore, it is possible to plot  $\log(q_e)$  vs  $\log(C_e)$ , Freundlich isotherm constants will be obtained by specification of width of origin and slope.

- **Temkin Isotherm**

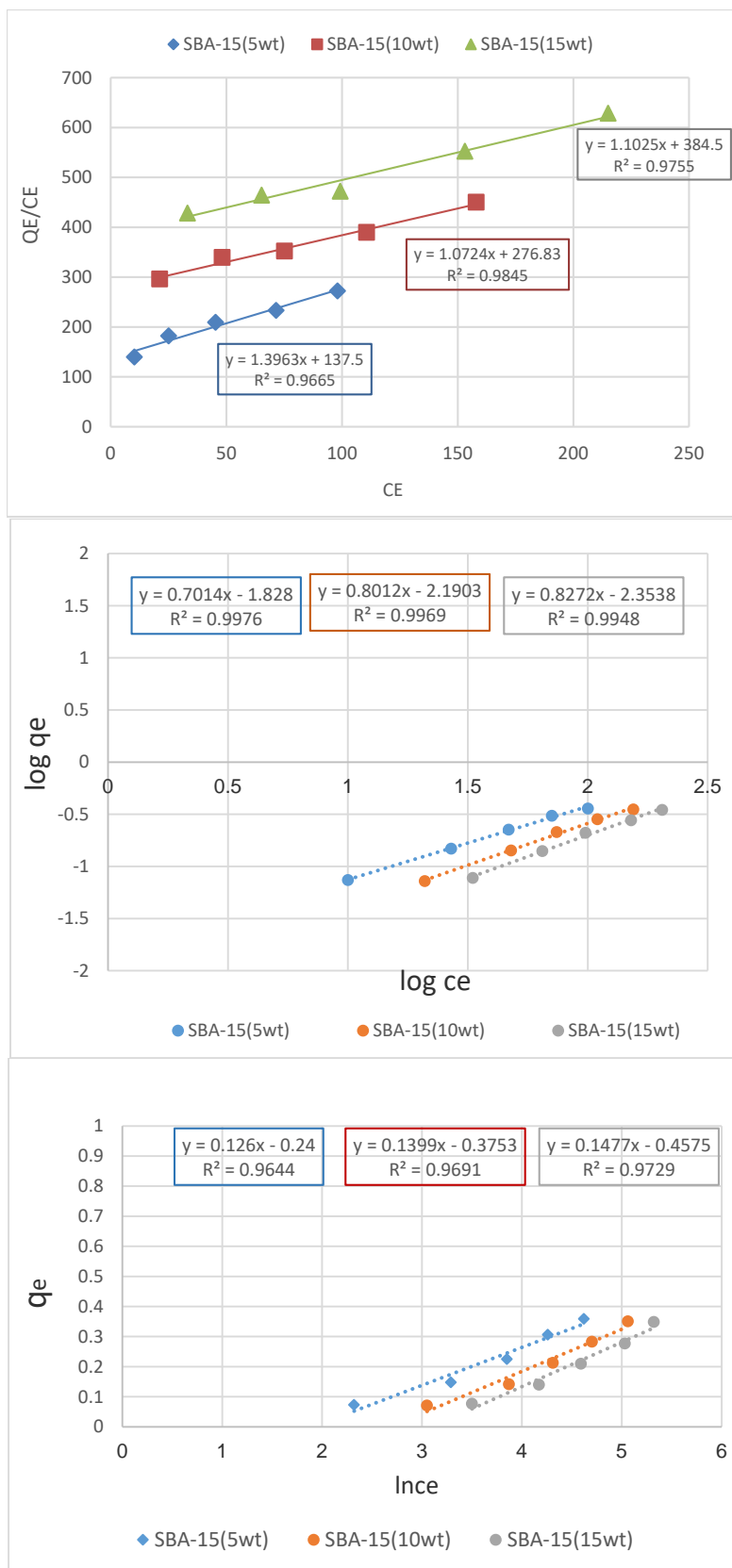
Following supposition of Adsorption Energy of Temkin isotherm is a relation of surface coverage.

$$\frac{x}{m} = A + B \log C_e$$

In this relation,  $A$  and  $B$  will be isotherm coefficient. In 1985 studies, it was specified that isotherm will be used in a limited range of ionic concentration.

Linear relation of isotherm has a line form. Therefore this form will be used.

$$\frac{x}{m} = q_e = A + B \log C_e$$

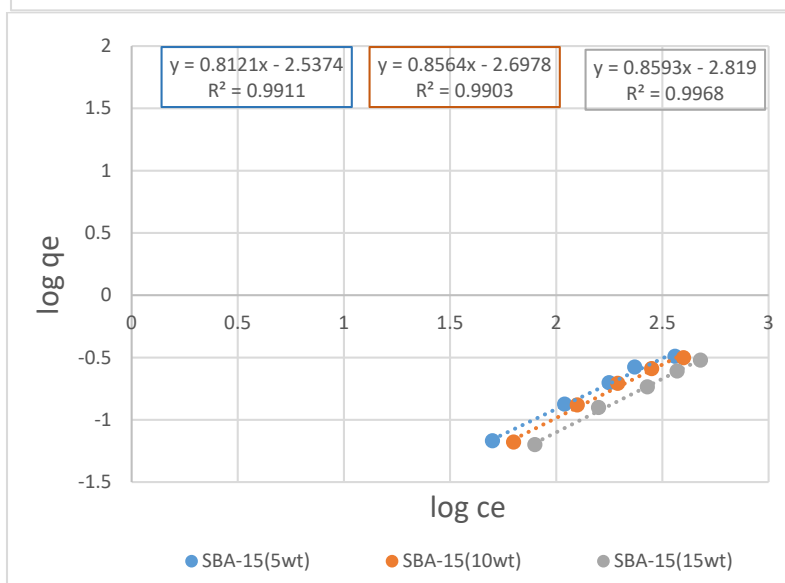
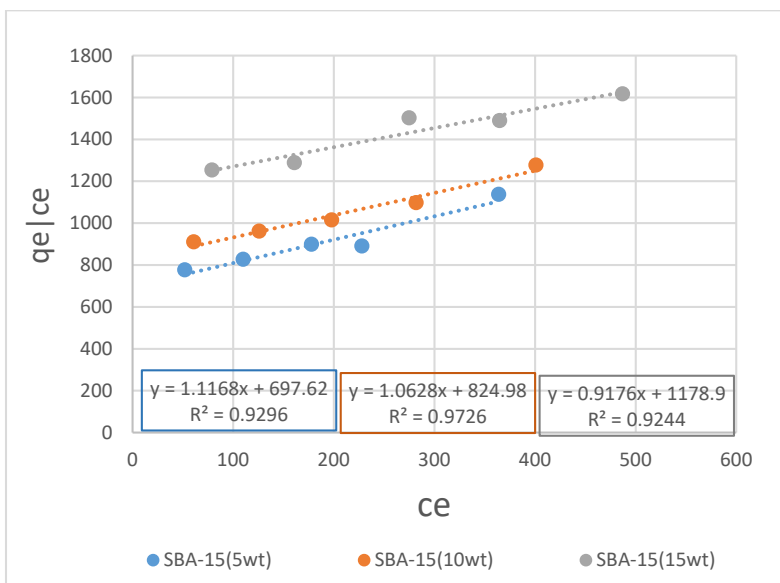


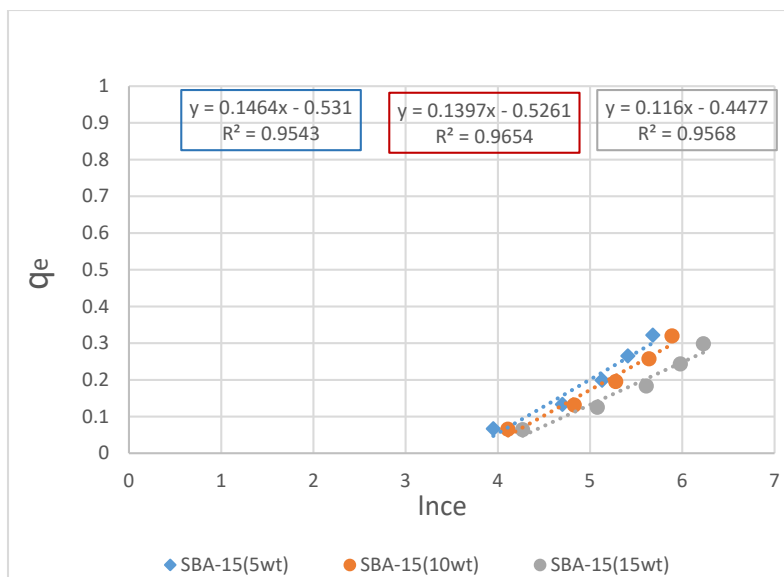
**Figure 8.** isotherm plot of IPM ga surface absorption with different SBA -15 at temperature 25C



**Table 2.** Thermodynamic Isotherm parameters of Absorbent SBA at temperature 25C

Langmuir	$q_m$ (mg/g)	$b$ (L/mg)	$R^2$
SBA-15(5wt)	0.7044	0.0104	0.976
SBA-15(10wt)	0.932	0.00389	0.984
SBA-15(15wt)	0.907	0.00259	0.975
Frundlich	$K_f$ (mg/gr)	$n$	$R^2$
SBA-15(5wt)	0.0148	1.42	0.997
SBA-15(10wt)	0.00645	1.24	0/996
SBA-15(15wt)	0/00442	1/20	0.994
Temkin	A	B	$R^2$
SBA-15(5wt)	0.24	0.126	0.964
SBA-15(10wt)	0.375	0.375	0.969
SBA-15(15wt)	0.457	0.147	0.972





**Figure 9.** isotherm plot of IPM ga surface absorption with different SBA -15 at temperature 50C

**Table 3.** parameters of thermodynamic isotherm at temperature 50 to remove with absorbent SBA 15

Langmuir	$q_m$ (mg/g)	$b$ (L/mg)	$R^2$
SBA-15(5wt)	0.906	0.00158	0.969
SBA-15(10wt)	0.94	0.00128	0.964
SBA-15(15wt)	1.09	0.00077	0.965
Frundlich	$K_f$ (mg/gr)	$n$	$R^2$
SBA-15(5wt)	0.0029	1/23	0.991
SBA-15(10wt)	0.002	1/16	0.99
SBA-15(15wt)	0.0015	1/163	0.996
Temkin	A	B	$R^2$
SBA-15(5wt)	0.471	0.132	0.954
SBA-15(10wt)	0.508	0.135	0.965
SBA-15(15wt)	0.453	0.113	0.956

## Results and Conclusion

Iso propyl Mercaptan had hazardous environmental effect and it is corrosive for industrial equipment. In this project removing isopropyl mercaptan by using meso pore with application of nano zinc particle is studied. High area of meso pore make it suitable for absorption. In this project, SBA-15 meso pore absorbent with coprecipitation project in which nano particle of oxide placed on absorbent with weight 5-10-5% by post method. It was detected by XRD, BET and ICP. Absorbent and de-absorbent plot of specific area nitrogen SBA-15 show for 438,271, 309 and 333  $m^2g^{-1}$ . Reduction of area shows that existence of nano particles of zinc oxide on absorbent pores. Studies of effect, initial concentration, loading nano particle and time shows that increasing of temperature decreases percentage of IPM gas removing. Since increasing temperature motivate gas molecule moving. Therefore increasing initial concentration decreasing absorption trend. Increasing nano particles of zinc oxide on absorbent, will block active sites too more. Because acclimation happens and results show that maximum amount of absorption of gas is for 5% nano particles. The more sulfur removing is due to proper distribution, proper ZnO particle size. Isotherm equation of surface absorption is important for designing an absorption system. Several equation at 25 and 50C and different loads were analysed by Langmuir, Freundlich, Temkin isotherm. For Langmuir, it was supposed that surface absorption of absorbent (Mercaptan iso propyl) occurs by absorption in single layer on uniform area without any reaction between absorbed species. According to calculation, considering  $R^2$ ,  $K_f$ ,  $n$  for mercaptan isopropyl, it can be concluded

that iso propyl surface absorption follows Freundlich isotherm model. Freundlich isotherm model occurs for chemical-physical absorption on non-uniform area by surface absorption in multi layer. So it doesn't follow Langmuir or Temkin. Therefore removing mercaptan iso propyl using nano particle of zinc oxide on the base of SBA-15 follows Freundlich model.

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