

Adsorption of Hydrogen Sulphide on the Zeolite type A Synthesized from Iraqi Kaoline

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Abstract

Three types of zeolite A were prepared from Iraqi kaoline which are 3A, 4A and 5A by ion exchange method. They were characterized by XRD and atomic absorption techniques. They were used as adsorbents to examine their applicability for H₂S adsorption. The adsorption process was performed in a static form and constant volume system which constructed from stainless steel. The effect of zeolite type and temperature on the adsorption properties of H₂S at -5, 25 and 55 °C was studied. The zeolite type 5A has the highest adsorption value (79.384 μmol/g) and the three types may be arranged in a sequence toward H₂S adsorption as 5A > 4A > 3A. The amount of H₂S adsorbed increased as temperature decreased from 55 to -5 for all samples. Langmuir, Freundlich and Toth isotherm equations model were applied for the adsorption data in order to determine the affinity and the heterogeneity of the three adsorbents. The heterogeneity parameters of the model equation applied indicated that 5A sample was more heterogeneous compared to other zeolite types.

Key words : Adsorption , Zeolite , H₂S , Iraqi , Kaoline.

Introduction

Zeolites are crystalline, porous three dimensional aluminosilicates of the alkali (mainly Na and K) and alkaline – earth (mainly Ca) metals. Their crystal structure is based on three dimensional frameworks of (SiAl)O₄ tetrahedra with all four oxygens shared by adjacent tetrahedral^[1]. This results in a channel structure with molecular dimension of 3 to 10 Å. Because some of the Si⁺⁴ is substituted by Al⁺³, there is a net negative charge which is balanced by extra framework exchangeable cations, mainly Na⁺, K⁺, Ca⁺² or cavities and surrounded by water molecules. The water molecules loosely held in the pores and most zeolites can be reversibly dehydrated and their cations readily exchanged. Zeolite has an empirical formula of :-



where M⁺ is usually Na or K, M⁺² is Mg, Ca, or Fe and g and z are variable multipliers. Rarely Li, Sr or Ba may substitute M⁺ or M⁺². The tetrahedral Si/(Si+Al) ratio is one of the major compositional variables, with some zeolite (e.g mordenite) being at the silica – rich end and others being more aluminous^[2].

Zeolites have three properties that make them unique and deserving separate category; They are highly crystalline with well defined structure enclosing the aluminum silicate framework cavities occupied by large ions and water molecules, the cavities opening ranging from 0.8- 1 nm diameter which are the order of molecular dimension. Size and shape

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of these pores determine which molecules enter the cavities and which are excluded, so they are called molecular sieves. Cations within the cavities are easily replaced with a large number of different valency cations which exert large number of electrostatic or polarizing forces across the small dimension of the cavity and the introduced cation into

the cavities by ion exchange will have separate activities of their own, This facilitates the opportunity of dual function catalysts involving acidity with other activities^[3]

Among clay minerals, kaolinite is the most common phyllosilicate involved

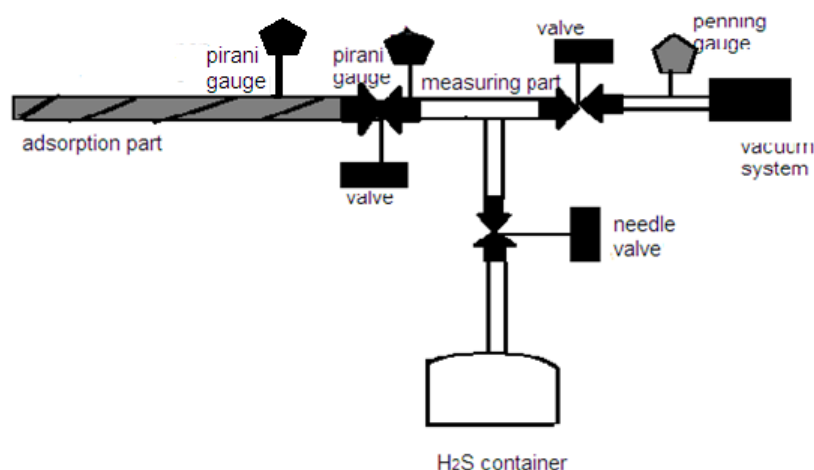


Fig (1) A block diagram of the adsorption system

RESULTS AND DISCUSSION

The amount of major components of the zeolite 3A, 4A and

5A present in the structure was found by atomic adsorption spectroscopy, Table (1).

Table (1):-Atomic absorption data of kaoline ,zeolite 3A,4A and 5A

Constituents	Weight (%) kaoline	Weight (%) 3A	Weight (%) 4A	Weight (%) 5A
SiO ₂	50.0	38.2	44.21	40.05
Al ₂ O ₃	32.02	27.60	26.68	26.93
Na ₂ O	0.33	3.01	11.70	2.97
K ₂ O	0.51	10.80	0.54	0.45
MgO	0.12	1.72	0.27	1.04
CaO	0.32	1.87	0.14	11.02
TiO ₂	1.02	0.44	1.34	1.06
Fe ₂ O ₃	1.4	1.50	1.06	0.19
L.O.I	11.92	13.77	13.06	16.92

Comparing the above data of kaolin and zeolite of the components, especially sodium, calcium and potassium, showed that the ion exchange process was successful. The x-ray diffraction

patterns of the prepared types 3A, 4A and 5A zeolite are show in figures (2,3 and 4). This pattern is just a plot of the x-ray intensity diffracted from the sample versus the diffraction angle (Bragg's angle, 2θ).

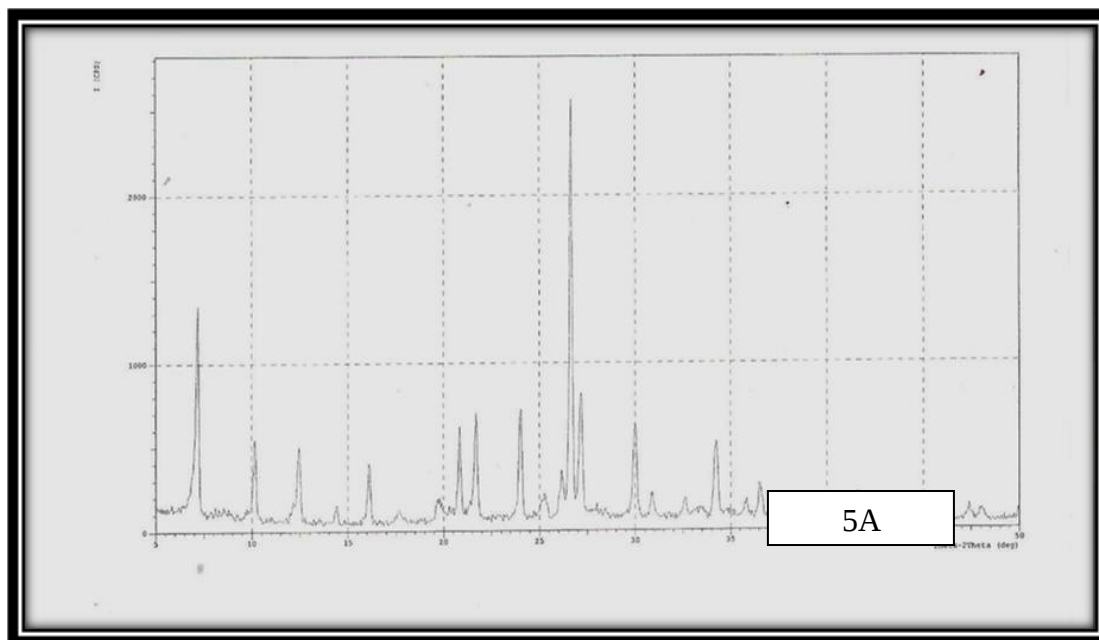


Fig (2):- the x-ray diffraction of zeolite 5A

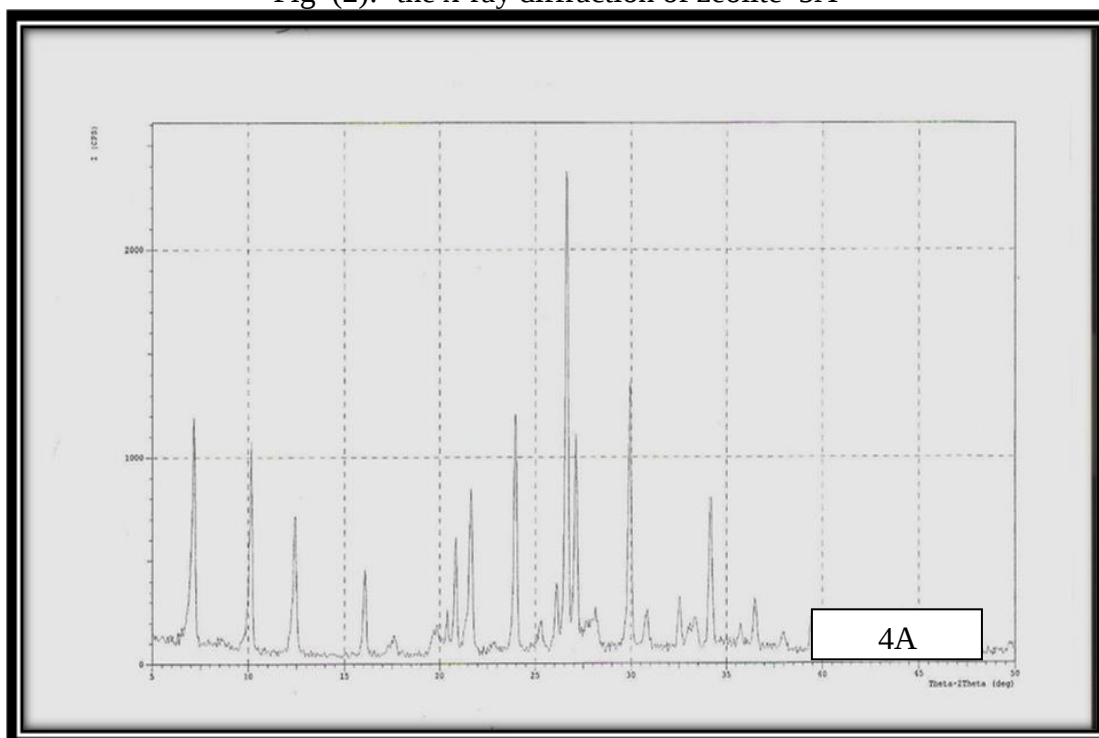


Fig (3):- the x-ray diffraction of zeolite 4A

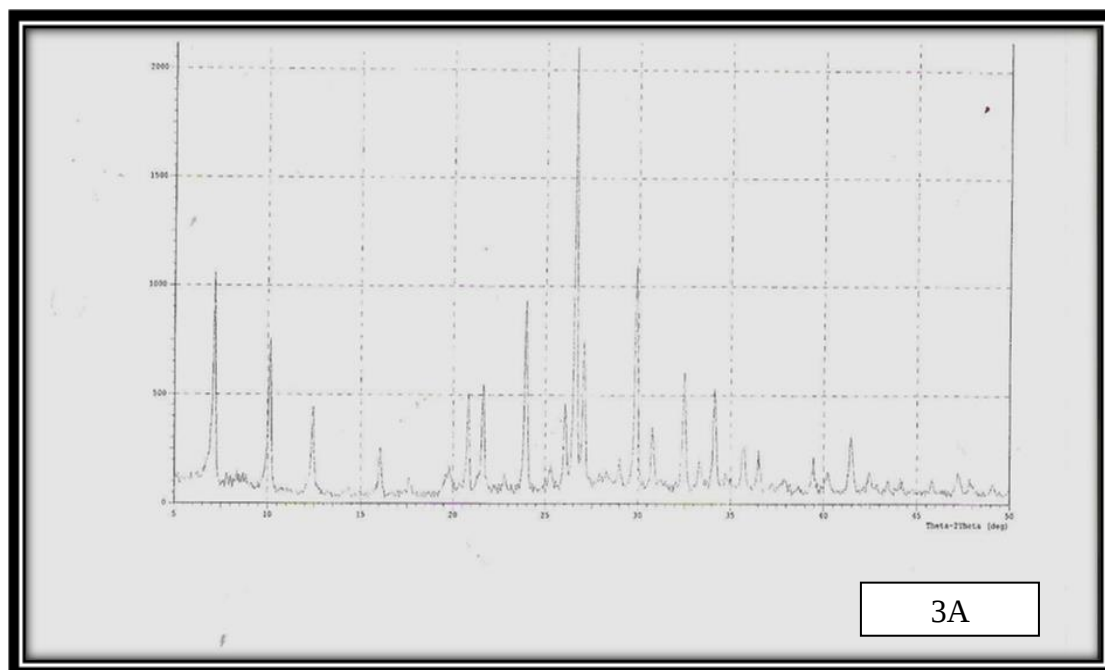


Fig (4):- the x-ray diffraction of zeolite 3A

From the X-ray diffraction patterns, it can be observed that the prepared zeolite has a good crystallinity and nearly has the same crystal structure as the standard type and the crystallization of the samples were completed.

The x-ray diffraction of the prepared zeolite type 4A has a small peak at the angle ($2\theta = 4^\circ$) with intensity 1300 and at $2\theta = 10^\circ$ with intensity 1009 but the characteristic peaks for this type is at the angle ($2\theta = 27^\circ$) with intensity of 2400 and at angle ($2\theta = 30^\circ$) with intensity of 1400.

Also zeolite type 5A and 3A were analyzed by x-ray diffraction as shown in Figures (2,3 and 4). The prepared zeolite type 5A has a small peak at the angle ($2\theta = 5^\circ$) with

intensity 1190 and at ($2\theta = 28^\circ$) with intensity of 2500 while type 3A has a characteristic peak for this type is at angle ($2\theta = 5^\circ$) with intensity 1100 and angle ($2\theta = 26^\circ$) with intensity 2100. The structures of zeolite type 3A and 5A were similar to the structure of zeolite type 4A with some differences in the cation kind and oxygen atom connection as explained by Reed's (1956).^[19]

The experimental data obtained from the adsorption of H_2S are listed in Table (2), and the adsorption isotherms are presented in figure (5).

Table (2) :-The experimental data for adsorption of H₂S gas

T(K)	3A			4A			5A		
	ΔP mbar	P_{eq} mbar	n_{ad} mol/g μ	ΔP mbar	P_{eq} Mbar	n μ mol/g	ΔP mbar	P_{eq} mbar	n μ mol/g
268	0.13	0.07	0.1773	0.114	0.026	0.766	0.085	0.025	0.2417
	0.17	0.21	0.4093	0.226	0.044	2.284	0.28	0.04	1.038
	0.3	0.60	0.815	0.535	0.085	5.877	0.684	0.076	2.983
	1	1.5	2.184	1.3	0.2	14.609	1.34	0.16	6.794
	1.1	5.4	7.0227	3.08	0.52	35.298	4.28	0.52	31.950
	0.50	8.5	9.222	5.1	1.3	69.55	7.5	2.5	76.033
	—	—	—	0.7	7.8	74.257	0.4	7.6	79.384
298	0.146	0.044	0.2097	0.487	0.033	2.172	0.087	0.023	0.1263
	0.24	0.16	0.5543	0.744	0.056	5.489	0.094	0.046	0.263
	0.3	0.7	0.985	3.44	0.56	20.829	2.68	0.32	4.1627
	1.1	1.5	2.5644	4.9	0.21	25.287	3.8	1.2	13.055
	1.2	5.2	7.561	1.0	9	27.353	0.9	6.1	19.623
	2	8	8.475	—	—	—	—	—	—
328	0.182	0.058	0.1503	0.176	0.044	0.714	0.024	0.017	0.0406
	0.25	0.21	0.357	0.24	0.08	1.6873	0.268	0.032	0.494
	0.33	0.62	0.6295	0.57	0.15	3.9993	0.518	0.062	1.3713
	0.9	1.8	1.3732	2.52	0.68	14.2193	3.45	0.35	7.199
	0.6	6	3.356	1.0	9	14.2193	6.8	4.2	18.711

Figure(5) shows that the isotherms for 4A and 5A are of type (L or I) indicates a high energy of adsorption and characteristic of adsorbent which contains microporosity, while the isotherm for 3A is of type (S or II) which indicates a small affinity between zeolite 3A and the gas.

The temperature effect on the adsorption was carried at -5 ,25 and 55

°C .The results (Table 2 and Figure (5) indicate that when the temperature increased the amount of H₂S adsorbed decreased .The decreasing trend of adsorption with temperature is mainly due to the weakening of adsorptive forces between the active sites of adsorbent and adsorbate species.

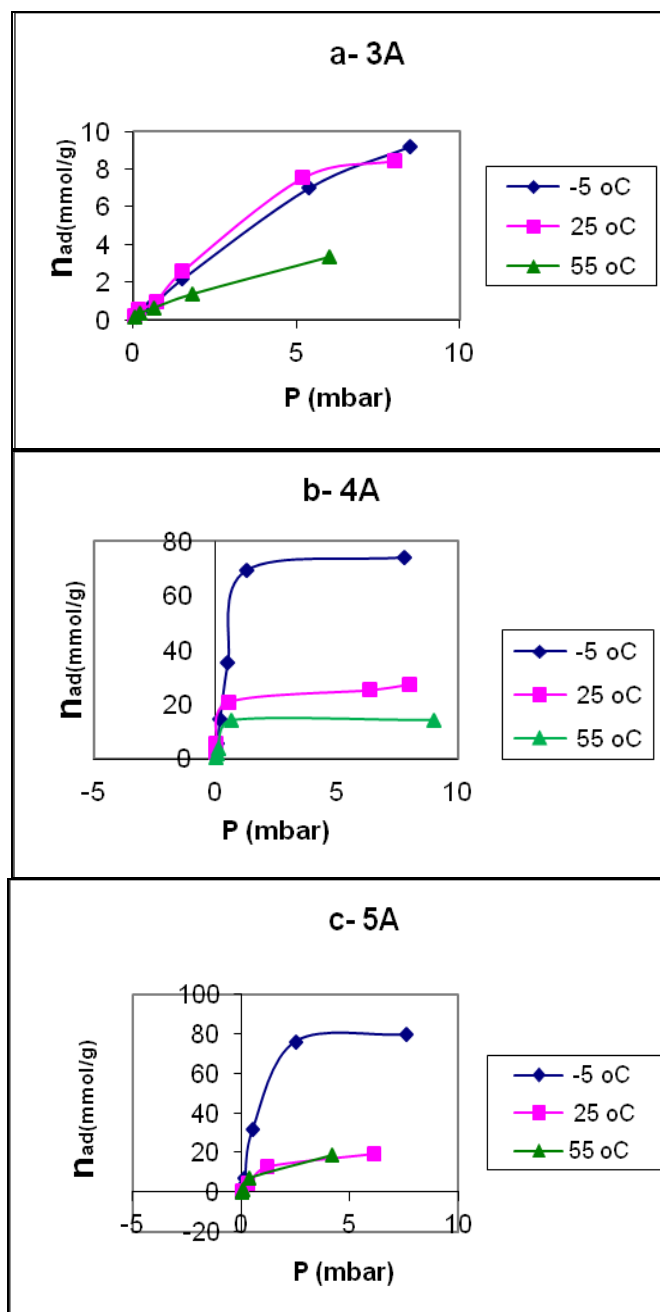


Fig (5):- The adsorption isotherms of the three zeolite at different three temperature

a- for 3A, b-for 4A,c- for 5A

Three model equations Langmmir , Freundlish and Toth were applied to the adsorption data to get information regarding the heterogeneity of the adsorbent surface .These equations are:-

$$\frac{P_{eq}}{n_{ad}} = \frac{1}{n_m b} + \frac{P_{eq}}{n_m} \dots\dots\dots (Langmmir - equation)$$

$$\ln n_{ad} = \ln K_f + \frac{1}{n} \ln P_{eq} \dots\dots\dots (Freundlish - equation)$$

$$n_{ad} = \frac{n_T P_{eq} K_T}{(1 + (K_T P_{eq})^t)^{\frac{1}{t}}} \dots\dots\dots (Toth - equation)$$

These isotherms are fitted employing the non – Linear fitting method using the software (Statistica Module Switcer) .Figure(3) presents how well

the equations fit the data for H_2S – adsorbent system at $(25)^\circ\text{C}$. The values of the constants are listed in the Table (3) along with R^2 values.

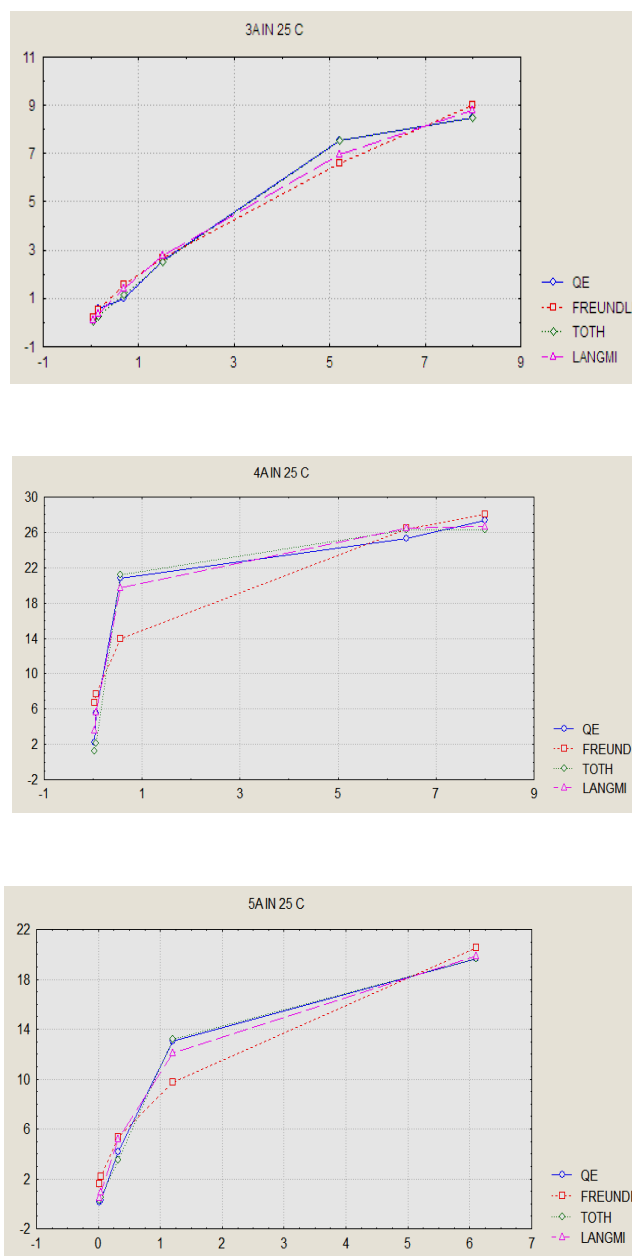


Fig (6) :-Comparison of various isotherm equation for the adsorption on three zeolite type A at 25°C

Table(3):-The values of the constants and R^2 values

T	Sample	Langmuir			Freundlich			Toth			
		n_m	B	R^2	K_f	$1/n$	R^2	n_T	T	K_t	R^2
268	3A	26.045	0.066	0.9992	1.657	0.815	0.9974	11.555	2.677	0.126	0.9998
	4A	86.247	1.521	0.979	39.045	0.369	0.8995	71.903	93.476	0.9509	0.9988
	5A	95.829	1.010	0.9898	29.402	0.524	0.911	77.709	81.179	0.761	0.9986
298	3A	17.531	0.126	0.9942	2.009	0.723	0.9885	8.655	5.018	0.193	0.9989
	4A	27.411	2.621	0.9952	16.275	0.261	0.9293	26.320	85.736	1.439	0.9865
	5A	23.647	1.145	0.9957	8.984	0.458	0.967	19.623	70.048	0.561	0.9991
328	3A	7.605	0.131	0.9969	0.917	0.723	0.9995	2.087	0.179	0.002	0.9991
	4A	16.144	3.161	0.950	8.560	0.276	0.814	14.219	60.315	1.748	0.9991
	5A	22.136	1.314	0.9990	9.170	0.506	0.987	18.711	104.44	1.097	0.9997

The affinity constants (b , K_f and K_t) are a measure of how strong an adsorbate molecule is attracted onto surface, The highest band K_f values for H_2S adsorption are obtained for the adsorption (4A) and the adsorbents may be arranged according to b , K_f and K_t values as $4A > 5A > 3A$.

The parameters (n & t) characterizes the system heterogeneity and the larger the parameter, the more heterogeneous is the system. According to Table (3), (4A) has the highest value indicating that H_2S -4A pair is more heterogeneous when compare to other adsorbent - H_2S pairs.

Also, it is seen that the highest adsorption capacity (n_m & K_t) belongs to 5A and the order is changed as follows $5A > 4A > 3A$. The results of R^2 and Figure (5) indicates that the equilibrium data are well fit with the

three models of adsorption, but Langmuir and Toth models may be more appropriate to that described by Freundlich.

Thermodynamics

The free energy change of adsorption (ΔG°) was calculated by using Langmuir constant, equation (1) ⁽¹⁸⁾, enthalpy change (ΔH°) and entropy (ΔS°) of adsorption were calculated, equation(2):-

$$\Delta G^\circ = -RT \ln K_{eq} \dots \dots \dots (1)$$

$$\ln K_{eq} = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \dots \dots \dots (2)$$

ΔH° and ΔS° were obtained from the slope and intercept of a plot of $\ln K_{eq}$ against $1/T$, figure (7), Table (3) the $\ln K_{eq}$, $1/T$ and K_{eq} for H_2S gas K_{eq} the results obtained of the three thermodynamics parameter are listed in Table (4).

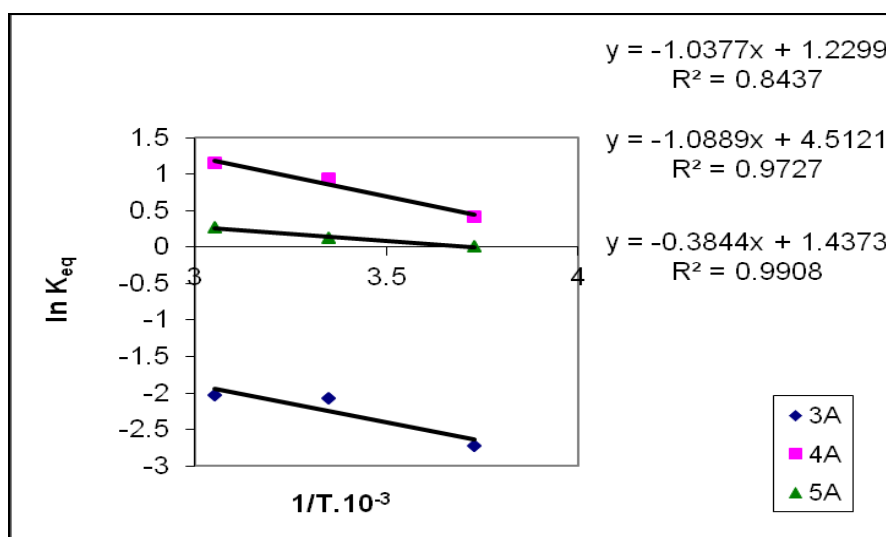


Fig (7):-The Van 't Hoff plot of adsorption on the three zeolite A

Table (3) The K_{eq} , $\ln K_{eq}$, $1/T$ for H₂S gas adsorption onto zeolite type A

K _{eq}			ln K _{eq}			1/T
3A	4A	5A	3A	4A	5A	
0.0656	1.5214	0.9738	-2.724	0.419	-0.027	268
0.1265	4.6211	0.8730	-2.067	1.531	-0.136	298
0.1308	3.1613	1.3135	-2.034	1.1509	0.273	328

Table (4) Thermodynamic parameters for H₂S gas adsorption onto zeolite type

Adsorbent	ΔH° KJ/mole	ΔS° J/ mole	ΔG° KJ/mole		
			-5°C	25°C	55°C
3A	8.627	10.23	6.056	5.132	5.542
4A	9.079	37.7	-0.934	-2.387	-3.138
5A	3.196	11.9	-0.0221	-0.335	-0.744

The negative values of ΔG° of H₂S adsorption on (4A & 5A) indicated the spontaneous nature of the adsorption, while the positive values on (3A) indicated the non spontaneous process.

The positive value of ΔH° on the three zeolite reveals the sorption is endothermic and mainly absorption, The positive values of ΔS° of the adsorption also on the three zeolite indicate an increase of randomness at H₂S-zeolite interface during sorption process.

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امتزاز غاز كبريتيد الهيدروجين على ثلاثة انواع من الزيولايت نوع A محضرة من الكاؤولين العراقي

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الخلاصة

حضرت ثلاثة انواع من الزيولايت من الكاؤولين العراقي وهي 3A و 4A و 5A بطريقة التبادل الايوني ثم شخّصت باستخدام تقنيتي حيود الاشعة السينية والامتصاص الذري . استخدمت هذه الانواع كسطوح مازة لمعرفة قدرتها على امتزاز غاز كبريتيد الهيدروجين H_2S , حيث اجريت عملية الامتزاز في منظومة مصنوعة من الفولاذ المقاوم للصدأ من النوع الساكن وذات حجم معروف مسبقا . تم دراسة تأثير كل من نوع الزيولايت ودرجة الحرارة على الصفات الامتزازية ، وظهرت النتائج ان الزيولايت 5A يعطى اعلى كمية امتزاز ($79.384 \mu\text{mol/g}$) من بين الانواع الثلاثة والتي يمكن ترتيبها نسبة الى امتزازها لغاز H_2S كالآتي:-

$$5A > 4A > 3A$$

وكانت كمية الامتزاز تزداد بنقصان درجة الحرارة من (55 الى -5)° م لجميع النماذج المستخدمة . تم تطبيق معادلات كل من لنكماير وفرندلش وتوث على نتائج الامتزاز لغرض ايجاد ميل المادة الممتزة تجاه غاز H_2S ومدى انتظام السطح. وظهرت المعلمات الدالة على عدم انتظام السطح وان الزيولايت 5A كان الاعلى من بين النماذج الاخرى لا منتظما.