

## **Preparation of zeolite types 4A and 5A from Iraqi kaolin to remove sulfur and water from LPG**

**تحضير زيولايت نوع 4A و 5A من الكاؤولين العراقي لازالة الكبريت والماء من الغاز النفطي المسال**

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### **Abstract:-**

In this work the 4A and 5A types of zeolite were prepared from locally available materials and characterized by X-ray diffraction and atomic absorption techniques .The prepared zeolites were used to remove H<sub>2</sub>S and to dry water from liquefied petroleum gas LPG using adsorption technique. The adsorption was investigated using flow method which was performed in laboratory adsorption unit made from stainless steel. The results obtained from column adsorption process was fitted with the most commonly used model (Adams-Bohart model) to describe adsorption data. Zeolite 5A was the most effective adsorbent for H<sub>2</sub>S (90% removal) compared with standard zeolites used in the North Oil Company (Beji- Iraq).

### **الخلاصة**

تم خلال هذا البحث تحضير الزيولايت نوع 4A ( و 5A ) من مواد متوفرة محليا (الكاؤولين ) . تم تشخيص الزيولايت المحضرين بتقنيتي حيود الاشعة السينية والامتصاص الذري . استخدم الزيولايت بنوعيه لازالة الكبريت من الغاز النفطي المسال (LPG) وتجفيفه من الماء باستخدام تقنية الامتزاز . استخدمت طريقة الجريان للتحري عن عملية الامتزاز والتي اجريت بمنظومة امتزاز مختبرية مصنوعة من الحديد المقاوم للصدأ . تم تحليل النتائج العملية بمطابقتها مع اكثر المعادلات شهرة وهي معادلة Adams-Bohart . وقد اظهر الزيولايت نوع 5A اعلى كفاءة في ذلك حيث وصلت النسبة المئوية للازالة بحدود 90% وتمت مقارنته مع زيولايت قياسي (5As) مستخدم في شركة نفط الشمال (بيجي- العراق).

### **Introduction:-**

Zeolites are materials widely known for their ion exchange properties [1]. They are good examples of how the structure at an atomic scale can determine macroscopic properties, and how a detailed knowledge of structure can favor performance prediction. The Si/Al framework ratio of the zeolite determines its maximum ion exchange capacity; however the real capacity may be lower if a proportion of the charge compensation cations are inaccessible for the exchanging ion [2]. The aperture dimensions control exchanging ion entry into zeolite cavities, and may be a limiting factor during the ion exchange process [3].

Liquefied petroleum gas (LPG) is the fuel of choice for inhabited areas and for leisure applications. LPG consists of a mixture of propane and butane in various ratios depending on country and season [4]. Natural gas and LPG contain sulfur components, either naturally occurring, or added deliberately as odorant to odorize the otherwise odorless gas. Sulfur levels in LPG can be much higher when compared to natural gas [5].

The sulfur removal task for LPG is more challenging than it is for natural gas. Propane, butane and heavier hydrocarbons are potential competitors for the sulfur compounds for adsorption sites, decreasing the adsorption capacity. Impurities such as H<sub>2</sub>S in light hydrocarbons usually cause hazardous odors, corrosion problems and air pollution; therefore elimination of these impurities is

very important [6]. Zeolite adsorbents are used to dry the natural gas or liquefied petroleum gas to prevent freezing and corrosion in pipeline, remove sulfur compounds from the natural gas or liquefied petroleum gas to prevent corrosion in burners, remove compounds that are obnoxious or toxic such as the odoriferous hydrogen sulfide and mercaptans that form sulfur dioxide pollutants when burned for home cooking and heating [7].

In the present work, two types of zeolite were prepared and characterized using atomic absorption and x-ray techniques. The prepared zeolite were used to remove H<sub>2</sub>S and H<sub>2</sub>O from LPG using adsorption method. The adsorption data were analyzed according to Adams-Bohart equation.

### Experimental

#### Preparation of zeolite type 4A and 5A

The raw kaolin from Doukhla site in the west part of Iraq, was calcined at 550 °C for about 3 hours to convert it to metakaolin. The metakaolin was treated with sodium hydroxide solution (8M) in a ratio of 1:2 and refluxed heated to 95 °C with a continuous vigorous stirring for 8 hours in order to insert the sodium ion in the metakaolin structure where the following reaction occurs :-

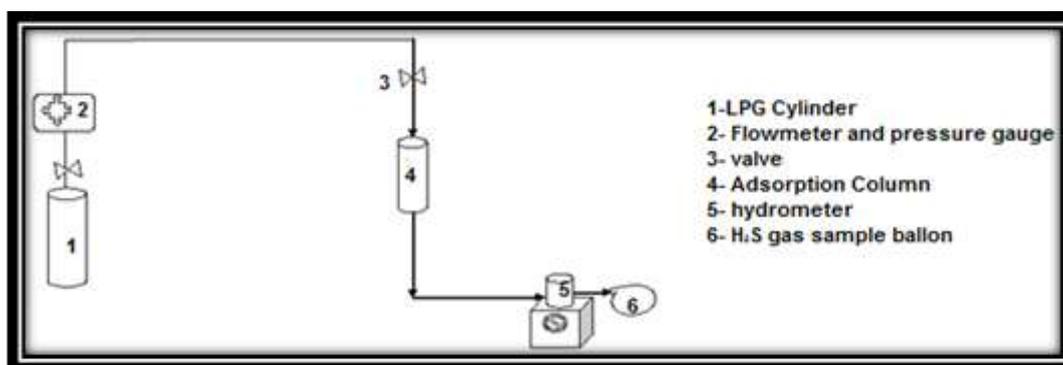


5A was prepared from 4A type using (1M) CaCl<sub>2</sub> solution.[8] The treated kaolin slurry was left to settle for two hours and washed four times with distilled water to remove the excess sodium hydroxide. Then it was filtered by any suitable mean and dried in an oven at 110 °C for four hours.[9]

The obtained zeolite powder was crushed milled and a suitable grain size was mixed with 20% raw kaolin as a binder and 40% water to make the paste that can be easily dealt with and passed through a laboratory extruder to obtain extrudates, then dried at 110 °C for 1.5 hours. Finally the formulated zeolite was calcined for about 3 hours at 550°C.[10]

### Adsorption Unit

The laboratory adsorption unit was designed and installed by the Petroleum Research and Development Center /catalyst and zeolite research department. This unit was used to examine the performance of the prepared zeolites (4A and 5A) and standard zeolite( 5As ). Figure (1) shows the block diagram of the unit.



**Figure (1) The laboratory adsorption unit**

The laboratory unit consists of flow gas control board, adsorption column, and hygrometer. The gas control board contains the flow meter to control the gas flow rate and pressure gauge to control pressure inside the adsorption column.

The adsorption column made from stainless steel with a diameter of 2.5 cm and length of 37.5 cm. Gauze plate of fine mesh was placed in the lower end of the column. The prepared zeolite were placed inside the column and a layer of plastic cylinders was placed below the packed zeolite to keep a good distribution of the gas inside the column. The hygrometer device (Shaw, ALPHA moisture system, England) was used to measure the humidity of the feed gas and outlet gas at different intervals during adsorption process. A gas cylinder was used to provide the LPG feed to the adsorption unit. 50 grams of zeolite granules were weighed in a ceramic crucible, dried at 250 °C for 3 hours, and kept to the next day in a desiccator containing silica gel to prevent the humidification of the zeolite.

### RESULTS AND DISCUSSION

The amount of major components of the zeolite 5A present in the structure were found by atomic absorption spectroscopy. The results are listed in Table (1).

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

Constituent	Weight % kaolin	Weight % 4A	Weight % 5A
SiO <sub>2</sub>	53.08	44.21	40.05
Al <sub>2</sub> O <sub>3</sub>	33.6	26.68	26.93
Na <sub>2</sub> O	0.28	11.90	0.098
K <sub>2</sub> O	0.49	0.48	0.45
MgO	0.32	0.30	0.29
CaO	0.29	0.28	10.89
TiO <sub>2</sub>	1.02	1.00	0.97
Fe <sub>2</sub> O <sub>3</sub>	1.24	1.15	1.14
L.O.I	7.22	13.06	14.92

Comparing the above data of the components, for kaolin and zeolite especially sodium, calcium, showed that the ion exchange process was successful. The x-ray diffraction patterns of the prepared types 4A & 5A zeolites are shown in Figures (2 and 3). The pattern is just a plot of the X-ray intensity diffracted from the sample versus the diffraction angle (Bragg's angle, 2θ).

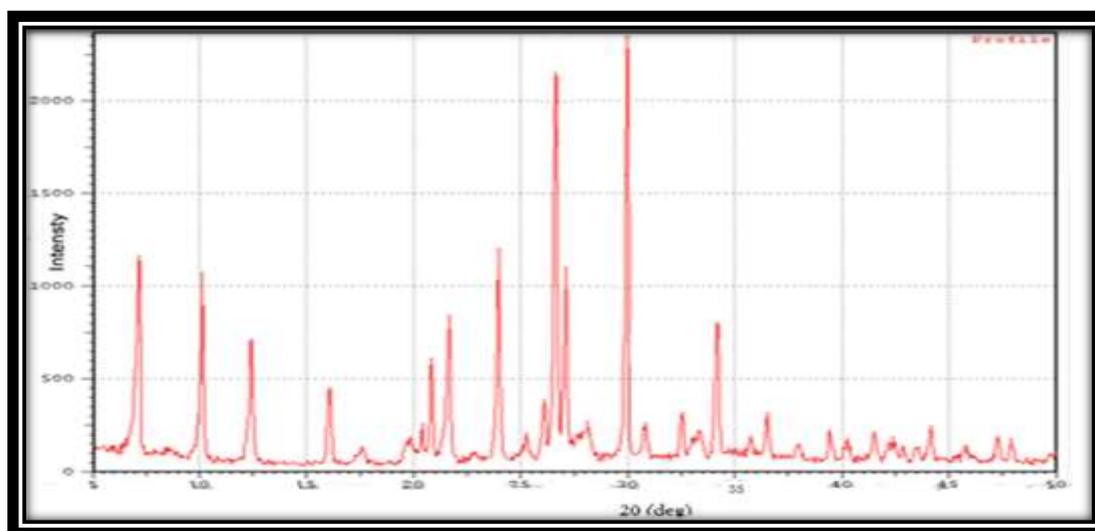
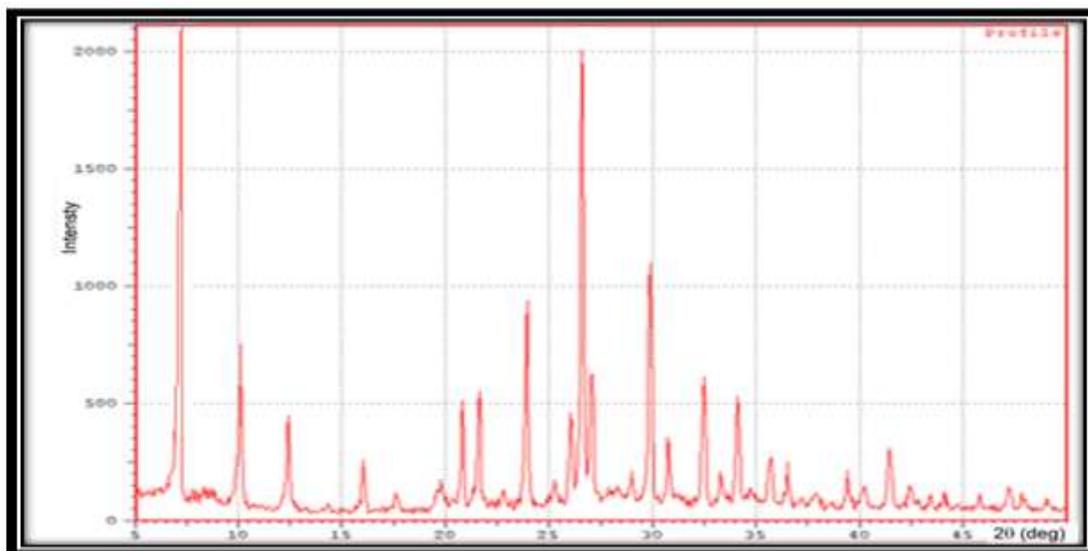


Figure (2) X-ray diffraction of the prepared Zeolite 4A



**Figure (3) X-ray diffraction of the prepared Zeolite 5A**

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 [11].

The X-ray diffraction of the prepared zeolite type 4A which has a small peak at the angle ( $2\theta = 10^\circ$ ) with intensity of 1120 and at ( $2\theta = 27^\circ$ ) with intensity of 2420, but the characteristic peaks for this type are at the angle ( $2\theta = 30^\circ$ ) with intensity of 3240 and at angle ( $2\theta = 34^\circ$ ) with intensity of 820.

X-ray diffraction diagrams showed that zeolite type 5A has a high degree of crystallinity and contains amount of quartz. The characteristic peaks of the prepared zeolite type 5A are at the angle ( $2\theta = 7.3^\circ$ ) with intensity of 2500, at ( $2\theta = 26^\circ$ ) with intensity of 2000 and at ( $2\theta = 27^\circ$ ) with intensity of 850.

### **Physical Properties**

The physical properties such as Crushing strength, Bulk density, Real density and Porosity were determined and shown in Table (2).

**Table (2) Physical properties of the prepared 4A, 5A and 5As of zeolites**

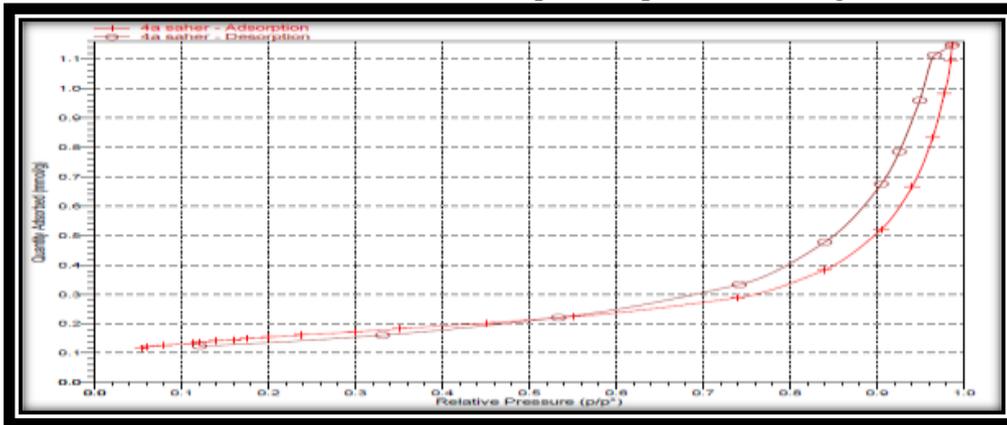
<b>Test</b>	<b>5A</b>	<b>4A</b>	<b>5As</b>
<b>Crushing Strength (N/mm)</b>	<b>23.630</b>	<b>21.48</b>	<b>25.116</b>
<b>Bulk density(g/cm<sup>3</sup>)</b>	<b>0.693</b>	<b>0.58</b>	<b>0.776</b>
<b>Real density(g/cm<sup>3</sup>)</b>	<b>2.339</b>	<b>2.22</b>	<b>2.242</b>
<b>Porosity (%)</b>	<b>67.550</b>	<b>63.12</b>	<b>65.410</b>

From this table, the results indicate that the values of the four physical properties of prepared samples were close to the values of standard sample.

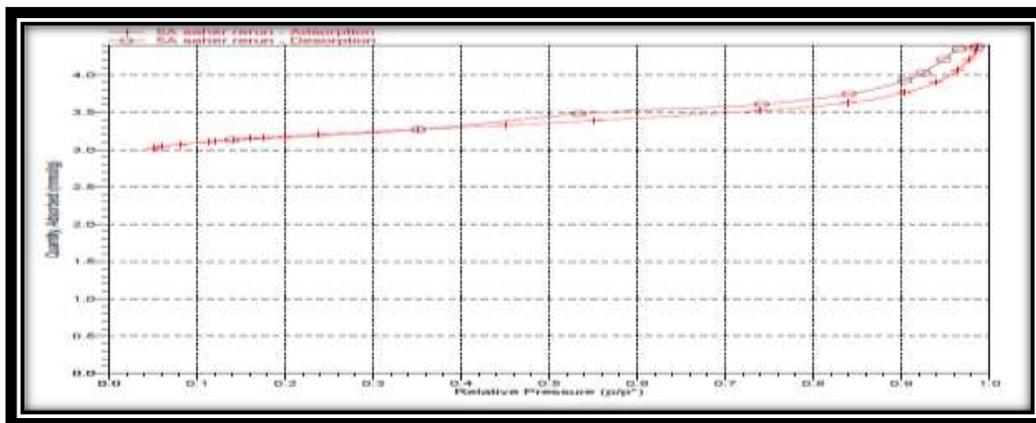
**N<sub>2</sub> Adsorption –Desorption Analysis**

The successful use of the zeolite types as adsorbents or catalysts is impossible without detailed study of their porous structures as well as adsorption properties in regard to adsorbates of different types. The zeolite has two types of porosity, the primary porosity (or microporosity) which caused by the specific crystal building of zeolite mineral grains. The second porosity is connected with size of zeolite and other mineral grains presented by meso and macropores [12].

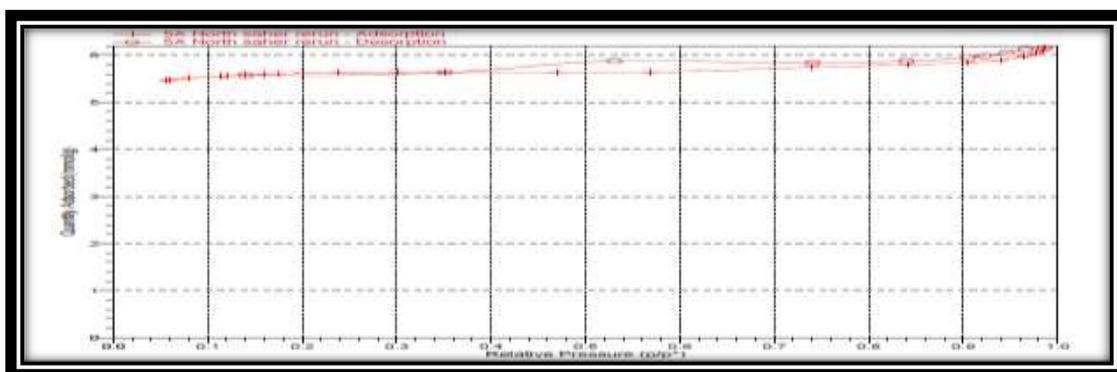
The samples of zeolite (4A, 5A) prepared and 5A standard were analyzed, the adsorption and desorption isotherms at 77 K obtained for these samples are presented in Figures ( 4,5 and 6).



**Figure (4) The N<sub>2</sub> adsorption – desorption isotherm of zeolite 4A**



**Figure (5) The N<sub>2</sub> adsorption - desorption isotherm of zeolite 5A**



**Figure (6) The N<sub>2</sub> adsorption -desorption isotherm of standard zeolite 5A**

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The shape of the 4A isotherm was type IV, while the shape of 5A and 5As isotherms were type I according to the classification of IUPAC. The shape of 5A isotherm indicates volumes the filling of micropores and the presence of mesopores, while the shape of 4A isotherm indicates the presence of mesopores only [13].

The shape of hysteresis loop of the 4A isotherm is type H<sub>3</sub> according to classification of IUPAC which is a characteristic of a sloping adsorption and desorption branches covering a large range of  $p/p^0$  with underlying type II isotherm. This interpret means that the pores of 4A zeolite is slit-like shape. The shape of hysteresis loop of the 5A and 5As isotherm are type H<sub>4</sub> which is a characteristic underlying type I isotherm with large range of the hysteresis loop. This indicates that the pores of 5A zeolite is slit-like shape too [13].

Table (3) shows the specific surface area and porosity parameters for the three samples.

Table (3) the surface area and porosity parameters for the three samples.

Sample	Surface area m <sup>2</sup> /g	Pore volume Single point. cm <sup>3</sup> /g	Avarage pore size Single point. A
4A	111.96	0.039	127.62
5A	285.420	0.151	27.26
5A <sub>s</sub>	300.59	0.211	22.15

The results in Table (3) showed that zeolite 4A gave unexpected low surface area which may be due to the block of the channel of the zeolite with nitrogen molecules. [14] The diameter of N<sub>2</sub> molecule (3.64A°) is comparable to the effective channel diameter of the 4A zeolite. The results of porosity parameters indicate that zeolite 5As has the highest value of pore volume and the sequence are as follows; 5As > 5A > 4A

Also, the results of pore size distribution showed that the pore size of the three samples ranged from < 20 A° to 500 A° which indicate that they have micro and mesopores with high percentage of mesopores in the case of 4A and high percentage of micropores in the case of 5A and 5As.

### **Adsorption of H<sub>2</sub>S and H<sub>2</sub>O**

The removal of H<sub>2</sub>S and H<sub>2</sub>O by the prepared zeolite 4A, and 5A was investigated using the continuous method (flow method) in order to test the practical applicability of the prepared zeolite.

During each run, samples were taken from the sample points at different minute intervals at the beginning of the experiment until the experiment was completed. The experimental time for each run was approximately four hours in order to assure the formation of a breakthrough curve [15]. The residual H<sub>2</sub>S and H<sub>2</sub>O in the samples were measured using Tutwiler method and Hygrometer respectively. The experiments were performed at 0.5 liter/minute flow rate, 12 cm bed height, and 204 and 450 ppm initial concentration for H<sub>2</sub>S and H<sub>2</sub>O respectively. All the experiments were carried out at room temperature (25 °C). The results obtained for H<sub>2</sub>S are reported in Table (4), while for H<sub>2</sub>O adsorption on zeolites (4A, 5A and 5As) are reported in Table (5).

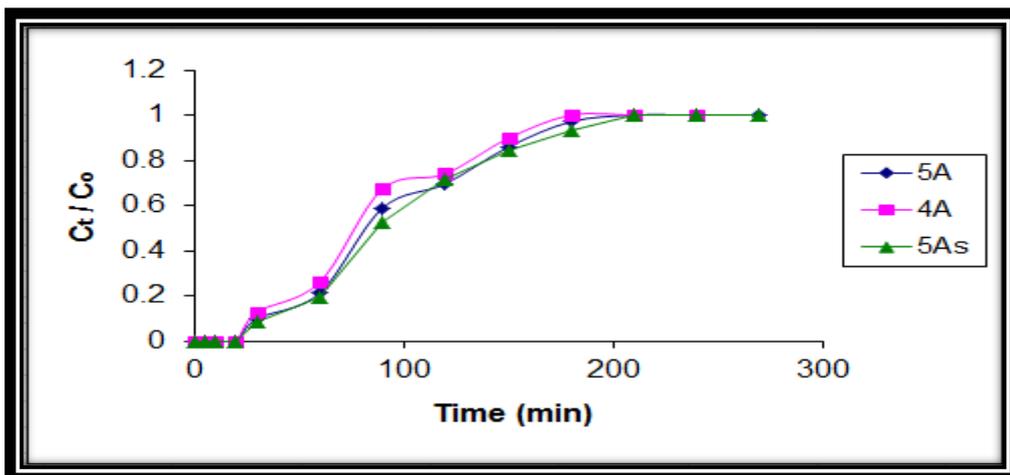
**Table (4) The variation of residual H<sub>2</sub>S concentration in the LPG sample with time during the adsorption on zeolite 4A , 5A and 5A standard**

Time (min)	5A			4A			5As		
	H <sub>2</sub> S C <sub>t</sub> (ppm)	H <sub>2</sub> S C <sub>t</sub> /C <sub>o</sub>	Ln C <sub>t</sub> /C <sub>o</sub>	H <sub>2</sub> S C <sub>t</sub> (ppm)	H <sub>2</sub> S C <sub>t</sub> /C <sub>o</sub>	ln C <sub>t</sub> /C <sub>o</sub>	H <sub>2</sub> S C <sub>t</sub> (ppm)	H <sub>2</sub> S C <sub>t</sub> /C <sub>o</sub>	ln C <sub>t</sub> /C <sub>o</sub>
0	0.0	0.000	---	0.0	0.000	---	0.0	0.000	----
5	0.0	0.000	----	0.0	0.000	----	0.0	0.000	----
10	0.0	0.000	----	0.0	0.000	----	0.0	0.000	----
20	0.0	0.000	----	0.0	0.000	---	0.0	0.000	----
30	20	0.098	-2.322	26	0.127	-2.060	18	0.088	-2.428
60	43	0.211	-1.557	53	0.259	-1.348	39	0.191	-1.655
90	120	0.588	-0.531	137	0.672	-0.398	107	0.525	-0.645
120	142	0.696	-0.362	151	0.740	-0.301	146	0.716	-0.335
150	175	0.858	-0.153	183	0.897	-0.108	172	0.843	-0.171
180	198	0.971	-0.029	204	1.000	0.000	190	0.930	-0.071
210	204	1.000	0.000	204	1.000	0.000	204	1.000	0.000
240	204	1.000	0.000	204	1.000	0.000	204	1.000	0.000
270	204	1.000	0.000				204	1.000	0.000

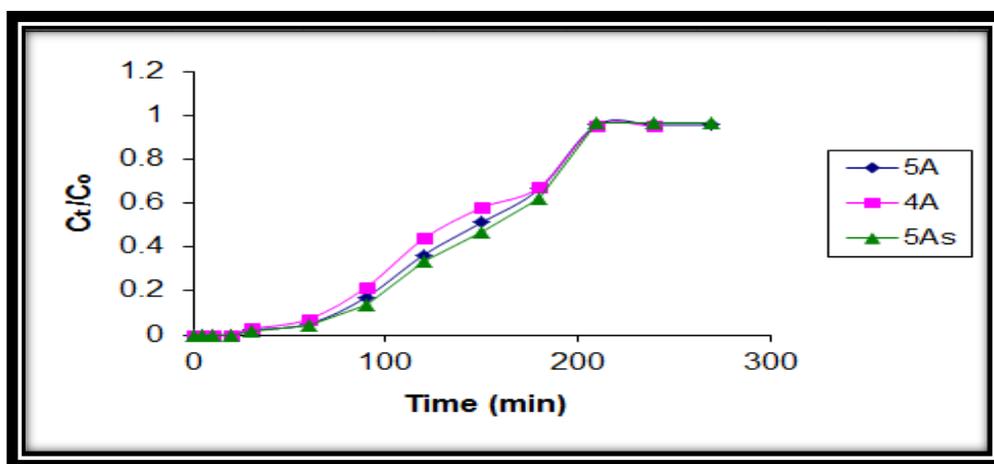
**Table (5) The variation of residual H<sub>2</sub>O concentration in the LPG sample with time during the adsorption on zeolite 4A , 5A and 5A standard**

Time (min)	5A			4A			5As		
	H <sub>2</sub> O C <sub>t</sub> (ppm)	H <sub>2</sub> O C <sub>t</sub> /C <sub>o</sub>	ln C <sub>t</sub> /C <sub>o</sub>	H <sub>2</sub> O C <sub>t</sub> (ppm)	H <sub>2</sub> O C <sub>t</sub> /C <sub>o</sub>	ln C <sub>t</sub> /C <sub>o</sub>	H <sub>2</sub> O C <sub>t</sub> (ppm)	H <sub>2</sub> O C <sub>t</sub> /C <sub>o</sub>	ln C <sub>t</sub> /C <sub>o</sub>
0	0.0	0.000	---	0.0	0.000	---	0.000	0.000	----
5	0.0	0.000	----	0.0	0.000	----	0.000	0.000	----
10	0.0	0.000	----	0.0	0.000	---	0.000	0.000	----
20	0.0	0.000	----	0.0	0.000	----	0.000	0.000	----
30	10	0.022	-3.807	12.0	0.027	-3.624	8	0.018	-4.029
60	22	0.049	-3.018	32.0	0.071	-2.644	18	0.040	-3.219
90	77	0.171	-1.765	97.0	0.216	-1.535	62	0.138	-1.982
120	164	0.364	-1.009	197.0	0.438	-0.826	151	0.336	-1.092
150	230	0.511	-0.671	260.0	0.578	-0.549	210	0.467	-0.762
180	299	0.664	-0.409	302.0	0.671	-0.399	278	0.618	-0.482
210	430	0.956	-0.045	427.5	0.950	-0.051	435	0.967	-0.034
240	430	0.956	-0.045	427.5	0.950	-0.051	435	0.967	-0.034
270	430	0.956	-0.045				435	0.967	-0.034

The behaviour of the two types of zeolite in a fixed –bed column was studied to determine the breakthrough point. The breakthrough curves were constructed as C<sub>t</sub>/ C<sub>o</sub> versus time and the curves for adsorption of H<sub>2</sub>S on the two zeolites are shown in Figure (7), while for adsorption of H<sub>2</sub>O on the same zeolites are shown in Figure (8).



**Figure (7) The breakthrough curves for H<sub>2</sub>S adsorption on 4A , 5A and 5As standard zeolites**



**Figure (8) The breakthrough curves for H<sub>2</sub>O adsorption on 4A, 5A and 5As standard zeolites**

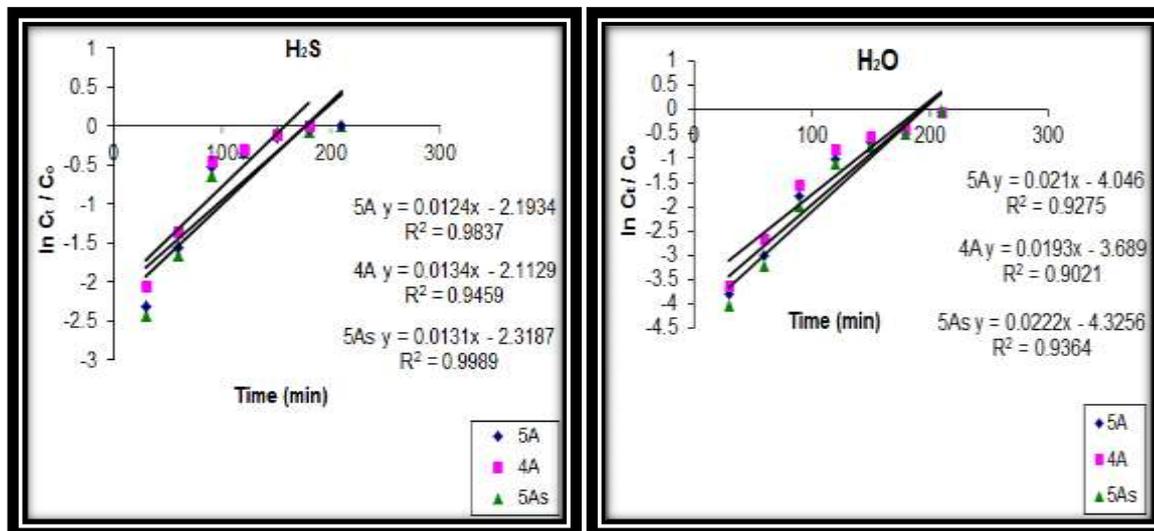
The breakthrough time for the column operation was defined as the time when effluent concentration of H<sub>2</sub>S or H<sub>2</sub>O began to increase higher than zero. It can be seen from Figures (7) and (8) that there was a period of time when the residual concentration of H<sub>2</sub>S and H<sub>2</sub>O remained zero and then the residual concentration started to increase. The breakthrough time of H<sub>2</sub>S and H<sub>2</sub>O for 4A, 5A and 5As was 30 min.

The experimental results obtained from column adsorption process were fitted with the most commonly used model (Adams- Bohart Model) to describe adsorption data [16]. They established the fundamental equation that describes the relationship between C<sub>t</sub>, C<sub>o</sub> and time for the initial part of the breakthrough curve in an open system. This equation is as follows:-

$$\ln \frac{C_t}{C_o} = K_{AB} C_o t - K_{AB} N_o \frac{H}{U} \quad (3-14)$$

where C<sub>t</sub> and C<sub>o</sub> are the outlet and inlet adsorbate concentration (mg/l) respectively, K<sub>AB</sub> is the rate kinetic constant (l mg<sup>-1</sup> min<sup>-1</sup>), N<sub>o</sub> is the adsorption capacity (mg/l) of the bed, H is the bed height and U is the linear flow rate obtained from dividing the flow rate by the column section area.

From this equation, values describing the characteristic operational parameters,  $K_{AB}$  and  $N_o$  of the column can be determined from the slope and intercept by the plot of  $\ln C_t / C_o$  versus time at a given flow rate and bed height. Adams- Bohart plots for the removal of  $H_2S$  and  $H_2O$  onto the two zeolite types are presented in Figure (9).



**Figure (9) The plot of  $\ln C_t / C_o$  for  $H_2S$  and  $H_2O$  versus time for the three types of zeolites**

The data obtained from linear plot of Adams and Bohart equation for the two adsorbate on the three adsorbent are given in Table (6).

**Table (6). The parameters of Adams – Bohart model for adsorption of  $H_2S$  and  $H_2O$  on the three types of zeolite A**

Sample	$H_2S$			$H_2O$		
	$K_{AB} \cdot 10^4$ L.mg <sup>-1</sup> .min <sup>-1</sup>	$N_o$ mg /L	$R^2$	$K_{AB} \cdot 10^5$ L.mg <sup>-1</sup> .min <sup>-1</sup>	$N_o$ mg /L	$R^2$
4A	1.019	268.38	0.926	5.911	756.67	0.959
5A	1.127	275.38	0.940	6.133	783.09	0.967
5As	1.176	278.20	0.965	6.444	791.59	0.971

The high correlation coefficients indicate that the experimental data for the adsorption of  $H_2S$  and  $H_2O$  on all adsorbents used in the present work fit well Adams- Bohart model. It is also understood from Table (5) that the higher adsorption capacity was obtained on zeolite 5A.

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