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Microwave-Assisted Synthesis of Zeolites A From Iraqi Cheap Raw Materials as Adsorbents for H_2S Gas

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Abstract:-In the present work , Iraqi Kaolin were used as an alternative cheap material for the synthesis of three types of zeolite (3A, 4A and 5A) by using microwave heating techniques. The prepared zeolite powders were shaped in cylindrical rods form by extrusion with 1 mm diameter and 3 mm height which were dried at 110°C for 1hour and calcinated at 550°C for 3 hours.Zeolites are appropriate adsorbents e.g. in this work they were used for H_2S gas adsorption. The adsorption was performed in a static form and constant volume stainless steel system. The results obtained indicated that zeolite type (5A) has the higher adsorption capacity and the sequence of the three zeolites is : 5A> 4A> 3A. The equilibrium data fit with Langmuir, Freundlich and Toth models of adsorption and the linear regression coefficient R^2 was used to elucidate the best fitting isotherm model. Kinetics of the adsorption was also investigated over a wide range of pressures and temperatures.

Key words: Microwave-Assisted , Zeolites , Iraqi , Cheap Raw Materials ,Adsorbents for H_2S Gas

Introduction

Kaolin is one of the most versatile industrial materials with the principal mineral of kaolinte having the chemical formula of $Al_2Si_2O_3(OH)_4$ and consisting of a single sheet of silica tetrahedral and single sheet of alumina octahedral both of which combine to form the kaolin unite layer.(1) It can be conveniently used as an ideal raw material for the synthesis of zeolite especially for zeolite A.(2)

Zeolite are microporous crystalline hydrated aluminosilicates, which can structurally be considered as inorganic polymers bulit from an infinitely extending three – dimensional network of tetrahedral TO_4 units, where T is Si^{+4} or Al^{+3} ,each aluminum ion that is present in the zeolite framework yields a net negative charge which is balanced by an extra framework cation, usually from group IA or IIA.(3)

Microwave heating techniques are now widely used in many application of chemical researchs including organic / inorganic synthesis due to their fast and energy efficient techniques to avoid competitive reactions in many known processes.(4)

Microwave heating represents a relatively new approach in zeolite synthesis .(5) The first attempts with microwave heating have been made for the most typical representative of an alumino-silicate type of zeolite, the zeolite A, by Jansen et al.(6)They were able to grow zeolite crystal within a reduced crystallization time, but with no significant improvement of the crystal size and quality.(7)

In this work , we report the preparation of zeolite 3A, 4A and 5A powder from Iraqi kaolin by microwave technique and their extrudates were used for studying the adsorption capacity of H_2S gas.

Experimental

Preparation of Zeolite : The raw kaolinite from Doukhla site in the west part of Iraq, was calcinated at 550 °C for about 3 hours to convert it to metakaolinite.

The metakaolinite was treated with sodium hydroxide solution (8M) with a ratio of 1:2 and refluxed in microwave with power 200 for 2hours with a continuous vigorous stirring in order to insert the sodium ion in the metakaolinite structure . 3A and 5A were prepared from 4A type using 1M of each KCl and $CaCl_2$ solution respectively.

The treated kaolin slurry was left to settle for two hours and washed four times with distilled water to remove the excess alkaline hydroxide . Then it was filtered by any suitable mean and dried in an oven at 110 °C for 4 hours.(8)

The obtained zeolite powder was crushed milled and a suitable grain size 150 mesh 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 hour. Finally the formulated zeolite was calcined for about 3 hours at 550 °C. (9)

-The Adsorption System

The system used in this work was constructed from stainless steel and presented earlier in the previous paper .[10] It consisted of a number of specialized parts, involving vacuum apparatus ,adsorption tube , measuring part, and pressure and temperature control units . The adsorption tube was constructed of Pyrex glass tubing , 40 cm in length and 1cm in internal diameter. An electrothermal heating tape (type Heat –by –the yard:Electrothermal engineering Limited, London) was used for heating the reaction system. The system was in static form and the H_2S vapor could be brought into contact with the adsorbent fixed as a bed in the adsorption tube.

Three grams of the adsorbent was transferred into the adsorption tube, then dried under vacuum of 10^{-2} mbar for at least 10 hours at 250 °C. After establishing a vacuum of 10^{-2} mbar in the system , the reactor was cooled to the temperature at which the experiment started .The experiment was done by dosing the amount of H_2S supply to the measuring section in small doses and allowed to contact with zeolite specimen .The uptake of H_2S was followed at each temperature until its pressure remained virtually constant. The variation of pressure was measured continuously by pirani pressure gauge .

RESULTS AND DISCUSSION

The experimental data obtained from the adsorption of H_2S are listed in Table (1),and the adsorption isotherms are presented in Fig (1).

Table 1. The experimental data for the adsorption of H2S gas on the three zeolite

	3A			4A			5A		
T(K)	ΔP mbar	P_{eq} mbar	n_{ad} µmol/g	ΔP Mbar	P_{eq} Mbar	n_{ad} µmol/g	ΔP mbar	P_{eq} mbar	n_{ad} µmol/g
268	0.05	0.21	0.169	0.08	0.11	0.358	0.1	0.1	0.409
	0.15	0.25	0.507	0.21	0.14	1.147	0.18	0.13	1.296
	0.42	0.34	2.097	0.47	0.23	2.744	0.39	0.21	3.397
	0.92	0.58	5.209	1.06	0.42	6.758	0.98	0.44	8.136
	1.7	1.9	13.435	2.8	1.2	16.177	1.8	1.6	18.864
	2.2	5.6	23.850	4.1	2.9	28.393	1.9	3.5	37.19
298	0.07	0.15	0.243	0.1	0.13	0.313	0.09	0.11	0.332
	0.21	0.19	0.772	0.24	0.16	0.981	0.19	0.14	1.032
	0.43	0.29	2.165	0.44	0.28	2.457	0.45	0.25	2.689
	0.96	0.54	4.907	0.88	0.62	5.797	0.94	0.46	6.152
	2.2	1.3	8.649	1.9	1.6	9.362	2.2	1.1	8.105
	3.0	3.0	12.221	1.7	3.7	16.082	2.6	3.2	16.159
328	0.09	0.13	0.185	0.05	0.20	0.298	30.1	0.13	0.465
	0.18	0.19	0.682	0.15	0.27	0.833	0.24	0.14	1.679
	0.45	0.4	1.352	0.4	0.40	2.899	0.56	0.18	7.791
	0.65	0.85	4.477	0.78	0.72	5.367	1.15	0.35	8.790
	0.6	5.6	6.436	1.5	1.9	9.114	2.4	1.6	10.851
	0.4	5.8	7.742	0.4	6.8	14.852	0.2	6.4	15.834

Fig(1) shows that the isotherms for the three type (3A, 4A, 5A) are of type (L or I) indicating a high energy of adsorption and characteristic of adsorbent which contains microporosity.

The temperature effect on the adsorption was carried at -5 ,25 and 55 °C .The results (Table 1 and Fig 1) indicate that when the temperature increased the amount of H_2S 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.

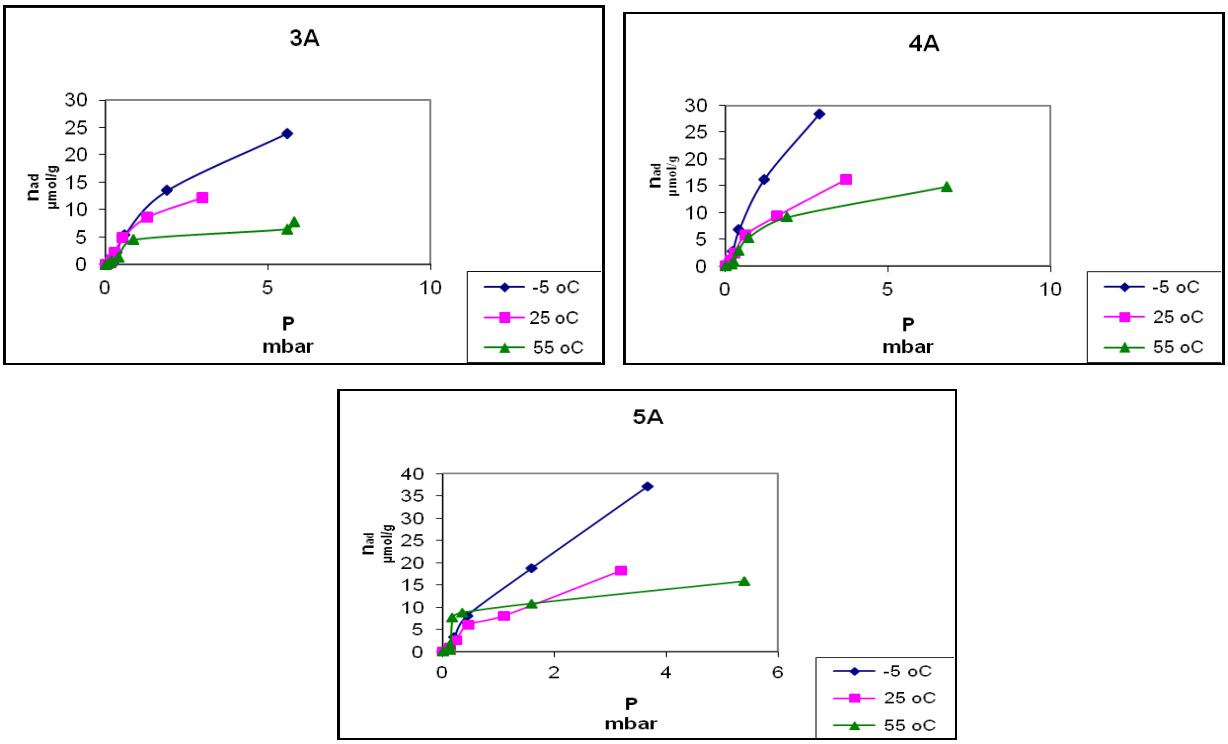

Fig. 1. The adsorption isotherms of the three zeolite at temperatures (-5, 25, 55 ºC)

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:-

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

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

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

Where n_{ad}(µmol/g) is the amount of H_2S adsorbed and P_{eq} (mbar) is the equilibrium pressure of H_2S gas .n_m and b are the Langmuir constants which means the maximum adsorption capacity or the theoretical monolayer saturation capacity and the adsorption affinity respectively. K_f and n are the freundlich constants which corresponding to adsorption capacity and intensity of adsorption respectively .n_T , k_T and t are the Toth constant which corresponding to adsorption capacity, adsorption affinity and parameter describing energetic heterogeneity of the adsorbent surface, respectively.

These isotherms are fitted employing the non – Linear fitting method using the software (Statistica Module Switcer) .Fig(2) presents how well the equations fit the data for H_2S –adsorbent system at (25) °C. The values of the constants obtained from the three equation are listed in the Table (3) along with R^2 values.

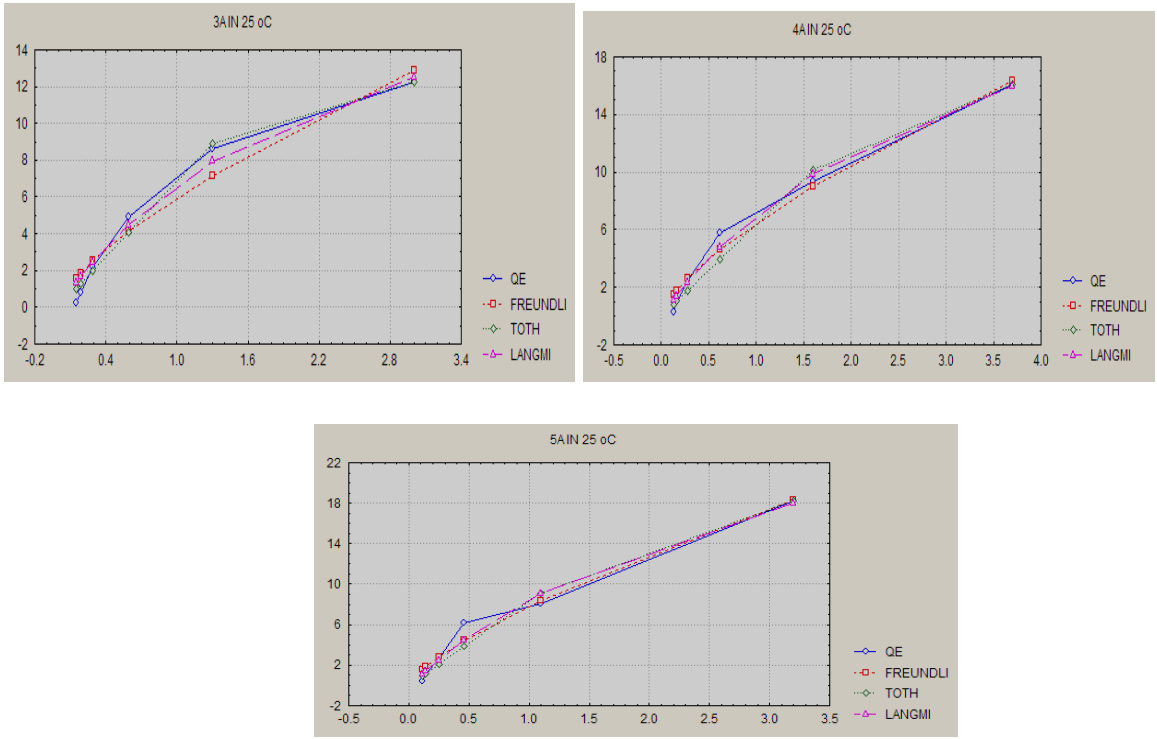

Fig. 2 .Comparison of various isotherm equation for the adsorption on three zeolite type A at 25 ºC

Table 2. Langmiur ,Freundlich and Toth constants for the adsorption of H_2S on the three zeolite

T	Sample	Langmiur			Freundlich			Toth			
		n_m	B	R^2	Kf	1/n	R^2	n_t	t	Kt	R^2
268	3A	46.303	0.194	0.9917	6.804	0.746	0.9823	43.337	23.850	0.496	0.9947
	4A	71.293	0.131	0.9962	12.313	0.808	0.9914	157.426	28.393	0.478	0.9974
	5A	135.074	0.108	0.9967	12.904	0.845	0.9970	53.675	37.194	0.330	0.9953
298	3A	22.258	0.428	0.9874	5.976	0.7002	0.9718	89.315	12.221	0.561	0.9923
	4A	29.920	0.309	0.9940	6.492	0.706	0.9898	89.631	16.082	0.395	0.9867
	5A	37.128	0.296	0.9893	7.834	0.729	0.9886	119.064	18.220	0.457	0.9837
328	3A	8.858	0.749	0.9714	2.995	0.507	0.949	50.341	7.089	0.679	0.9844
	4A	20.517	0.399	0.9886	5.149	0.573	0.9674	1.637	16.465	0.407	0.9906
	5A	16.193	0.2128	0.9009	8.655	0.345	0.8732	80.167	18.343	0.1869	0.8905

The affinity constants (b , K_f and K_t) are a measure of how strong an adsorbate molecule is attracted onto surface, the highest values for H_2S adsorption are obtained for the adsorption on (3A) and the adsorbents may be arranged according to b, K_f and K_t values as 3A >4A >5A. The result of K_f is different because the freundlich equation is applicable in the range of pressure is not wide .Therefore ,it is generally valid in the narrow range of the adsorption data. [13]

The parameters (1/n & t) characterize the system heterogeneity and the lower the parameter, the more heterogeneous is the system .According to table (2) , (3A) has the lower value of t 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 & n_t) belongs to 5A and the order is changed as follows 5A> 4A> 3A.

Among the tested three equations, the better and perfect representation of the experimental results of the adsorption isotherms is obtained using the Toth model ,although the Langmuir and freundlich equations provide a reasonable fit ,Table (2) and Fig(3).

Reaction Kinetics

Kinetic of the interaction between the H_2S gas and the three types of zeolite was studied by measuring the variation of the pressure of H_2S gas (reactant) , in the range (2×10^{-1} - 7×10^{0} mbar) with time at the constant temperature in the range (-5 – 55 $^{\circ}$C) .

A check of the pressure dependence (the order) value was made by plotting the logarithm of H_2S pressure (lnP_{H2S}) at a constant temperature as a function of time for different zeolite .Typical such plots are indicated in Fig (3) .Also, the plotting of 1/p versus time was checked and presented in Fig (4) .

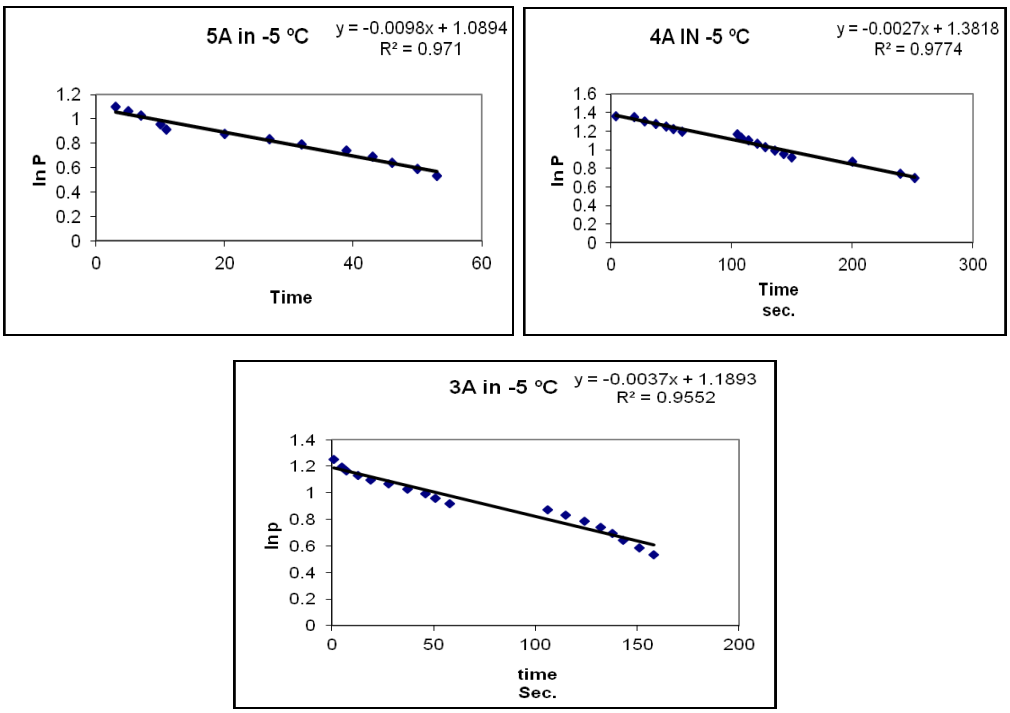

Fig. 3. First order plot for adsorption of H_2S gas on the three zeolites

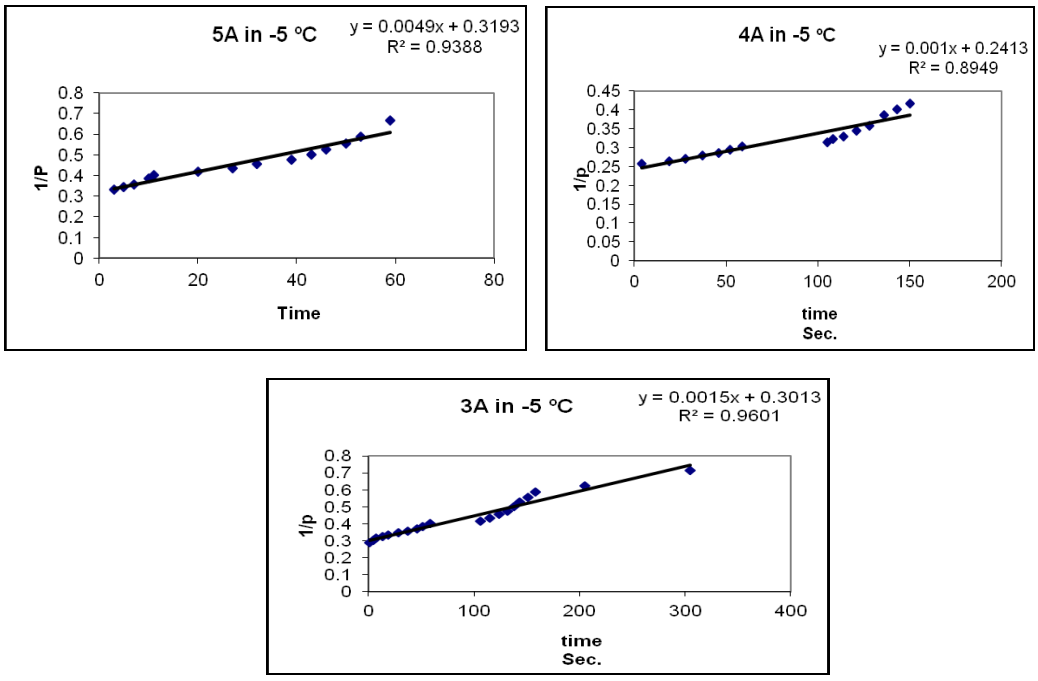

Fig. 4. Second order plots for adsorption of H2S gas on the three zeolites

The plots reveal that the first – order kinetics with respect to H_2S gas is the best fit model for the adsorption of H_2S onto the three zeolites as the correlation coefficient R^2 for first order is higher than R^2 for second –order .Also, the kinetic of interaction was studied by calculating the amount of H_2S gas adsorbed (product) and applying the following equations:-

The pseudo first order reaction is described by[11] :-$\ln (n_{ad,eq} - n_{ad,t}) = \ln n_{ad,eq} - k_1 t$

where $n_{ad,eq}$ and $n_{ad,t}$ are respectively the amount of H_2S (µmol/g) adsorbed on zeolite at equilibrium and at time t, k_1 is the rate constant (s^{-1}) .

The equation of pseudo second –order reaction has the following form[12]:-

$$t/n_{ad,t} = 1/k_2 n^2_{ad,eq} + t/q_{ad,eq}$$

Where k_2 is the equilibrium rate constant of pseudo second-order adsorption (gμmol^{-1}s^{-1}) .

The straight line plots of pseudo first and second order have been tested Fig(5) and (6) and the rate parameters obtained from the slope and intercept are listed in Table (3).

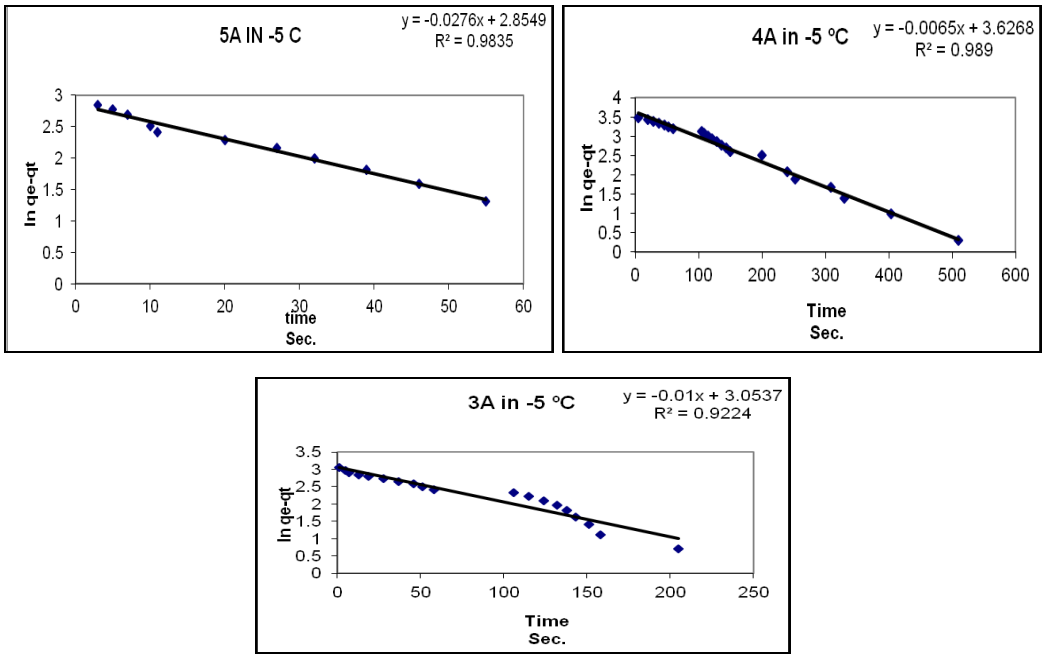

Fig. 5. pseudo first- order plots for adsorption of H_2S gas on the three zeolites

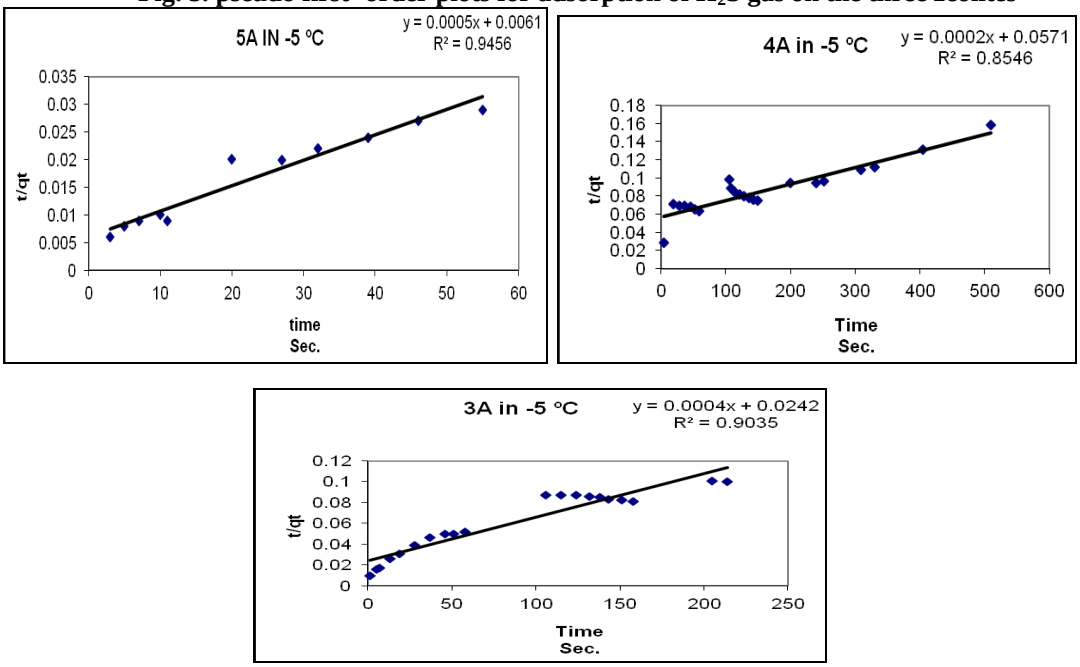

Fig. 6 . pseudo second- order plots for adsorption of H2S gas on the three zeolites

Table 3. Kinetics parameters for the adsorption of H_2S gas on the three type of zeolite.

Sample	$n_{ad,eq}$ (exp)	Pseudo first –order			Pseudo second -order			Intrapartical	
		$n_{ad,eq}$	k_1	R^2	$n_{ad,eq}$	k_1	R^2	K_D	R^2
5A	37.194	17.37	0.01	0.983	50.00	0.0819	0.946	1.361	0.877
4A	28.399	37.59	0.0065	0.989	70.71	0.0035	0.855	1.605	0.938
3A	23.85	21.194	0.0276	0.922	44.72	0.0165	0.904	1.424	0.979

The result of table (3) reveals that the first order is the best fit model for this system as the R^2 for first order is higher than R^2 for second order.

The possibility of intraparticle diffusion as a rate limiting step was checked by using the equation :- [14]

$$n_{ad,t} = K_D\, t^{1/2}$$

Where K_D is the intraarticle diffusion rate constant .Fig(7) shows the plot of $n_{ad,t}$ versus $t^{1/2}$ and the values of K_D are given in table (3) .

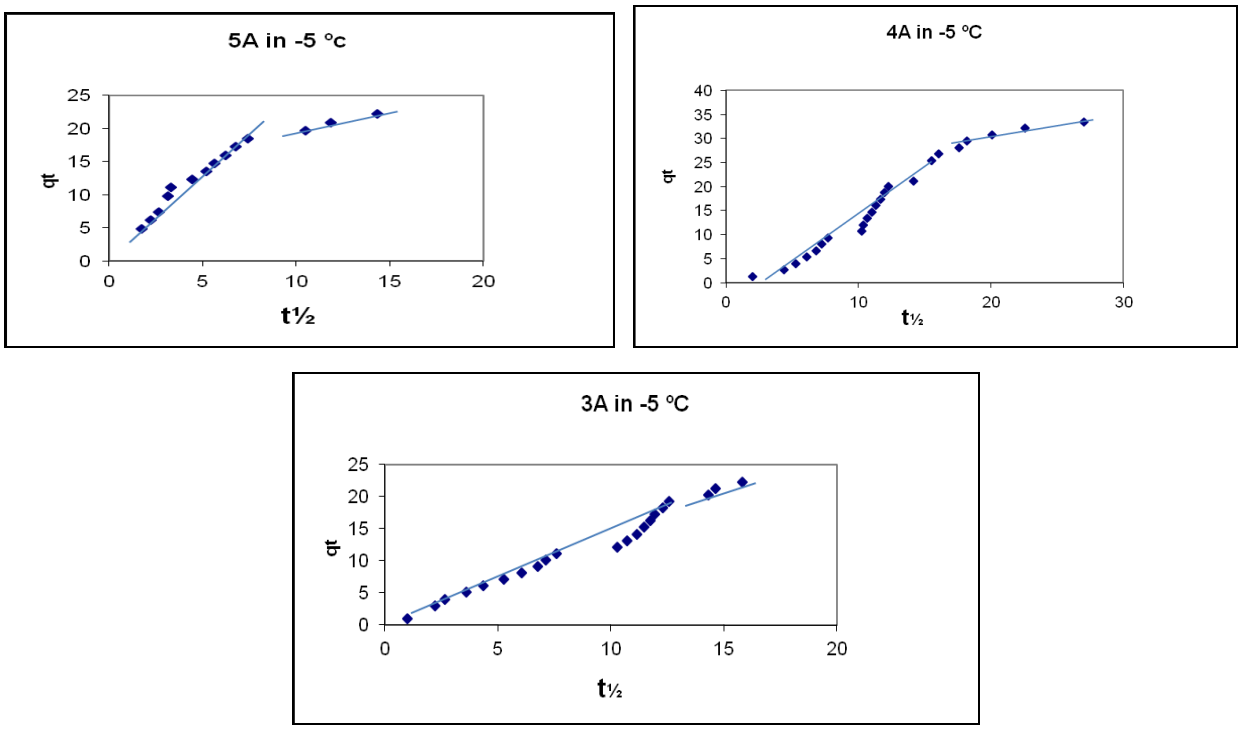

Fig. 7. Intrapartical diffusion kinetics for adsorption of H_2S gas on the three zeolites.

Fig (7) show deviation of lines from the origin which indicate that the intraparticle diffusion and surface adsorption are operating during the adsorption of H_2S .gas on the zeolites. The second linear region is the final equilibrium stage where intra-particle diffusion slows down due to the extremely low pressure of adsorbate

References

1- Adamis Z. and. Williams R.B.(2005). "Bentonie, kaolin, and selected clay minerals " report ,world health organization Geneva .

2- Chunfang Du and Huaming Y.(2010). ,J. American Mineralogist , vol.95 :741-746 ,

3- Valer ,N., (2002). Licentiate Thesis, Lulea University of Technology, Sweden.

4- Mathavee S. ,Erdogan G., Sujitra W. (2004)., J.Materials Chemistry and Physics ,83: 89-95.

5- Slangen P. M. ,Jansen J. C. and Van Bekkum , H.(1997)."The effect of aging on the microwave synthesis of zeolite NaA". J. Microporous Materials ,9:259-265.

6- Jsnsen, K., Arafat, A., Barakat, A. K. and Van Bekkum H.(1992). "Microwave techniques in zeolite synthesis". synthesis of microporous materials (Eds.M. L.Occelli,H. E. Robson).Van Nostrand Reinhold, Nw York I:507.

7- Stenzel CH., Brinkmann M., Muller J. , Schretten R. , Venot Y. and Wiesbeck W. , (2001). Journal of microwave power & Electromagnetic Energy Vol.36: 3-8.

8- Vian Y. Jarjees (2011). M.Sc Thesis, Baghdad University, College of Science for women.

9- Nada S. Ahmed, (2000). M.Sc Thesis, Baghdad University, College of Engineering.

10- Sameer H. Kareem ,Fouad A. AL-Saady and Naema A.Hilkmat,(2012). " Catalyze direct reaction of methanol with silicon" ,Journal of the Association of Arab Universities for Basic and Applied Sciences , ,In Press.

11- Onal Y ,Akmil –Basar C., and Sarici-Ozdemir (2007). "Investication kinetic mechanisms of adsorption malachite green outo activated carbon ", J.Hazared mater.,vol.146:194-203.

12- Baskaralingam P., Pulikesi M.,Elango D.,Ramamurthi V. and Sivanesan S. (2006). "Adsorption of acid dye onto oranobentonite" J.Hazard.Mater.,vol.13128:.138-144,

13- Duong D.Do , (1998). "Adsorption Analysis ;Equilibria and kinetics " ,ICP , London.

14- Muhammad A.M.,Sana I., and Muhammad N.A. (2010). "Removal of various dyes from aqueous media onto polymeric gels by adsorption process:Their kinetics and thermodynamics ", Desalination , 263:249-257 .

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استخدام المايكروويف في تحضير زيولايت كمادة مازة لغاز كبريتيد الهيدروجين من مواد خام عراقية رخيصة

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الخلاصة :-

في البحث الحالي تم استخدام الكاوؤلين العراقي كبديل رخيص لتحضير ثلاثة انواع من الزيولايت هي 3A, 4A, 5A باستخدام تقنية المايكروويف تم تشكيل مسحوق الزيولايت المحضر على شكل قطع اسطوانية بطول3 ملم وقطر1 ملم باستخدام باثقة مختبرية ، ثم جفف وكلسن بدرجة حرارة ١١٠ م° لمدة ساعة واحدة ودرجة ٥٥٠ م° لمدة ثلاث ساعات على التوالي . يعتبر الزيولايت كمادة مازة مناسبة حيث استخدم في هذا البحث لامتزاز غاز كبريتيد الهيدروجين . اجريت عملية الامتزاز في منظومة مصنعة من الحديد المقاوم للصدأ من النوع الثابت وبحجم ثابت ايضا . ودلت النتائج التي تم الحصول عليها بان الزيولايت من النوع 5A يمتلك اكبر سعة اامتزاز وان قابلية امتزاز الانواع الثلاثة تجاه غاز H_2S يمكن ترتيبها على النسق 5A> 4A> 3A .استخدمت ثلاثة معادلات لتقييم عملية الامتزاز هي لانكماير Langmuir ، فرندلش Freundlich ,، وتوث Toth واستخدم العامل R^2 لاختيار المعادلة المناسبة .تم البحث والتحقق من المعلمات الكمية على مدى واسع من درجات الحرارة والضغط