

## The Effect of Surfactant on Zeolite Preparation from Iraqi Kaolin

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### Abstract:

In this study, zeolite type A was successfully prepared from kaolin; as a source for silica and alumina. The effect of a cationic surfactant (hexadecyltrimethylammonium Bromide (CTABr) was studied during the preparation of zeolite type A from kaolin clay (structurally modified). The addition ratio was (0.2, 0.4, 0.6, 0.8) CTABr. Also, CTABr was added with different amounts of (25, 75, 150 and 300) mg/l to commercial zeolite type A (surface modified). The prepared samples were characterized using FTIR, surface area and adsorption capacity.

The results indicated that the adsorption capacity was decreased as the concentration of CTABr is increased. The minimum adsorption capacity was 8.4109 % gH<sub>2</sub>O / gzeolite using 300 mg/l of surfactant, while it was reached 6.907% gH<sub>2</sub>O / gzeolite by using 0.8% CTABr of kaolin within the preparation.

Furthermore, the increased amounts of CTABr causes to increase the surface area of **surface modified zeolite** where it was increase from (19.938 to 23.8655, 24.377 and 25.2174 (m<sup>2</sup>/g achieving an increase of 22.6, 25.2 and 29.6% respectively, A large increase more than 100% in the surface area was obtained for the **structurally modified** samples by increasing the CTABr concentration from (13.0113 to 24.0935, 25.7594, 26.2719 and 27.12) m<sup>2</sup>/g.

### الخلاصة:

في هذه الدراسة تم تحضير زيولايت نوع A من الكاؤولين كمصدر للسيليكا والالومينا. حيث تم دراسة تأثير إضافة مركب الشد السطحي الموجب خلال تحضير زيولايت نوع A المحضر من الكاؤولين بنسب (0.2, 0.4, 0.6, 0.8) من الكاؤولين ومقارنته مع الزيولايت المحضر بدون الإضافة. كذلك دراسة إضافة CTABr بكميات مختلفة (25, 75

الامتزاز. (300, 150) مغ/ لتر الى زيولايت نوع A التجاري، وتشخيص النماذج بواسطة FTIR ، المساحة السطحية و سعة

تشير النتائج الى ان سعة الامتزاز تقل بأزدياد تركيز CTABr , حيث كانت اقل سعة امتزاز % 8.4109 غم ماء/ غم زيولايت بأستخدام 300 مغ/ لتر من مركب الشد السطحي , بينما يصل الى % 6.907 غم ماء/ غم زيولايت عند أستخدام CTABr بتركيز 0.8 % من الكاؤولين.

أضافة الى ذلك, ان الزيادة بكمية CTABr تؤدي الى زيادة المساحة السطحية للزيولايت التجاري المعدل من (19.938 الى 23.8655 , 24.377 و 25.2174 م<sup>2</sup> غم وكانت الزيادة بنسبة (22.6 , 25.2 و 29.6) % على التوالي. حيث تم الحصول على زيادة اكثر من 100% بالمساحة السطحية للنماذج المحضرة من الكاؤولين بزيادة تركيز CTABr من (13.0113 الى 24.0935 , 25.7594 , 26.2719 و 27.12) م<sup>2</sup> غم.

### **Introduction:**

Zeolite is the one of the most significant materials in chemistry, their application as catalysts being most important in relative industrial processes. Zeolite has been exploited as industrial catalysts in many petroleum derived chemical processes (e.g., isomerization, catalytic cracking, hydrocracking, aromatics alkylation, disproportionation, methanol to gasoline, dewaxing, etc.) and fine chemical processes (selective oxidation of olefins or fragrance synthesis, etc.).[1]

In fact, zeolites are microporous materials with regular pores and cavities of molecular dimensions (3–15) °A formed by heteroatoms in tetrahedral coordination essentially silica and alumina connected through oxygen atoms. The chemical composition of zeolite tuned by introducing other heteroatoms such as Co , Sn, Fe, Cu, etc., both in framework positions, as well as, the nature of the catalytic active sites (redox centers or acid-base).[1]

Zeolite can be produced from natural minerals; also it can be chemically synthesized. It contains negative charges in its framework and the charges are normally balanced by alkali or alkali-earth ions.[2]

The zeolite morphology had been an important factor for determination for the adsorption properties and the corresponding catalytic activity. Making smaller spherical crystals, rather than layer and needle-shaped crystals, can be useful for the corresponding catalysis, because

all active sites can be easily exposed to the reactant. Furthermore, the controlling of the zeolite morphology is very important when the hydrothermal synthetic approach is utilized.[3]

Zeolite type A, classified into three different kinds (3A, 4A and 5A) all of them has the same general formula but different in cation type. When 75% of sodium in zeolite is replaced by potassium it's referred to 3A, alternatively replacing of sodium by calcium referred to zeolite type 5A.[4]

### **Surfactant-Modified Zeolites:**

Mixture of a surfactant used to prepare a mesoporous zeolite with high microporosity and acidity was reported by Karlsson et al 1999. They suggested that the cation could direct the crystallization of the zeolite while the surfactant could simultaneously direct the formation of the mesopores by micellation.[5]

The cationic surfactant could modify zeolite surface to increase its capacity to retain anion. The molecules of surfactant form bi-layers on external surface of zeolite, the lower layer held by electrostatic interaction between the negatively charged zeolite surface and the positively charged surfactant head groups and the upper layer is bound to the lower layer by hydrophobic forces between the surfactant tail groups in both layers. Under the surfactant bi-layer arrangement, the zeolite reverses its surface charge resulting in a higher affinity for negatively charged anions, and the sorption and retention of anions are attributed to surface anion exchange. The surfactants are attached only on the external surface of the zeolite caused by the cation exchange sites situated inside the pores are in stoke for cation exchange.[6]

Modified zeolite combines the cation sorption properties typical for zeolites, with the ability to absorb anionic species and non-polar organics, besides anion exchange properties. Some of the applications of modified zeolite are removal of BTEX and removal of phenols.[7]

There are many works focused on modified zeolite:

surface modification of a natural Chilean zeolite with cetyltrimethylammonium bromide and investigated the adsorption efficiency for the removal from aqueous solution of an anionic surfactant, sodium dodecyl benzene sulfonate (SDBS).[8]

Zeolite A by hydrothermal transformation of natural Jordanian kaolin with various concentrations of NaOH solutions at 100 °C for 20 h. They used the metakaolinization process at 650 °C. The results indicated that the products contain zeolite A as the major constituent phase, the amount of untransformed metakaol in probably decreases with increasing concentration of NaOH.[9]

Therefore, the main aim of the present work was to study the effect of a cationic surfactant (hexadecyltrimethyl-ammonium Bromide (CTABr) on characterization of zeolite type A.

### **Experimental Work:**

This study was made in two ways: first, by adding CTABr with different amounts of 25, 75,150,300 mg/l to commercial zeolite A and is designated as "**surface modified commercial zeolite A**". the other way, by adding CTABr during the preparation of zeolite A from kaolin clay as ratios of (0.2, 0.4, 0.6, 0.8) of the kaolin, and compared with the one prepared with no addition, and is designated as "**structurally modified zeolite A**".

### **Chemicals Components:**

The chemical components used in this study were Commercial Zeolite 4A (from BAIJI Refinery), Kaolin (from Iraqi Surveying & Mining commission), Hydrochloric Acid HCl (35%, from Gainland Chemical Company GCC, UK), Sodium Hydroxide NaOH (98%, from Riedel-De Haen Ag Seelze-Hannover) and hexadecyltrimethylammonium-bromide (CTABr).

### **Addition of CTABr during Preparation Step**

- 1- The Iraqi kaolin clay was crushed by using electrical mill then grained and sieved to the grain size 150 micron.
- 2- The sieved kaolin and a dilute solution of hydrochloric acid (1N) putted in a two

- necks round bottom flask with a solid to liquid ratio (3 g: 10 ml).
- 3- The mixture was agitated and heated at 100°C for 30 minutes by magnetic stirrer heater with an oil bath, condenser and thermocouple.
  - 4- The slurry was filtered after 30 minutes in Buckner funnel with a vacuum pump. The clay treated was washed with deionized water and filtered many times until the filtrate was neutral.
  - 5- The kaolin was dried at 110°C for 7 hours, then dried kaolin was calcined at 550°C for 2 hour to convert kaolin to metakaolin.
  - 6- The metakaolin was treated with sodium hydroxide solutions (2N) with ratio (1 g: 5 ml), and then the mixture put in sealed vessel of polyethylene mixed by a magnetic bar for 10 minutes until the mixture became homogeneous and then the mixture was aged for 24 hours at room temperature.
  - 7- After ageing, the reaction mixture was agitated and heated by the magnetic stirrer heater at 90 °C for 2hours.
  - 8- When the reaction was ending, the slurry was filtered in Buchner funnel using vacuum pump and washed with deionized water then filtered several times till the pH reaches 10.5.
  - 9- The filter cake was dried at 100°C for 4 hours then calcined at 550°C for 4 hours.
- [10]

In case of preparing zeolite with CTABr, the steps from (1-8) are followed and then the surfactant is added during the preparation at different ratios (0.2, 0.4, 0.6, and 0.8) as a percentages of kaolin weight.

#### **Addition of Surfactant to Commercial Zeolite A:**

- 1- Zeolite was mechanical ground with a mortar to a fine particle size.
- 2- The grounded zeolite was mixed with (CTABr) solution in a 1:50 (solid: liquid) ratio. The concentrations of CTABr solutions used for the preparation were 25, 75,150, and 300 mg/ L.
- 3- The solution was agitated for 6 hours at 150 rpm on an orbital shaker. The solution

was filtered, and the solid residue was washed with distilled and dried in furnace at 110° C for 4 hours.

### **Characterization**

The physical and chemical properties of zeolites were characterized using X-ray powder diffraction (SHIMADZU type), Fourier Transform IR Radiation technique, surface area and pore volume (Burnauer, Emmett and Teller /BET), adsorption capacity and chemical analysis using ICP.

### **Results and discussion:**

#### **Surface modified commercial Zeolite A:**

Commercial zeolite A was used in this study, where the CTABr was added in different amounts of 25, 75,150 and 300mg/l.

The participation of CTABr on the surface of zeolite is investigated by comparing FTIR pattern of both commercial zeolite (S1) and modified zeolite samples (S6 and S10). The FTIR pattern for selected samples are shown in figures (1to 3). Also the distinguishable functional groups can be found in Table (1).The designation of samples and the results of commercial and prepared zeolite are presented in Table (2).

For the parent zeolite, major peaks of Si-O-Si and Si-O-Al bending and stretching, major bands of the aluminosilicate appear in the range 500 cm<sup>-1</sup> to1300 cm<sup>-1</sup>.The bending vibration of water molecules HOH adsorbed on zeolite appears in (1635cm<sup>-1</sup>) and the stretching vibration of OH group appears in range (3610 cm<sup>-1</sup>) to (3387 cm<sup>-1</sup>) as showing in Figure (1).

That peak at 403.14cm<sup>-1</sup> is assigned to the structure insensitive internal TO<sub>4</sub> tetrahedral bending peaks of zeolite A. Peaks (1633.75cm<sup>-1</sup>) and (3033.16cm<sup>-1</sup>) are referred to the external linkage asymmetrical stretching and internal tetrahedral symmetrical stretching respectively. The peaks (4685.25 cm<sup>-1</sup>) is assigned to the external linkage asymmetrical stretching. The typical groups for zeolites seem in range (461 cm<sup>-1</sup>) to (1298 cm<sup>-1</sup>) and the

peaks of Si-O-Al and Si-O-Si were (461, 555, 669, 1012 and 1646)  $\text{cm}^{-1}$ . These groups are distinguished also in all samples of zeolite after modification, which is important to remain these bands in the same positions when the surfactant is added to prepared zeolite.[11]

**Table (1) Active bands of Zeolite in the present work**

Band (Standard)	Band $\text{cm}^{-1}$ Prepered Zeolite (S10)	Band $\text{cm}^{-1}$ Prepered Zeolite with surfactant (S6)
457	465.38	461.28
555	555.27	555.27
657.42	657.42	669.68
718.71	722.80	722.80
1007	1020	1012.91
1462.38	1470	1458.30
1654.43	1646.25	1646.28
2720.89	2724	2855.73
2917.03	2915	2920
2950	2952	2949.71
3435	3430	3374.67

The bands belonging to CTABr are found within the zeolite indicating that the presence of the surfactant did not alter the zeolite main structure. The vibration bands of the surfactant can be grouped into two types: those associated with methylene tails and those with alkylammonium head groups. The peak around ( $3015 \text{ cm}^{-1}$ ) was assigned to the symmetric stretching mode of the trimethylammonium head group  $\text{CH}_3\text{-N}$ . In the FTIR spectrum of the crystalline CTABr the most intense absorption bands at around  $2915$  and  $2850 \text{ cm}^{-1}$  arise from the  $\text{CH}_2$  asymmetric and symmetric ( $\text{CH}_2$ ) stretching vibration modes of methylene groups respectively, which are corresponding with the bands ( $2920$  and  $2855.73 \text{ cm}^{-1}$ ) in the modified zeolite (S6). The bands around ( $2946$  and  $2871 \text{ cm}^{-1}$ ) are due to the asymmetric and symmetric stretching modes of terminal  $\text{CH}_3\text{-R}$  group respectively, which can be observed in modified zeolite as the bands ( $2949.71 \text{ cm}^{-1}$ ). [8]

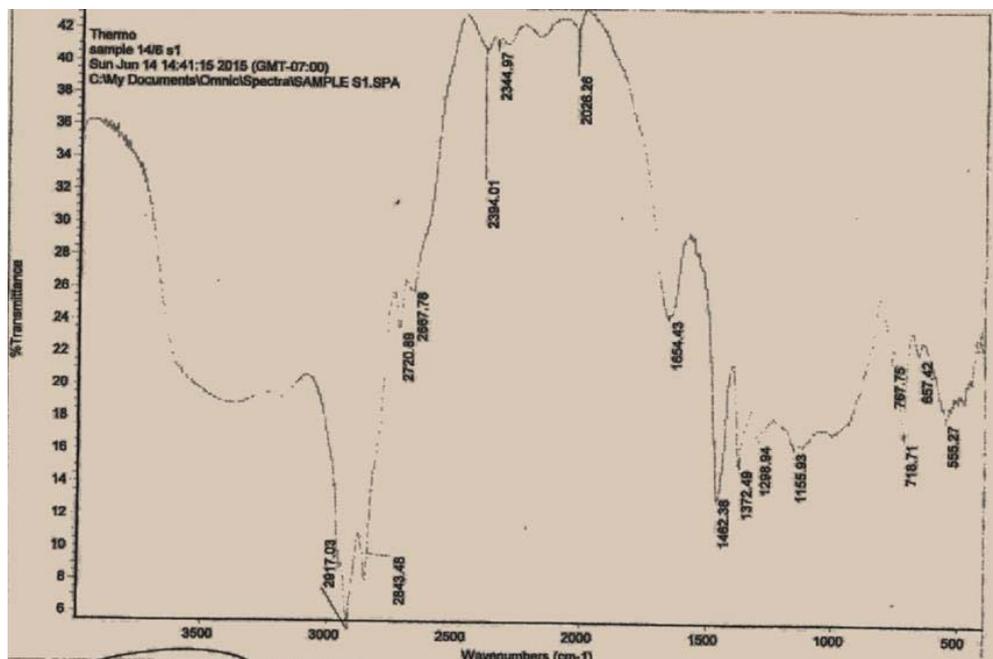


Fig. (1) FTIR Spectrum of S1

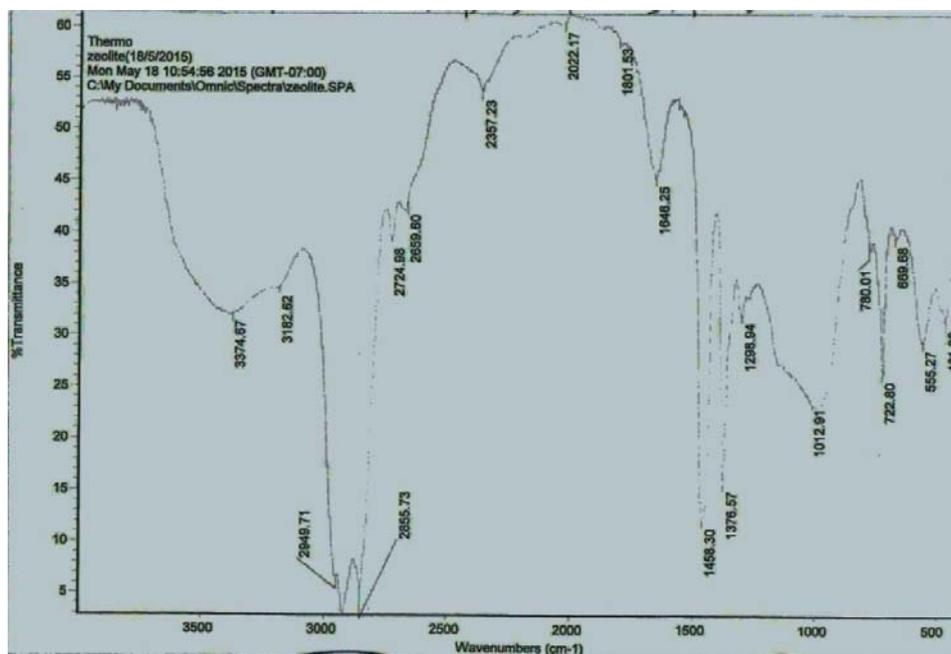


Fig. (2) FTIR Spectrum of S6

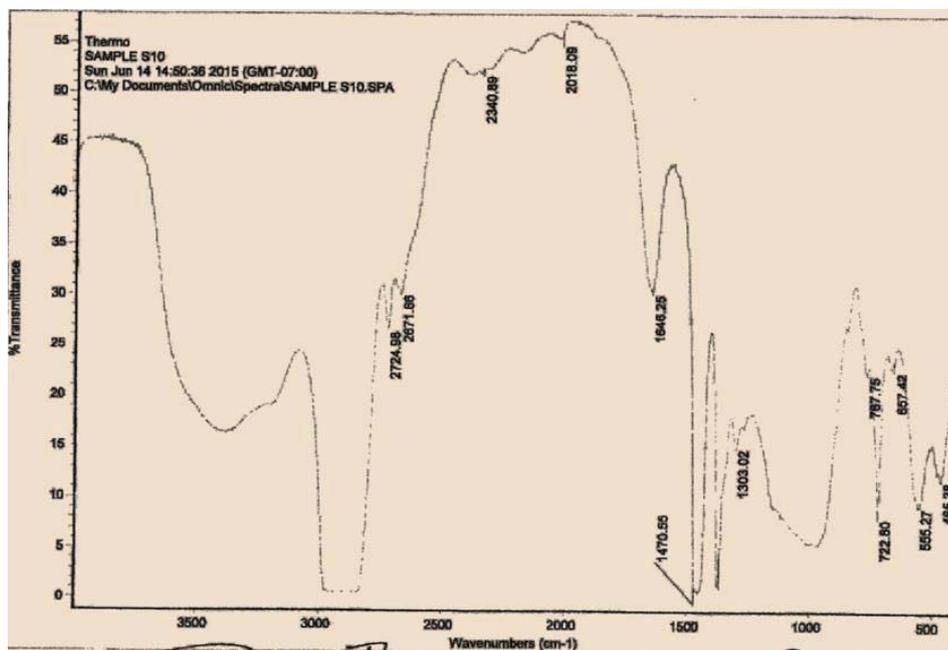


Fig. (3) FTIR Spectrum of S10

**Table (2) Sample designation and results**

Zeolite	CTABr Concentration	Surface Area m <sup>2</sup> /g	Adsorption Capacity % g <sub>H2O</sub> / g <sub>zeolite</sub>	Efficiency %
S 1	Commercial Zeolite A	19.938	14.18	64.31
S 2	25 mg/ L	19.457	19.7084	89.5837
S 3	75 mg/ L	23.8655	17.7589	80.722
S4	150 mg/ L	24.377	11.9045	54.111
S 5	300 mg/ L	25.2174	8.4109	38.2315
S6	(0.4 percentages of kaolin weight) from CTABr	25.7594	9.5441	43.3825
S10	Zeolite prepared from kaolin	13.0113	14.6701	66.08
S 11	(0.2 percentages of kaolin weight) from CTABr	24.0935	13.6812	62.1877
S12	(0.6 percentages of kaolin weight) from CTABr	26.2719	7.7552	35
S13	(0.8 percentages of kaolin weight) from CTABr	27.12	6.907	31.397

**Structurally modified ZeoliteA:**

In this study Zeolite A was successfully synthesized from kaolin clay (S10). Other samples (S6, S11, S12 and S13) were prepared by the addition of CTABr in various amounts.

It can be deduced from the chemical analysis that the SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> ratio is 2.6 and Na<sub>2</sub>O to Al<sub>2</sub>O<sub>3</sub> is 0.3 which can be related to type 4A zeolite with the presence of some impurities of other zeolitic materials.

A comparison is made between the structurally modified and the original zeolite by comparing the functional groups in FTIR spectrum in both samples. All the specific bands

of typical values present in the unmodified prepared zeolite can be found in the modified zeolite and this can be found in Table (1).

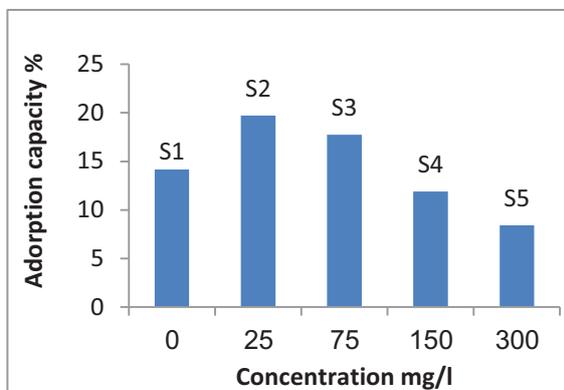
### The Effect of Surfactant on Adsorption Capacity:

The adsorption capacity of the samples modified by the two ways was investigated, the results can be found in Table (2). The commercial zeolite (S1) exhibited a value of 14.18 %  $g_{H_2O} / g_{zeolite}$  for the uptake of water vapor. For the surface modified samples, it can be seen that the adsorption for water vapor is increased at low loading of 25mg/l and then decreased as the concentration of CTABr is increased, it seems that using 25mg/l had improved the adsorption capacity to 19.7084%  $g_{H_2O} / g_{zeolite}$  as shown in figure (4), also the efficiency was calculated according to eq. below, it can be seen that the highest value of 89.5837% was obtained.

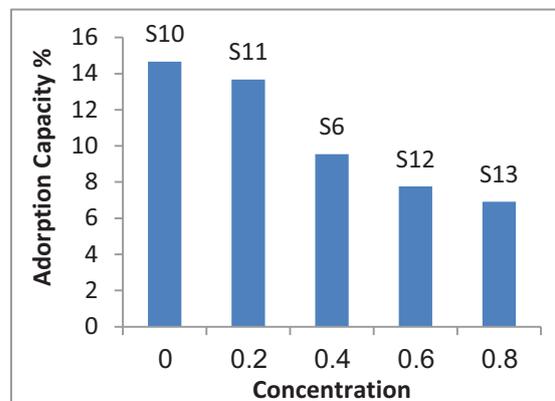
$$Efficiency = \frac{A.C}{22} * 100\%$$

This could be explained by the decrease in particle size affecting the morphology and pore opening being more susceptible to guest molecules. But the increase of the cationic surfactant CTABr furthermore, makes the surface positively charged and causes repulsion to polar water molecules, the polar negative part of CTABr is attached to the external surface of zeolite leaving the organic positive part micelles of surfactant.

In comparison between the prepared zeolite (S10) and commercial zeolite (S1) it was found that the adsorption capacities were almost similar. In order to investigate the effect of surfactant on adsorption capacity of *structurally prepared zeolite from kaolin*. The results indicated that maximum adsorption capacity is obtained at concentration of (0.2 percentages of kaolin weight) from CTABr as showing in Fig. (5). The structurally modified sample got the lowest water adsorption capacity of 6.907%  $g_{H_2O} / g_{zeolite}$  for the sample of (0.8 percentages of kaolin weight), it can be seen that the lowest value of 31.397% was obtained.



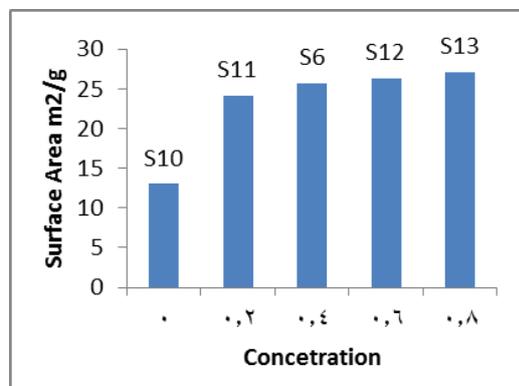
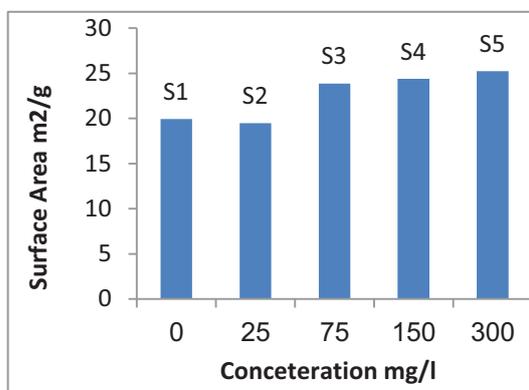
**Fig. (4) Effect of surfactant on adsorption capacity in commercial zeolite**



**Fig. (5) Effect of surfactant on adsorption capacity in modified zeolite**

### **The Effect of Surfactant on Surface Area**

The addition of 25 mg/l surfactant to commercial zeolite causes unpredicted change in surface area from (19.938 to 19.457m<sup>2</sup>/g) which could be attributed to the changes in particle size did not reach the level that can make a significant change in the surface area. While increased in amounts of CTABr causes to increase in the surface area from 19.938 to 23.8655, 24.377 and 25.2174 m<sup>2</sup>/g. For the structurally modified samples increasing in the CTABr concentration causes to sharp increase in the surface area from (13.0113 to 24.0935, 25.7594, 26.2719 and 27.12) m<sup>2</sup>/g and the highest value was for sample (S13) where an increase of higher than 100% is achieved figures (6 and 7) show the effect of the surfactant on surface area.



**Fig. (6) Effect of surfactant on Surface Area in commercial zeolite**

**Fig. (7) Effect of surfactant on Surface Area in modified zeolite**

### Conclusions:

- ❖ Zeolite A was prepared successfully from Iraqi kaolin.
- ❖ The results showed that the characteristic functional groups of the CTABr were found in the FTIR spectrum pattern of both the surface modified and the structurally modified zeolite A. This reveals the presence of the surfactant inside zeolite A.
- ❖ Surface modified commercial zeolite A showed a decrease in the adsorption capacity of water vapor and the min. was 8.4109%  $g_{H_2O} / g_{zeolite}$  while it was 6.907%  $g_{H_2O} / g_{zeolite}$  for the structurally modified zeolite.
- ❖ All samples which were treated with CTABr showed an increase in the surface area but the structurally modified samples had the higher increase than the surface modified reaching more than 100%.

**Nomenclature**

**CTABr** Hexadecyltrimethylammonium Bromide

**S 1** Commercial Zeolite A

**S 2** Commercial Zeolite A modified with 25 mg/ L (CTABr)

**S 3** Commercial Zeolite A modified with 75 mg/ L (CTABr)

**S4** Commercial Zeolite A modified with 150 mg/ L (CTABr)

**S 5** Commercial Zeolite A modified with 300 mg/ L (CTABr)

**S6** Zeolite prepared from kaolin with (0.4percentages of kaolin weight) from CTABr

**S10** Zeolite prepared from kaolin

**S 11** Zeolite prepared from kaolin with (0.2percentages of kaolin weight) from CTABr

**S12** Zeolite prepared from kaolin with (0.6percentages of kaolin weight) from CTABr

**S13** Zeolite prepared from kaolin with (0.8percentages of kaolin weight) from CTABr

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