

## Interaction between Kaolin and DMSO: FTIR, XRD , thermodynamic and Nano studies

Sabri M. Hussein\* , Omar H. Shihab\*\* and Sattar S. Ibrahim \*

\*University of Anbar – College of Science.

\*\*University of Anbar – College of Women Education.

**Abstract** :Intercalation of highly polar organic compound dimethylsulfoxide (DMSO) with kaolinite and the formation of interlamellar complexes has been studied, and characterized by X-ray diffraction (XRD), Fourier transform-infrared spectroscopy (FTIR). Interaction was found to be dependent on the particle size of kaolin raw material. Nature of interaction achieved through the formation of hydrogen bonds between DMSO and both AlOH and Si – O surface of kaolinite. Effect of temperature on equilibrium adsorption of methylene blue (MB) from aqueous solution using kaolin and kaolin – DMSO complexes also studied, the results were analyzed by Langmuir and Freundlich isotherms. Thermodynamic parameters such as  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  were calculated. Results suggested that the MB adsorption on kaolin was spontaneous and exothermic process.

**Key words:** organo-clays; intercalation; adsorption; adsorption isotherms; dyes; FTIR; XRD; TEM.

### Introduction

Kaolin is one of the clay materials widely used for a large number of applications such as in ceramics, paper coating, paper filling, paint extender, rubber filler, cracking catalyst or cements, oil refinery and water treatment [1], [2], [3], [4]. Kaolinite is the major mineral component of kaolin, which may usually contain quartz and mica and also less frequently feldspar, illite, montmorillonite, anastase, hematite, bauxite, zircon, rutile, kyanite, silliminate, graphite, attapulgite and halloysite [1],[2]. Kaolinite is a clay mineral with chemical composition  $Al_2Si_2O_5(OH)_4$ . It is a layered silicate mineral, with one tetrahedral sheet of being linked through oxygen atoms to one octahedral sheet of alumina [5]. Rocks that are rich in kaolinite are called kaolin. Kaolinite has a low shrink-swell capacity and a low cation exchange capacity. It is a soft, earthy material, usually white mineral produced by chemical weathering of aluminum silicate minerals like feldspar. In many parts of the world, it is colored pink, orange or red by iron oxide giving it a distinct rust hue.

Kaolinite like other clays are composed of fine grained minerals which are plastic at appropriate water content and hardens up when fired [6]. They have varying chemical composition depending on both physical and chemical changes in the environment where they are found. The industrial utilization of kaolinite is closely related to its

reactivity and surface properties and depends strongly on surface modification. Several methods have been suggested in literature to improve the properties of clay materials with thermo-chemical treatment [1], [2] or chemical activation [7], [4].

Some inorganic and organic compounds may penetrate into a newly formed interlayer space of kaolin – like layers and the factoids expand from 0.72 to 1.00 – 1.47 nm [8]. The penetrating species that break the strong electrostatic and van der Waals types of interactions between the kaolin – like layers may form H – bonding with inner surface hydroxyls and inner surface oxygen's. This was first inferred by comparing calculated and experimental basal spacing and later proved by FTIR and XRD spectroscopy.[9-12]

The layered kaolinite particles can be intercalated by small molecules , such as urea, potassium acetate, dimethylsulphoxide (DMSO), etc.[13-16]. The preparation of hybrid organic-inorganic materials by intercalation of organic molecules into kaolinite represents a clear possibility of new and interesting materials present unique properties [17]., furthermore, some small molecules that intercalated into kaolinite can be used for the precursors for the preparation of polymer – kaolinite compounds.[18]

### Experimental

Kaolinite used in this study was hydrated Aluminum silicate, provided from General

company for the manufacture of glass and ceramic ( ceramic factory). Chemical analysis of kaolin is shown in table (1), and the other organic material

is Dimethylsulphoxide (DMSO) provided from Merck Co. Germany.

**Table (1):** Chemical analysis of kaolin

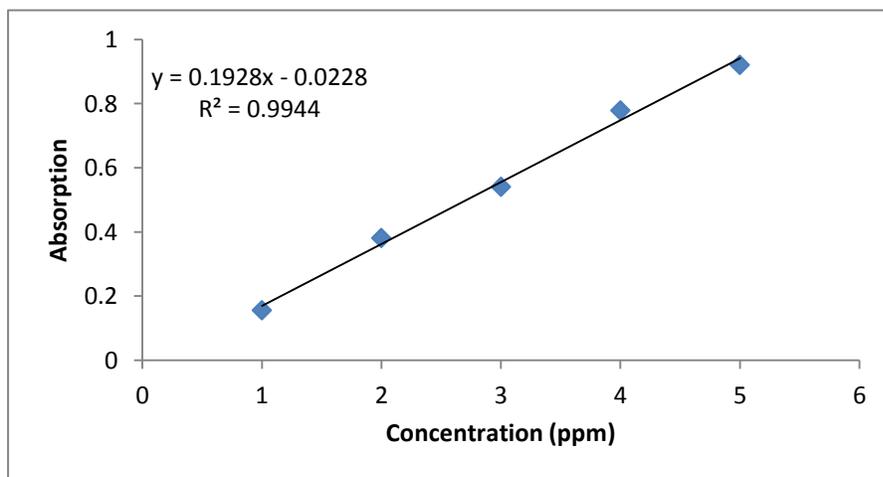
Constitunet	Wt %
SiO2	48.57
Al2O3	35.05
CaO	0.6
MgO	0.77
K2O	0.08
Fe2O3	1.34
TiO2	1.19
Moisture	0.08
Loss on ignition	12

**Preparation of Kaolin – DMSO Organoclay ( granular size 53 µm and 106 µm ).:**

- 1- 70 gm of grinded kaoline of granular size 53 µm was weight and placed at a beaker 500 ml.
- 2- 200 ml of DMSO was added to the clay and mixed very well.
- 3- The mixture was refluxed at 60°C for 48 hours, using a hot plate with magnetic stirrer.
- 4- The precipitate was filtered and washed 3-4 times by methanol.
- 5- The product was dried in oven at 50°C.
- 6- The dry clean precipitate, then was grinded and became ready for the required testing.
- 7- The kaolin of granular size 106µm was prepared using the same steps as above mentioned.

**Preparation of Methylen blue solution:**

1 gm of Methylen blue dye (MB) was dissolved in one liter of double distilled water to obtain 1000 ppm MB dye solution. UV-Vis spectra of this solution appeared an absorption band at  $\lambda_{max} = 660 \text{ nm}$  and from this solution different concentration of methylen blue were prepared to make standard curve as shown in figure (1). From this standard curve we calculat the concentration of unknown.



**Figure.1:** Standard curve for methylen blue solutions

### Steps of adsorption.

- 0.5 gm of the prepared organoclays was weighed, and placed at 25 ml volumetric flask.
- 10 ml of methylen blue solution dye of the required concentration was added to the clay and stirred very well.
- The flasks were placed at shaker water bath at different temperatures (10, 30, 40 and 50 °C) and stirred for 1 hour.
- The solutions were filtered.
- The absorption was measured for each filtered solution at wave length 660 nm.
- The adsorption required calculation according to (Langmuir and Freundlich isotherms ), from which the thermodynamic constant can be obtained (  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  ).

### Preparation of nano organoclays

- 1- 5 g of prepared organoclay were placed in a glass Beaker 250 ml.
- 2- Added 200 ml of a solution of DMSO concentration 2 M and Shake well.
- 3-The solution is placed on the ultrasonic for one hour and placed the amount of ice around the beaker.
- 4- Separating the precipitate from the filtrate using a centrifuge.
- 5- Dried the precipitate and then grinds it and conducted the tests required.

### Results and Discussion

Dimethylsulphoxide (DMSO) intercalation has been used to separate the chlorite fractions from the kaolinite minerals. The reason DMSO is so successful at separation the clay minerals is that the kaolinite after intercalation by DMSO expand from 0.72 to 1.12nm [8].

The corresponding FTIR spectra of kaolin and their complexes are shown in figures (2, 3). From these figures, one could observe some bands, which are very important for the kinetic process.

Band at 3621cm<sup>-1</sup> in each complexes are due to an inner hydroxyl group in kaolin bonded to S=O group of DMSO.[19] and it is unlikely to be significantly affected by the inclusion of DMSO molecules in the inter lamellar layers, because of its presence within the bulk of kaolin structure.

Bands at 3478 and 3428cm<sup>-1</sup>in the figure (3.19 C) and at 3471cm<sup>-1</sup>in the figure (3.20 C) are due to the formation of moderately strong H-bonding between some of inner surface hydroxyls of the kaolinite and the sulphonyl oxygen for DMSO.[17]

Band at 2938cm<sup>-1</sup> in each figures chart C of complexes are assigned to symmetric CH vibration in the complexes. The water bending vibration at 1631cm<sup>-1</sup>and 1646cm<sup>-1</sup> in figures (3.19 C, 3.20 C) respectively indicate one type of water molecule present.

Band at 914cm<sup>-1</sup> is due to Al—OH, and the bands at 752, 686, 543 and 466 cm<sup>-1</sup>are assigned to Si—O vibration.

Since DMSO is a small molecule with high dipole moment, its intercalation in to the kaolinite structure can be enhanced by microwave irradiation. [20]

### XRD for kaolinite 53, 106 µm- DMSO complexes.

Figure (4) show the XRD for kaolinite (A), kaolinite 53 and 106µm- DMSO complexes charts (B, C) respectively.

From these figure one could observe that:

The emergence of new peaks at a distance of 11.06079 Å<sup>0</sup>, 2θ= 7.9869 and 3.371850Å<sup>0</sup> under 2θ= 23.9112 in chart B, and in distance of 11.10646, 2θ= 7.9540 and 3.72325 Å<sup>0</sup> under 2θ= 23.8802 in chart C in the same figure these a new peaks are due to DMSO.

These signify that the DMSO molecules are directly intercalated in to the kaolinite mineral in agreement with the reported in the literature [21-23].

The basal spacing of kaolinite expands and it may be proposed based on this expansion that one of methyl groups of DMSO is keying in to distrigonal holes of the siloxane layer [21, 24-26]

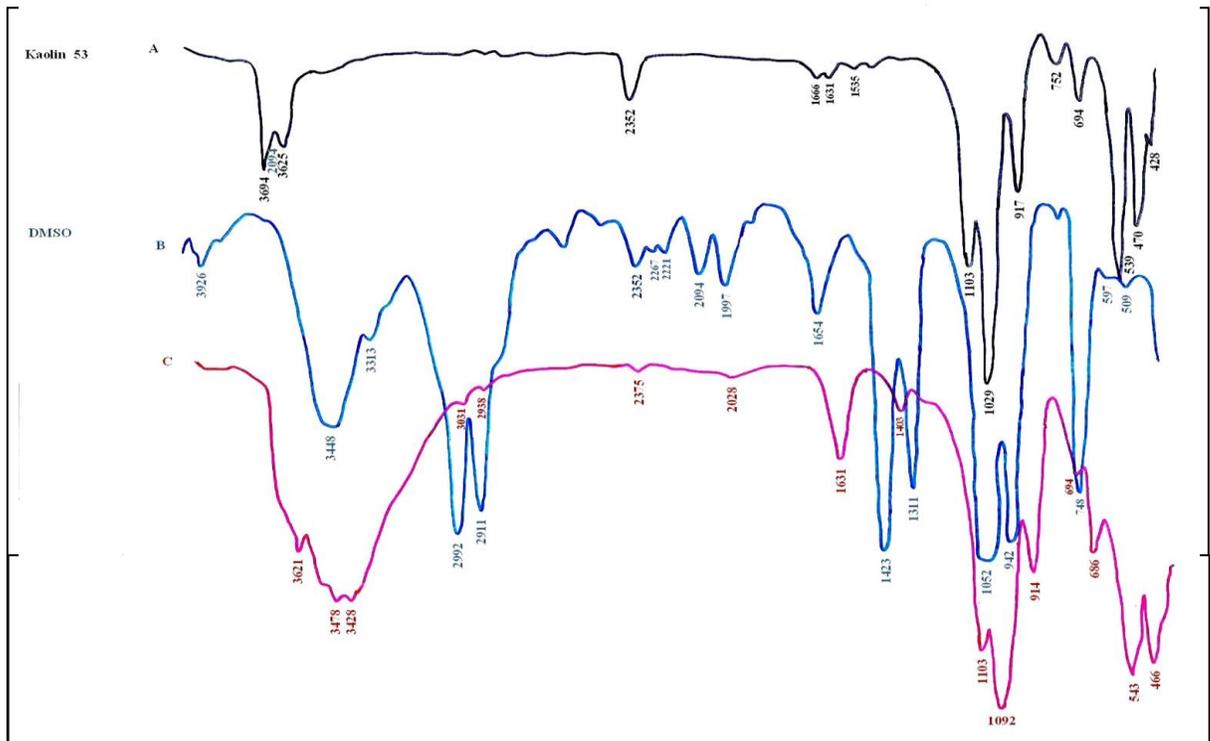
In order to check the effect of interlayer expansion on the uptake capacity of kaolinite, the clay was intercalated with Dimethylsulphoxide (DMSO) to increase the interlamellar space of kaolinite by breaking up the hydrogen bonds tightly interlinking the kaolinite lamellae.

According to these diagrams, upon intercalation, the characteristic peaks of kaolinite are changes in intensity its converting to low intensity when intercalated is happened, thus confirming the expansion of the interlayer space of kaolinite. [27]

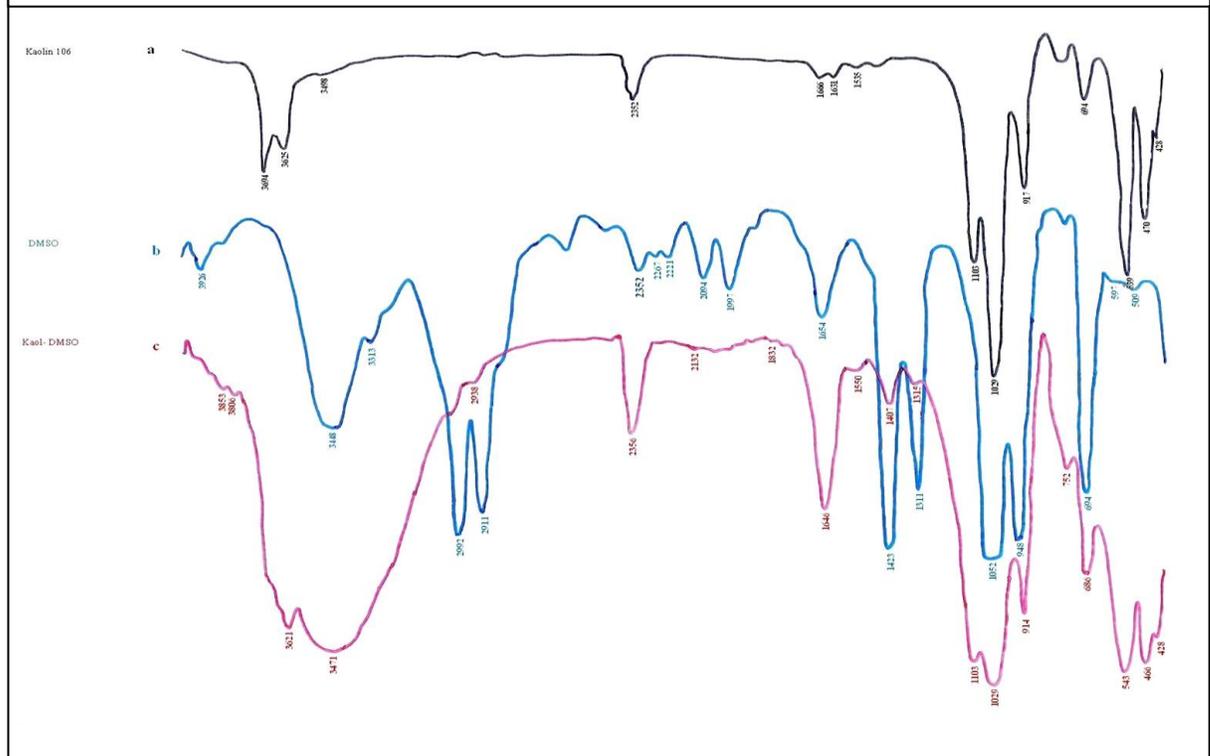
### Adsorption study

The isotherm of the Methylene blue adsorption by kaolin and organoclay were represented by applying the Langmuir and Freundlich adsorption models. It was found that the adsorption process on the kaolin and organoclay fits very well with the isotherm models Freundlich.

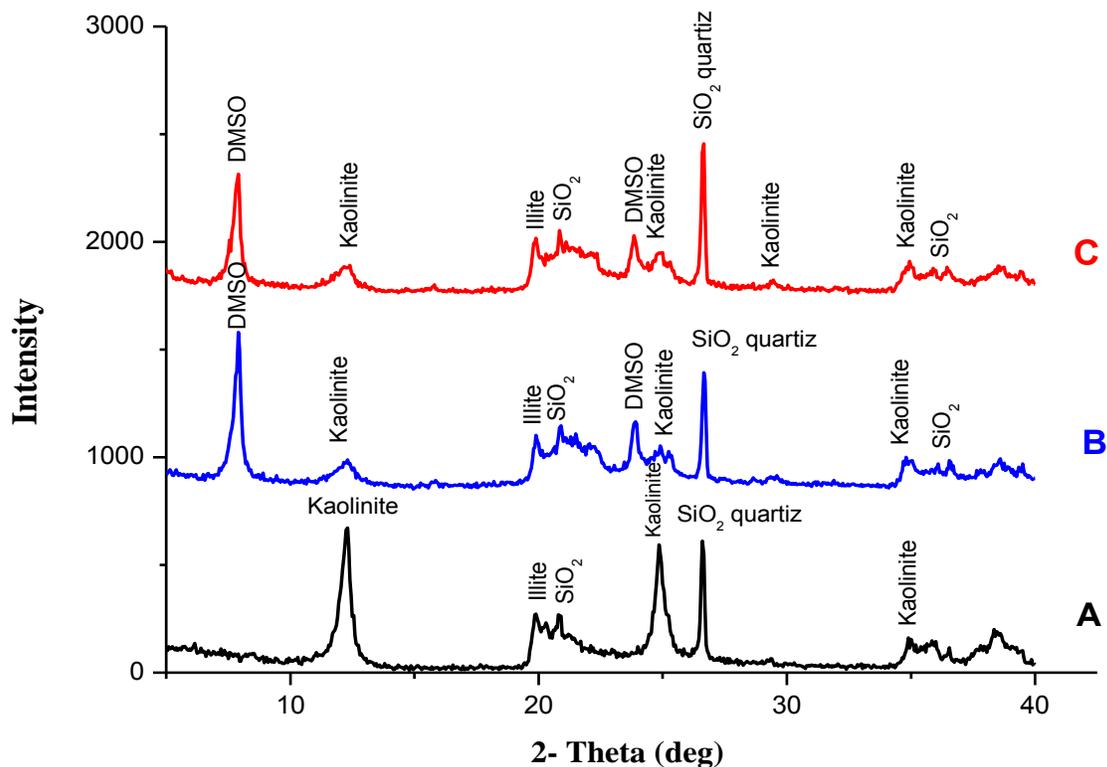
The relations of equilibrium values of logQ<sub>e</sub> vs. logC<sub>e</sub> and C<sub>e</sub>/Q<sub>e</sub> vs. C<sub>e</sub> for Methylene blue adsorption isotherms using kaolin and organoclay powders at different temperatures (10, 30, 40, 50 °C) are shown in figures (5- 8).



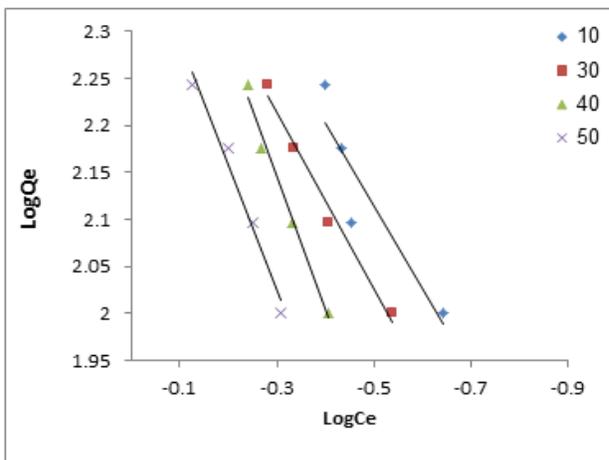
**Figure 2:** FTIR spectra of (A) kaolin 53µm, (B) DMSO and (C) Kaolin 53µm -DMSO complex



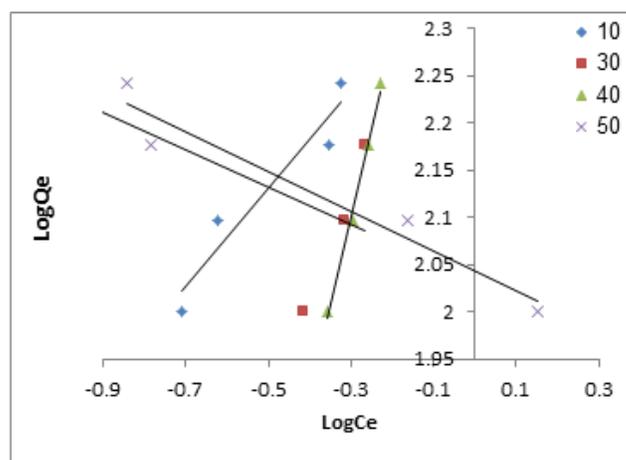
**Figure 3:** FTIR spectra of (A) kaolin 106µm, (B) DMSO and (C) Kaolin 106µm -DMSO complex



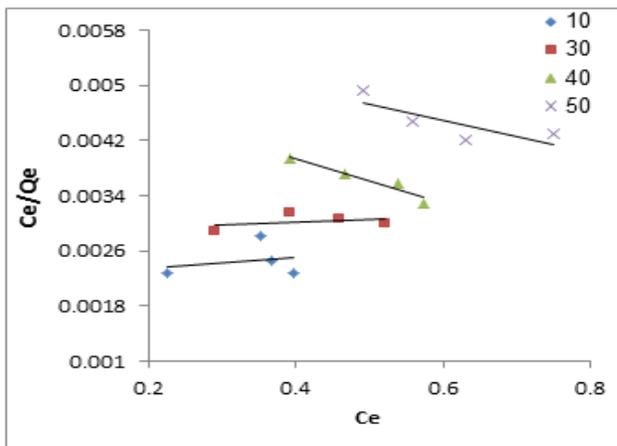
**Figure 4:** The XRD pattern of raw kaolinite (A), kaolinite 53 and 106 μm- DMSO complexes charts B and C respectively.



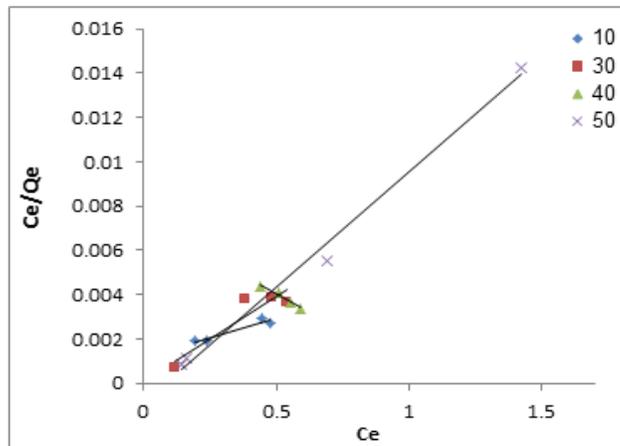
**Figure 5:** Frendlich isotherm for adsorption of MB on kaolinie 53μm- DMSO complex.



**Figure 6:** Frendlich isotherm for adsorption of MB on kaolinie 106 μm- DMSO complex.



**Figure 7:** Langmuir isotherm for adsorption of MB on kaoline 53µm- DMSO complex.



**Figure 8:** Langmuir isotherm for adsorption of MB on kaoline 106µm- DMSO complex.

The Freundlich linear isotherm is expressed in equation.

$$Q_e = K_f C_e^{1/n}$$

This isotherm is usually used in special cases for heterogeneous surface energy and it is characterized by the heterogeneity factor  $1/n$ .  $Q_e$  is the equilibrium value of methylene blue adsorbed per unit weight of kaolin powder, a liquid-phase sorbate concentration occurred at equilibrium and  $K_f$  as the Freundlich constant. Freundlich constants are shown in table (2) while the relations are clearly indicated that the Freundlich isotherm model fits the analyzed data according to its

correlation coefficients ( $R^2$ ).

The kaolin powder takes up methylene blue on a heterogeneous surface by multilayer adsorption as described by Langmuir. However, the Langmuir linear isotherm is expressed in equation.

$$C_e/Q_e = (1/K) + (a/K) C_e$$

Where  $C_e$  is the equilibrium concentration (mg/l),  $Q_o$  is the maximum amount of adsorption (mg/g) corresponding to complete monolayer coverage and  $K_L$  are constants related to the binding strength respectively or sometimes called Langmuir constants. The Langmuir constants are shown in table (3)

**Table: 2** Freundlich constant for adsorption of methylene blue

sample	Particle size µm	Freundlich constant	Temperature K			
			283	303	313	322
Kaolin	53	$K_f$	419.75	404.57	309.2	285.759
		$n$	1.315	1.207	1.331	1.360
		$R^2$	0.913	0.938	0.897	0.864
Kaolin - DMSO	53	$K_f$	244.34	108.14	461.31	110.407
		$n$	1.934	5.128	0.531	4.784
		$R^2$	0.912	0.422	0.989	0.938
Kaolin	106	$K_f$	319.15	1127.19	1879.31	434.51
		$n$	1.751	0.536	0.379	1.360
		$R^2$	0.880	0.983	0.970	0.864
Kaolin - DMSO	106	$K_f$	357.27	311.88	373.25	263.026
		$n$	1.137	1.068	0.703	0.758
		$R^2$	0.842	0.982	0.988	0.975

**Table 3.** Langmuir constant for adsorption of methylene blue

sample	Particle size $\mu\text{m}$	Langmuir constant	Temperature K			
			283	303	313	323
Kaolin	53	$K_f$	1000	1000	1000	500
		a	1	1	1	0.5
		$R^2$	0.535	0.411	0.504	0.64
Kaolin - DMSO	53	$K_f$	1000	0	142.8571	0
		a	3	0	-0.85714	0
		$R^2$	0.899	0.84	0.982	0.993
Kaolin	106	$K_f$	0	250	142.857	250
		a	0	-1.5	-1.714	-0.5
		$R^2$	0.817	0.933	0.933	0.345
Kaolin + DMSO	106	$K_f$	500	500	200	200
		a	0	0	-0.6	-0.4
		$R^2$	0.061	0.133	0.916	0.637

**Thermodynamic parameters**

Thermodynamic parameters such as  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  were calculated using adsorption equilibrium constant obtained from Langmuir isotherm and shown in table (4). for these adsorption processes are determined by using the following equations [3].

$$\Delta G^\circ = -RT \ln K$$

Where K is the thermodynamic equilibrium constant. The effect of temperature on thermodynamic constant is determined by:

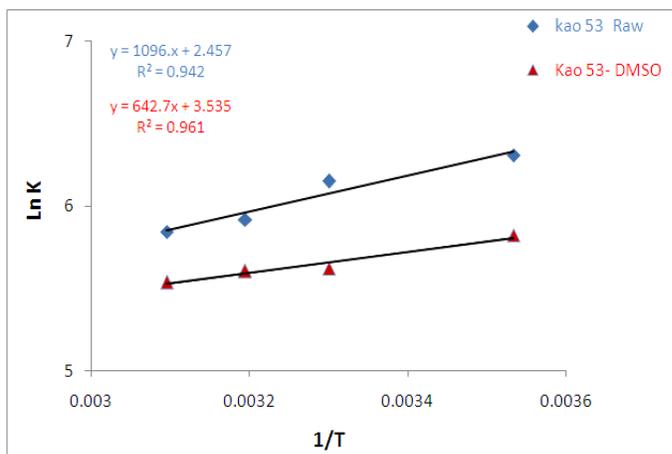
$$\ln K = \Delta S^\circ / R - \Delta H^\circ / RT$$

Where  $\Delta G^\circ$  is the free energy change

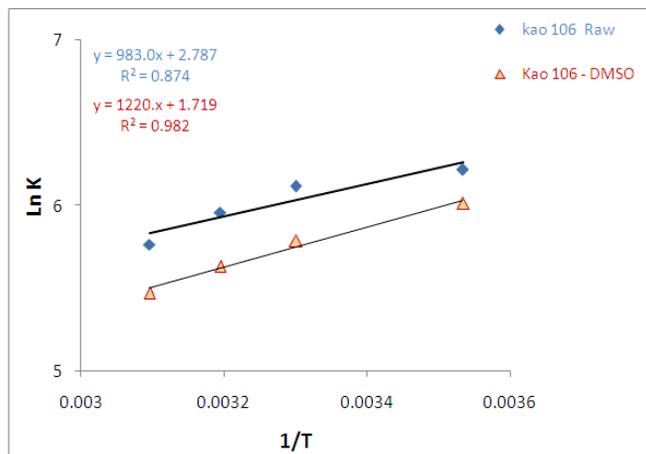
(kJ/mol); R is the universal gas constant (8.314 J/mol K) and T (K) is the absolute solution temperature.

The  $\Delta H^\circ$  and  $\Delta S^\circ$  values were calculated from slope ( $-\Delta H^\circ/R$ ) and intercept ( $\Delta S^\circ/R$ ) of the linear plot, of  $\ln K$  vs.  $1/T$  as shown in figures (9 and 10).

Results suggested that methylene blue adsorption on kaolin was spontaneous and exothermic process. Decrease a negative value of  $\Delta G$  with increase the value of  $\Delta H$  (- ve) indicate that the adsorption reaction was exothermic.



**Figure 9:** The relation between (1/T) and (LnK) for kaolin 53  $\mu\text{m}$  Raw and kaolin 53  $\mu\text{m}$  - DMSO complex



**Figure 10:** The relation between (1/T) and (LnK) for kaolin 106  $\mu\text{m}$  Raw and kaolin 106  $\mu\text{m}$  - DMSO complex

**Table: 4** Thermodynamic parameters at conc. 150 ppm Methylen blue

sample	Parical size $\mu\text{m}$	$\Delta\text{H}$ KJ/mol	$\Delta\text{S}$ KJ/mol.k	$\Delta\text{G}$ KJ/mol			
				283 K	303 K	313 K	323 K
<b>Kaolin</b>	<b>53</b>	-9.11214	0.020427	-14.8366	-15.4886	-15.4007	-15.6932
<b>Kaolin - DMSO</b>	<b>53</b>	13.26083	0.093034	-13.6943	-14.1581	-14.5762	-18.2953
<b>Kaolin</b>	<b>106</b>	-8.17266	0.023171	-14.6237	-15.4084	-15.503	-15.4777
<b>Kaolin - DMSO</b>	<b>106</b>	-0.965	0.014292	-14.1464	-14.5755	-14.6503	-14.689

Percentage of adsorption ( Q%) for kaolin and kaolin – DMSO at conc. 150 ppm of methylen blue are shown in table (5).

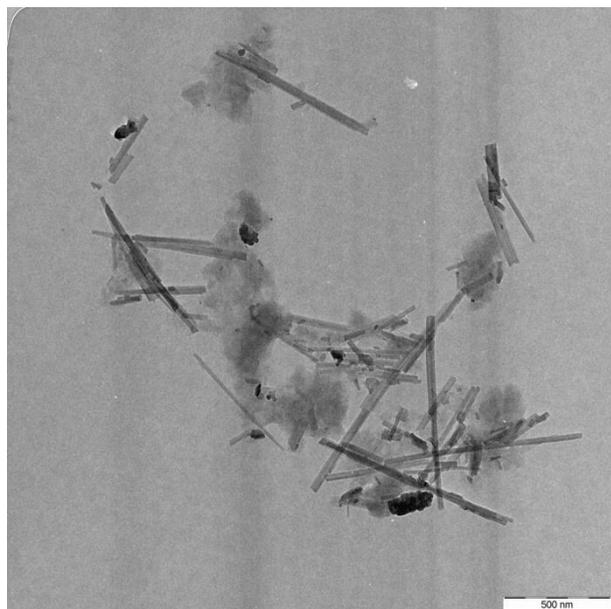
**Table: 5** Percentage of adsorption ( Q%) for kaolin and kaolin – DMSO at conc.150 ppm of methylen blue.

sample	Particle size $\mu\text{m}$	Q% at different temp.			
		283 K	303 K	313 K	322 K
Kaolin	53	99.81743	99.78631	99.73098	99.71024
Kaolin - DMSO	53	99.70332	99.63762	99.63071	99.89004
Kaolin	106	99.80014	99.77939	99.74136	99.68603
Kaolin - DMSO	106	99.75519	99.69295	99.64108	99.57884

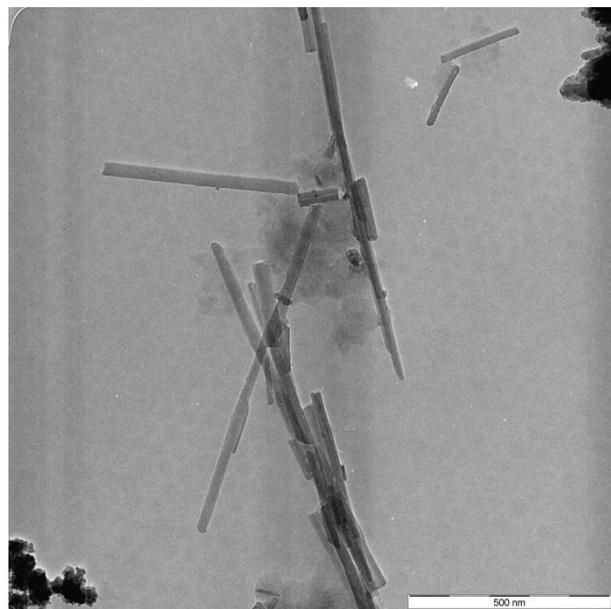
**Transmission Electron Microscopy (TEM)**

A typical TEM micrograph of kaolinite – DMSO complexes are presented in Figures (11 and 12). From this figures appeared formation of nanotube

it is also very clearly in the images. The average diameters ranging of nanotubes are from (14.15 - 20.61nm) in the figure (11) and from (24.15 - 27.64nm) in figure (12) .



**Figure 11.**TEM of Kaolinite 53µm DMSO complexes after using ultrasonic



**Figure 12.**TEM of Kaolinite 106µm DMSO complexes after using ultrasonic

## References

- [1] C. Belver, M.A. Munor, M.A. Vicente, Chem. Mater, 2002, 14 2033-2043.
- [2] G. Vaga, Epitoanyag, 2007, 59, 4-8.
- [3] A.M. Caulcante, L.G Torres, G.L.V. Welho, Braz. Journal of Chemical Engineering, 2005, 22, 2682-2865.
- [4] T.O. Salawudeen, E.O. Dada, S.O. Alagbe, Journal of Engineering and Applied Sciences, 2007, 2, 11, 1677-1680.
- [5] W.A. Deer, R.A. Howie, J. Zussman, An introduction to rock forming minerals, Harlow longman 1992.
- [6] G. Stephen, R.T. Martin, clay and clay minerals, 1995, 43, 2, 225-226.
- [7] A. Coma, A. Misfud, E. Sanz, clay miner, 1990, 25, 19.
- [8] S. Yariv, Organo-clay Complexes and Interactions, S. Yariv and H. Cross, Eds, Marcel Dekker, New York 2002, p. 90.
- [9] J. Kristóf, R. L. Frost, J. T. Klopogge, E. Horváth and M. Gábor, J. Therm. Anal. Cal., 56 (1999) 885.
- [10] S. Yariv, I. Lapidés, A. Nasser, N. Lahav, I. Brodsky and K. H. Michaelian, Clays Clay Miner., 48 (2000) 10.
- [11] S. Yariv and I. Lapidés, J. Therm. Anal. Cal., 80 (2005) 11.
- [12] Z. Yermiyahu, I. Lapidés and S. Yariv, Appl. Clay Sci., 30 (2005) 33.
- [13] Janek M, Emmerich K, Heissler S, Nuesch R. Thermally induced grafting reactions of ethylene glycol and glycerol intercalates of kaolinite. Chem Mater. 2007;19:684-93.
- [14] Frank Caruso. Chemistry of materials 20 years on and on the rise. Chem Mater. 2008;20:1-2.
- [15] Letaief S, Elbokl TA, Detellier C. Reactivity of ionic liquids with kaolinite: Melt intersalation of ethyl pyridinium chloride in an urea-kaolinite pre-intercalate. J Colloid Interface Sci. 2006;302:254-8.
- [16] Tonle IK, Diaco T, Ngameni E, Detellier C. Nanohybrid kaolinite-based materials obtained from the interlayer grafting of 3-aminopropyltriethoxysilane and their potential use as electrochemical sensors. Chem Mater. 2007;19:6629-36.
- [17] Gardolinski JE, Ramos LP, Desouza GP, Wypych F. Intercalation of benzamide into kaolinite. J Colloid Interface Sci. 2000;221:284-90.
- [18] Fang QH, Huang SP, Wang WC. Intercalation of dimethyl sulphoxide in kaolinite: molecular dynamics simulation study. Chem Phys Lett. 2005;411:233-7.
- [19] R. K. Vempati, M. Y. A. Mollah. G. R. Reddy, D. L. Cocke, H. V Lauer. Jr., J. Mater. Sci. 31 (1996) 1255.
- [20] Gardolinski, J., Filho, H. P. M. and Wypych, F. (2003 ) Thermal behavior of hydrated kaolinite. Quim. Nova., 26 (1): 30 – 35.
- [21] J. G. Thompson and C. Cuff. Clays Clay miner. 33. 490 (1985).
- [22] S. Olejnik, L. A. G. Alymore. A. M. Posner, and J. P. Quirk, J. Phys. Chem. 72, 214 (1968).
- [23] M. Raupach, P. E. Baron, and J. G. Thompson, Clays Clay Miner. 35, 208 (1987).
- [24] X. Zhang and Z. Xu. Mater. Lett. 61, 1478 (2007).
- [25] S. Yariv and I. Lapidés, J. Therm. Anal. Cal. 94, 433 (2008).
- [26] I. Lapidés and S. Yariv, J. Therm. Anal. Cal. 97, 19 (2009).
- [27] Dilek AKAR, Msc. Thesis. " Physiochemical characterization of the sorption of Cr<sup>3+</sup> and Sr<sup>3+</sup> ions on natural kaolinite and Clinoptilolite minerals (2005) pp.77.

## التداخل بين الكاؤولين والداي مثيل سلفوكسايد ( دراسة ترموديناميكية، حيود الأشعة السينية، طيف الأشعة تحت الحمراء ودراسة نانوية )

صبري محمد حسين      عمر حمد شهاب      ستار سالم إبراهيم

E.mail: [dean\\_coll.science@uoanbar.edu.iq](mailto:dean_coll.science@uoanbar.edu.iq)

### الخلاصة

تضمن البحث دراسة التداخل بين المركب العضوي القطبي ثنائي مثيل سلفوكسايد مع الكاؤولين بواسطة حيود الاشعه تحت السينية وطيف الاشعه تحت الحمراء. أظهرت نتائج الدراسة كون التداخل يعتمد على الحجم الحبيبي للكاؤولين وكون طبيعة التداخل تتم كنتيجة لتكوين أصرة هيدروجينية بين الثنائي مثيل سلفوكسايد ومجموعتي الهيدروكسيل العائدة للألمنيوم والسليكون على سطح الكاؤولين. تم دراسة تأثير درجة الحرارة على ثابت الامتزاز لصبغة المثلين الزرقاء في المحلول المائي للكاؤولين ومعقد الكاؤولين - ثنائي مثيل سلفوكسايد بواسطة استخدام ايزوثيرمات لانكمير وفريندليش. تم حساب المتغيرات الترموديناميكية ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) والتي أظهرت كون الامتزاز على سطح الأطيان العضوية المحضرة يكون تلقائي والتفاعل باعث للحرارة.