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APPLIED STUDIES AND MECHANICAL ANALYSIS OF THE SOILS AT MAKKAH AL- MUKARRAMAH AND RABIAGH CITIES AND THEIR POSSIBLE USES AS CATALYST.

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ABSTRACT

The twenty five selected air dried samples from the soils of the area between Makkah Al-mukarramah and Rabiagh cities were studied in details as catalyst. The sieving processes for the soil samples were carried out through different standard sieves in the 38-1000 μm range using the dry method. Samples number (4) and (1) from Rabiagh city were found to have the highest percentage of fraction which are less than 38 μm, therefore, sample (4) was chosen to study the catalytic effects on the polymeriation process. The polymerization of methyl methacrylate (MMA) and hydrolysis of methyl acetate reactions were studied in the presence of the treated Rabiagh sample (sample 4). It was found that the polymerization of MMA and hydrolysis of methyl acetate is increased with increasing the sample weight. This means that the rate of these reactions increased with increasing sample weight. Further studies on the kinetic polymerization of MMA and hydrolysis of methyl acetate reactions will be discussed later in a separate paper.

INTRODUCTION

Many synthetic and natural minerals are used in different purposes especially in chemical industries e.g., supported reagents **[Mc Killop, (1979)]** chromatographic separation **[Njopwouo, (1988)]**, catalysis for cracking for heavy oil **[Gonzjies, et al., (1999)]**

polymerization catalysis **[Al-Esaimi, (1997) and Moustafa, et al., (1976)]**, alkylation **[Njopwouo, (1988)]**, and condensation **[Azzouz, (1996)]**.

Mostafa et al. (1976) and Yamaguchi et al., (1974), reported the polymerization of methyl methacrylate in the presence of various metal oxides, sands and slags. The results indicates that the polymerization rates depend on the type of metal oxides used. Also, the data that the polymerization was performed at 30, 40, 50 and 60 °C using initior concentrations varying from 0.05 to 0.3 mol/L and the moleculear weights were determined viscosimetrically.

The aim of the present work is to study the mechanical analysis of the selected soils from the area between Makkah Al-mukarramah and Rabigh cities and the catalytic polymerization of methyl methacrylate (MMA) and hydrolysis of methyl acetate in the presence of the treated sample(4) from Rabigh city .

EXPERIMENTAL

Mechanical Analysis :

The selected soils from seven places in the area between Makkah Al-mukarramah and Rabigh cities Table (1) are investigated. The twenty five samples were taken from the soil depth ranging from 0– 20, 40–60, to 60–80 cm, dried in air and finely pass to a group of sieves ranging from 1000 to 39 μm (1000, 500, 250, 106, 90, 75, 53, 39 μm), for sieving using the dry method. Sample number (4) from Rabiagh city was grounded and then used for catalytic study experiments .

Materials:

MMA (Aldrich chemicals, LTD, England) stabilized with 0.1 % hydroquinone, was washed with sodium hydroxide.

The exchanged treated sample number (4) from Rabiagh city was prepared by standard ion-exchange method using solutions of $Al_2(SO_4)_3.12H_2O$ **[Al-Esaimi, (1992) and Al-Esaimi, (1997)]**. The exchanged sample was washed several times and then centrifuged before drying in a oven at 60°C for several days. It was then ground, sieved at 140 mesh (ASTM) and finally stored in a dry-air container.

Potassium persulphate ($K_2S_2O_8$) and methyl acetate were purchashed from BDH and used as initiator and a reactant, respectively.

Physical measurements:

Infrared absorption spectroscopy studies were carried out using KBr disc on a Pye Unicam Infrared spectrophotometer model (SP. 3-100) in the range 4000-600 cm^{-1} using KBr discs. The IR spectrometer was checked and calibrated using polyethylene film. X-ray powder diffraction (XRD) patterns were recorded using a Philips APD 1700 with Fe -filtered W K_α radiation .

Catalytic polymerization of MMA and hydrolysis of methyl acetate in presence of treated clay :

The reactions were carried out using the same method as reported earlier **[Al-Esaimi, (1992) and Al-Esaimi, (1997)]**. The conversion of polymerization was calculated using equation (1) :

$$\text{Conversion (\%)} = (Cp-C)\times 100 / M \qquad (1)$$

where Cp, C and M are the weight of the clay polymer composite, weight of clay and the weight of monomer, respectively, where the weight of MMA is 4.7g, but the calculations of the hydrolysis of methyl acetate were carried out using equation(2) :

$$\text{Conversion (\%)} = (Np/Nr) \times 100 \qquad (2)$$

where Np and Nr are the number of moles of the products and reactants, respectively, where the number of reactant moles is 0.102.

RESULTS AND DISCUSSION

Mechanical analysis

Table (1) represents the mechanical analysis of the selected soils from the area between Makkah Al-mukarramah and Rabiagh cities. The samples were taken from depth 0–20, 40–60, 60–80cm. The analysis indicates that the two samples from Rabiagh city number (4) and (1) have the highest percentage of the fine powder (less than 38 μm). Therefore, all further experiments such as XRD, IR and catalytic studies were carried out on sample (4) from Rabiagh city.

Table 1. Mechanical Analysis of the Soils For the Area Between Makkah-Al-Makmakarrma and Rabiagh cities.

Sample name	Number	The depth	>1000 µm	1000-500 µm	500-250 µm	250-106 µm	90-106 µm	90-75 µm	75-53 µm	53-38 µm	<38 µm
Usfan	1	0-20	1.60	3.19	16.37	99.77	16.61	19.17	23.30	16.31	3.49
	2	20-40	2.05	2.62	18.67	133.93	12.55	11.09	10.68	5.57	2.96
	3	40-60	8.10	15.30	25.10	103.1	9.20	13.20	13.4	7.20	5.00
Gdead	1	0-20	1.90	101.70	23.0	6.50	21.80	18.00	18.85	5.00	3.10
	2	20-40	13.0	21.5	66.7	71.80	8.00	7.00	2.20	8.50	1.00
	3	40-60	37.6	33.5	78.6	39.20	3.20	2.40	3.60	1.20	0.50
Khulays	1	0-20	1.30	5.50	53.90	92.9	13.70	13.00	12.50	5.20	1.70
	2	20-40	1.20	2.80	29.20	124.1	9.60	6.50	4.30	1.20	0.80
	3	40-60	1.00	2.00	41.40	112.7	13.6	10.60	13.20	4.20	1.80
Alkamal	1	0-20	35.00	41.50	24.60	39.00	10.36	13.19	23.20	10.00	3.00
	2	20-40	23.50	33.70	28.40	68.80	16.70	9.90	10.60	5.50	2.60
	3	40-60	21.00	30.50	39.50	69.00	11.8	10.40	11.30	5.20	1.00
Saaber	1	0-20	24.2	28.10	34.00	5.10	19.00	18.10	62.80	7.50	1.00
	2	20-40	12.00	27.20	42.20	74.4	13.50	11.20	9.00	9.00	1.30
	3	40-60	15.00	32.90	45.50	65.5	13.00	12.00	11.90	2.80	1.00

Table 1. Continued.

Sample name	Number	The depth	>1000 µm	1000-500 µm	500-250 µm	250-106 µm	90-106 µm	90-75 µm	75-53 µm	53-38 µm	<38 µm
Rabiagh	1	0-20	56.50	19.20	30.50	55..50	14.00	8.80	8.30	4.70	4.70
	2	20-40	67.50	24.80	32.80	48.50	7.50	5.80	3.80	4.50	4.50
	3	40-60	62.80	24.70	32.80	49.20	8.70	7.10	6.50	4.50	4.50
	4	0-20	71.80	35.30	19.80	-	40.80	10.50	5.50	5.70	5.70
	5	20-40	112.80	38.26	20.40	15.91	2.76	3.03	3.83	2.17	2.17
	6	40-60	118.90	37.66	19.37	13.55	1.98	3.23	2.60	1.92	1.92
Nouryah	1	0-20	24.60	28.60	33.80	73.20	9.50	9.40	11.80	5.90	2.80
	2	20-40	32.60	31.60	38.20	70.50	7.60	6.70	7.00	3.80	1.60
	3	40-60	86.29	24.48	28.13	46.48	3.96	3.44	3.45	2.14	1.57
	4	0-20	-	1.00	88.90	103.90	3.40	1.50	5.70	0.30	-

Characterization

X-ray diffraction (XRD)

The x-ray diffraction pattern in figure(1) for clay fraction of Rabiagh sample number (4) shows that the Kaolinite is the most abundant mineral component with lesser amounts of saponite, muscovite, and clinochlore. Kaolinite was identified by the diffraction peaks at 12.3, 100%; 19.8, 3.33%; 25.5, 50.0%, clinochore at 3.5, 26.67%; 24.7, 16.2% saponite at 10.5, 41.67%; 19.1, 20.0%; 28.7, 48.9%; muscovite at 7.2, 30.0%; 20.1, 6.65% **[Yamaguchi, et al., (1974) and Yamagishi, (1985)]**. The XRD data suggests that sample (4) contains a mixture of clay minerals.

Infrared spectroscopy :

The IR spectrum of sample 4 (figure 2) is dominated by several bands at 3697 and 3620 cm^{-1}**[Van der Marel & Beutelspacher (1976) and Wilson, (1990)]** together with supporting bands at about 700, and 800 cm^{-1}. Also, the spectrum shows a broad doublt band of chlorite at 3500 and 3420cm^{-1} and then broading at 3620 cm^{-1}. The observation of a weak bands at 825, and 750 cm^{-1} may suggest the presence of muscovite.

Catalytic studies

Effect of weight of catalyst

Polymerization of methyl methacrylate was studied in the presence of different of weights (2.0, 1.5, 1.0, 0.50, 0.25) of the treated Rabiagh clay and in the absence of catalyst to the reaction mixture using 0.03 mol/L of potassium persulfate at 60°C for 3hrs. Tables (2-3) show the conversion of methyl acetates and MMA at different weights. Figures (3-4) indicate that the conversion reaches a limiting value at 0.5g of catalyst in polymerization of MMA and hydrolysis of methyle acetate.

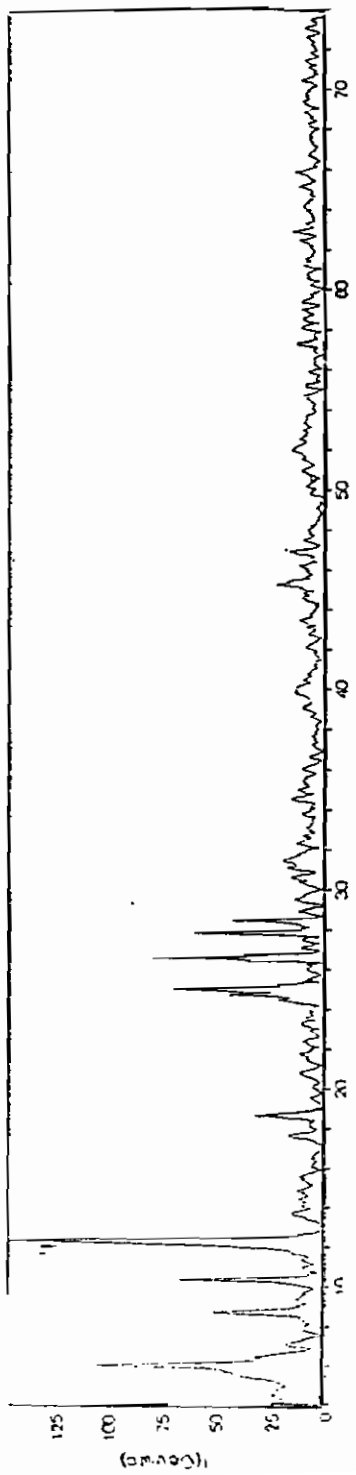


Figure 1 X-ray diffraction pattern of treated sample from Rabigh

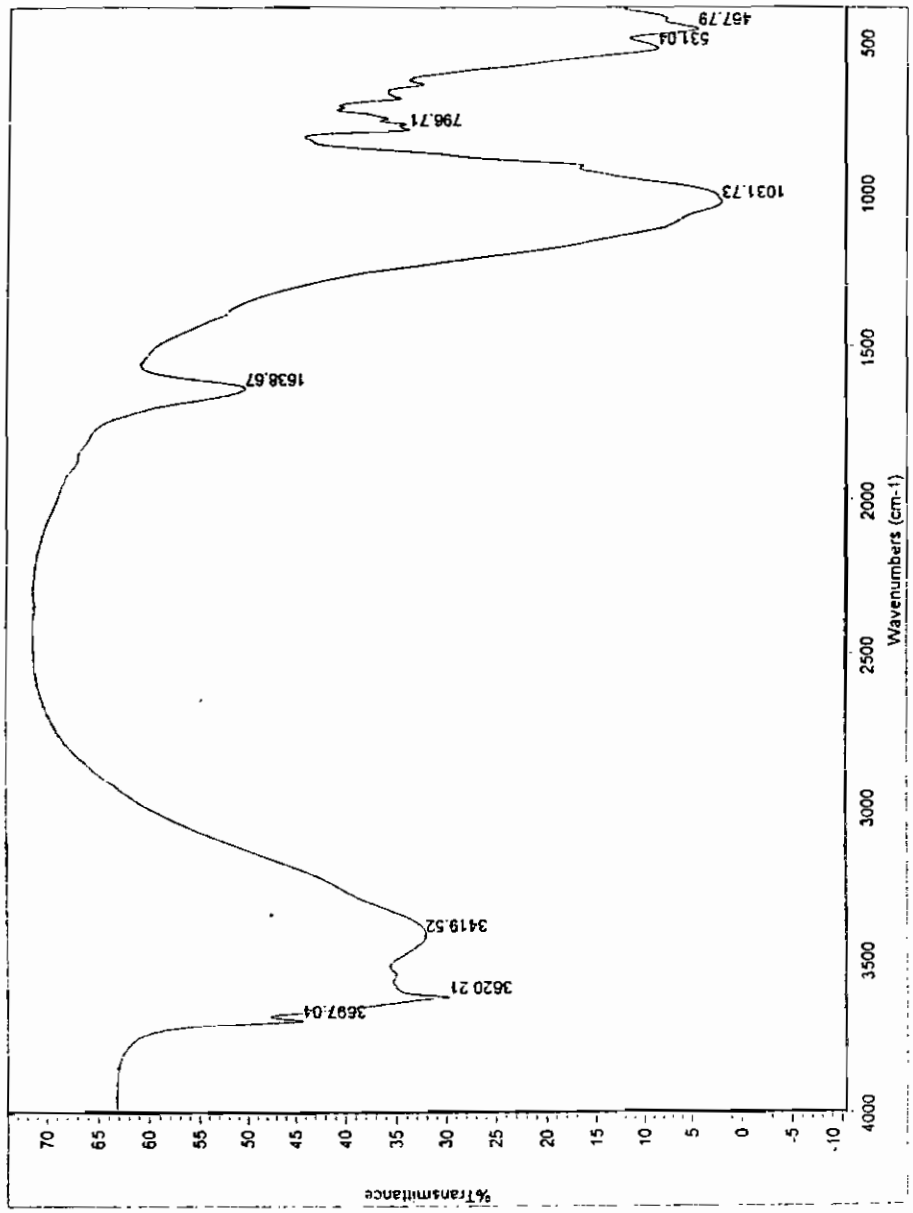
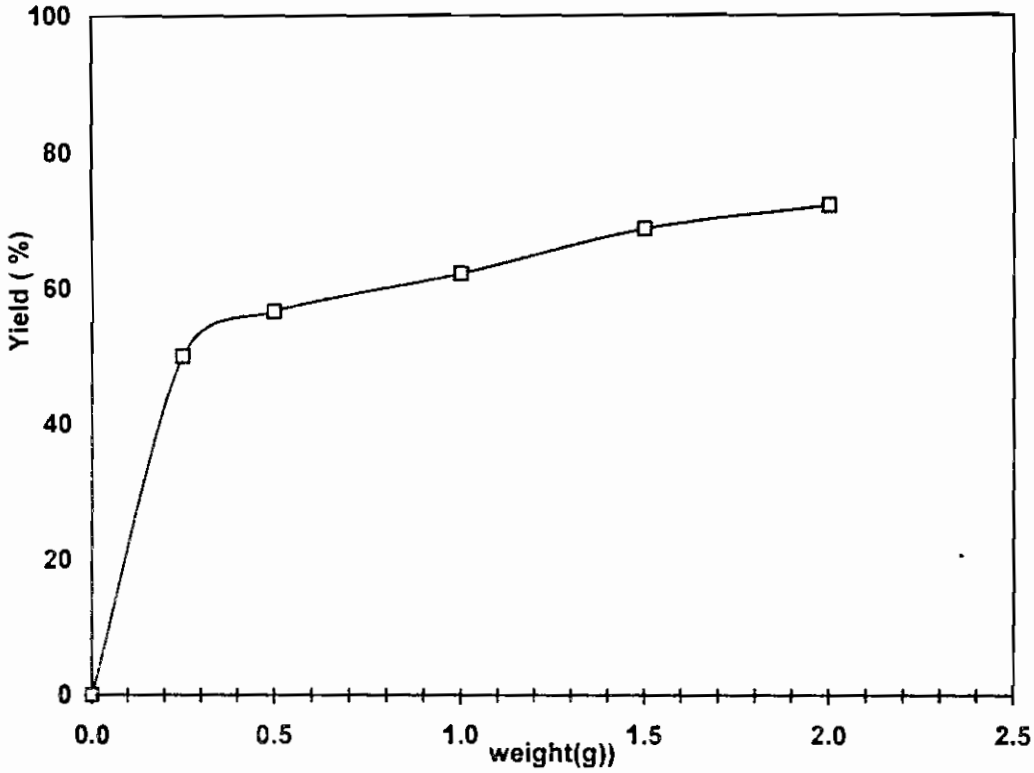
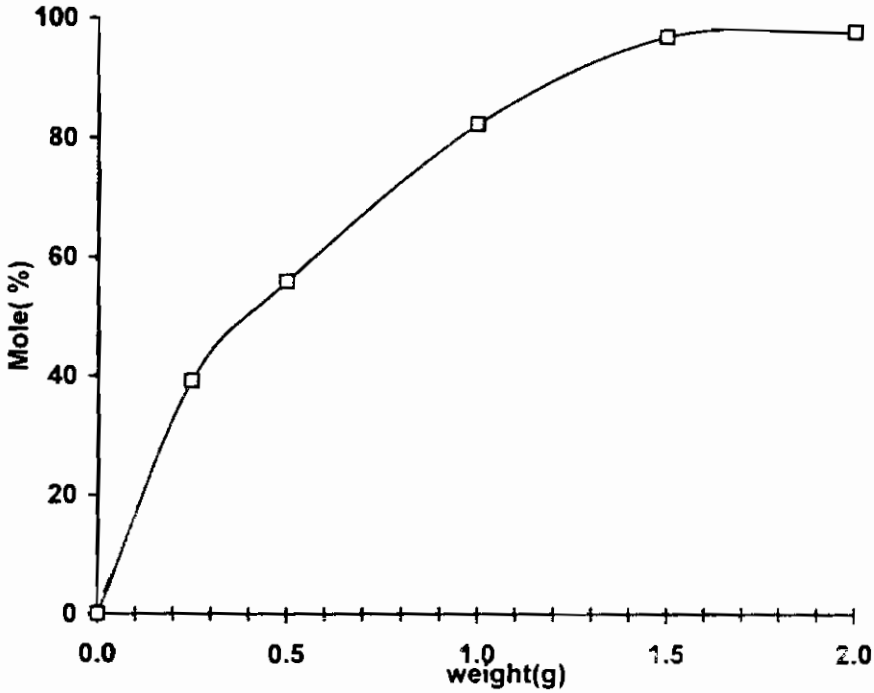


Figure (2) IR spectrum (600 - 4000 cm^{-1}) for treated sample from Rabigh



Figure(3) Effect of weight of treated clay from Rabiagh on the yield of Polymerization of MMA with 0.03 mol/L $K_2S_2O_8$ at 60^O C for 4h.



Figure(4) Effect of weight of treated clay from Rabiagh on the yield of hydrolysis of methyl acetates at 60^{O} C for 4h.

Table (2): The effect of weight of Rabiagh sample on polymerization of MMA.

Catalyst weight (g)	Product weight (g)	Weight (%) of product
0.00	2.05	43.6
0.25	2.35	50.00
0.50	2.66	56.60
1.00	2.92	62.20
1.50	3.22	68.50
2.00	3.39	72.12

Table (3): The effect of weight of Rabiagh sample on hydrolysis of methyl acetate

Sample Name Rabiagh (wt. in gram)	Mole Methyl acetate	(conversion %)
0.25	0.040	39.2
0.50	0.057	55.9
1.00	0.084	82.4
1.50	0.099	97.06
2.00	0.100	98.0

CONLUSIONS

XRD diffraction (XRD) and infrared spectroscopy (IR) *analysis of the* treated Rabiagh *sample was found to have* a mixture of different clay minerals such as Kaolinite (majour) *and little* of saponite, muscovite, and clinochlore. The *polymerization of MMA using potassium persulfate as initiator and* the hydrolysis of methyl acetate *increases by increasing weight* of the treated Rabiagh *sample which is used as a catalyst.* This indicates that the mixture of the clay minerals can be used as catayst in the polymerization of MMA. Therefore, further invetigation of kinetic polymerization of MMA and hydrolysis of methyl acetate reactions will be discussed in the next study.

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REFERENCES

Al-Esaimi, M.M., "Catalytic processes induced by modified-exchanged Montmorillonite", Ph.D. Thesis, University of Wales (Swansea), (1992).

Al-Esaimi, M.M., J. Appl. Polym .Sci., 64,367-372 (1997).

Azzouz, A., Dumitru,E., Hulea,V., Catrinescu,C., Carji,G., Prog.Catal, 5(1),1996.

Gonzjies, F., Pesquera, C., Benito, Hrrero, E., Pncio, C., and Appl.Catal, 181A ,1,71, (1999).

Lenarda, M., Straro, L., Pellegrini, G., Piovesan, L., and Ganzerla, R., J.Mol. Catal., A, 237, (1999).

Mc Killop, A., Young, D.W., Clay Minerals, 481, (1979).

Moustafa, A.B., Nosseir, M.H. and Nashed, N.E., Makromol. Chem., 52(1), 71, (1976).

Njopwouo, D., Roques, G., Wandji, R., 23, 35, (1988).

Yamaguchi, T., Tanaka, H., Moustafa, A.B., Ono, T., Ito, H., Itabashi, O., Endo, M., Ohuchi, M. and Saito, L., Chemistry and Industry, 619, (1974).

Yamagishi, A., "Use an Organic–Clay Mineral Complex For Chromatographic Separation of Optical Isomers., Prod. Inter .Clay Conf., Denver, 329-334, (1985).

Van der Marel, H.M, and Beutelspacher, H., "Atlas of Infrared Spectroscopy of Clay Minerals and Their Admixtures" (1976).

Wilson, M.J., "A Handbook of Determinative Methods in Clay Mineralogy" (1990).

سلسلة الدارسات التطبيقية على تربة المملكة العربية السعودية

أ – التحليل الميكانيكي لعينات تربة مكة المكرمة – رابغ
وامكانية الإستفادة منها كعوامل حفز.

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** جامعة ام القرى – كلية العلوم التطبيقية –قسم الكيمياء – مكة المكرمة –ص.ب ٤٤٩٦

تم اخذ خمس وعشرون عينة من العينات المنتقاة من ست مواقع من المنطقة المحصورة بين مدينة مكة المكرمة ومدينة رابغ وجففت هوائيا وتم نخلها من خلال مجموعة من المناخل القياسية بين ٣٨ – ١٠٠٠ ميكرون (بالطريقة الجافة). ومن التحليل الميكانيكي وجد أن هناك عينتين من عينات التربة تحت الدراسة بهما نسبة عالية أقطار حبيباتهما اقل من ٣٧ ميكرون . وقد وجد أن عينه رقم (٤) تزداد نسبة هذا الجزء حوالي ٥٠ % بعد طحنها. وتم استخدام هذه العينة فيما بعد في الدراسة الحفزية. وحيث تم اختيار بلمرة ميثيل ميثااكريلات والتحلل المائي لتفاعل خلات الميثيل في وجود عينة معالجة من رابغ لاختبار الخاصية الحفزيه لها. وجد أن تفاعل البلمرة للميثيل ميثااكريلات والتحلل المائي لتفاعل خلات الميثيل تزداد بزيادة وزن العينة المضافة لخليط كلا هذين التفاعلين لمزيد من الدراسة لهذه التفاعلات في وجود هذه العينات كحوافز سنتناولها بمشيئة الله في الأبحاث القادمة.