



Interactions Investigation of New Composite Material Formed from Bauxite and Melamine-Urea Formaldehyde Copolymer

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Abstract

In this study the Bauxite has been activated and used to prepare two complexes: Bauxite - urea and Bauxite - melamine, these complexes were merged and polymerized with formaldehyde to prepare the complex Bauxite polymer - urea - melamine - formaldehyde (modified Bauxite). In the Bauxite-urea complex XRD results indicate that the urea molecules penetrate among the layers of the crystal plane (110) of the Gibbsite mineral while in the Bauxite-melamine the interaction was at the outer surface of the Bauxite forming minerals because the relatively large volume of the melamine molecule. FT-IR results show the interaction of these two bases with Bauxite was mainly based on the hydrogen bonding and in less extent on the coordination between N loan pair atom and aluminum empty orbital in the above complexes. Finally the copolymer was formed around the micro-crystals of Bauxite minerals.

Key words: Bauxite, Composite Bauxite, X-Ray, SEM, AFM, FT-IR.

Introduction

Mineral-polymer composites have attracted large attention over the past thirty years in both applied and academic fields [1]. These materials occupy wide area in plastic industry, pollution treatment, insulators, and others [2, 3]. The discoveries of their characteristic structure at the nano scale carry additional latent applications seems in the horizon, this made them as a one of most important materials in the near future[4, 5]. The key step to reach this goal is learning how to functionalize a certain part of nano-crystals of minerals or utilize from their nano-scaled frames in the fabrication of new types of projected materials. Bauxite considered as one of the aluminum ores formed mainly from Gibbsite and Boehmite minerals. Bauxite is produced in large amounts as waste in alumina production so finding method to utilize of it is considered an important subject from economic point of view [6]. The aim of this work is synthesis of composite from Bauxite with urea-melamine formaldehyde copolymer then determine the way by which the polymer bind to Bauxite .

Experimental part

This study used the following devices: 1-Double beam UV- visible spectrophotometer type Shimadzu.1800,Japan. 2- FT-IR spectrometer type Shimadzu. I Raffinity-1(8400 s).3-A water bath 4.Balance(0.0001 g \pm) type Sartorius Lab. BL 210 S, Germany.4-laboratory oven type Daihan Labtech Oven LDO - 060E. 5-X-ray diffraction device Shimadzu 6000. 6-Atomic force microscope AFM- SPM AA3000 USA 20089.7-scanning electron microscope SEM. 8-microwave device. The chemicals used were (melamine from BDH, urea from Hannover, solution of formaldehyde and hydrochloric acid from Reidel-De Haen). The Bauxite is from the General Company of Geological Survey in Iraq.

Bauxite preparation: Bauxite was crashed into small pieces using a metal grinder milled using a ceramic mortar then wash several times with distilled water after that flooded with distilled water for 48 hours and finally washed using sexholet device to remove most of the adsorped ions. Bauxite dried in thermal oven at 90 C° for four hours, then re-grinding again and sieved to particle size less than 150 μ m. **Complexes of Bauxite–Melamine and Bauxite-Urea preparation:** Each complex was prepared by blending(20 gm)of Bauxite with(4 gm)of organic compound then placed in a mortar with the addition of two drops of distilled water to the mixture to complete the over lap process, the blending reached half an hour then left for 10 days in an airtight container to complete the interaction. **Preparation of (Bauxite -urea - melamine -formaldehyde) copolymer:** The polymerization proceed by mixing (20 gm) of BM complex and (20 gm) BU complex with (8.1 ml) of formaldehyde solution and (4 ml) of distilled water, all the materials were put in the mortar and blended with adding 8 drops of hydrochloric acid, this process will continue for half an hour with continuous stirring the mixture was then placed in a water bath at a temperature ranging between 90-100C° for five minutes where the material start to lose some water and hardening. The resulting rigid material was grinded and placed in a microwave for a minute (to homogenize the polymerization process in the sample, after cooling, the dry material returned to the microwave for a minute to make sure of the polymerization process is completed.

Discussion

The surfaces of Bauxite and modified Bauxite were characterized using X-ray diffraction (XRD), infrared spectrometry (FT-IR), atomic force microscope (AFM) and scanning electron microscopy (SEM). In addition XRD and FT-IR techniques have been used to characterize the Bauxite complexes with urea and melamine as well. The unit cell parameters of Bauxite main minerals Gibbsite and Boehmite were identified from figure(1) then listed in table(1), the values that tabulated agree with those reported in reference [7-8]. Unit cell parameters for

Gibbsite were $a = 8.75 \text{ \AA}$, $b = 5.075 \text{ \AA}$, $c = 9.65 \text{ \AA}$, and for Boehmite were. $a = 3.71 \text{ \AA}$, $b = 12.2 \text{ \AA}$, $c = 2.90 \text{ \AA}$. The value of d (which represents the distance between the crystal planes) has been calculated from Bragg's Law [9]

$$2d\sin\theta = n\lambda \dots \dots \dots (1)$$

Where (λ) represents the wavelength of X-ray radiation, n constant takes the value = 1, 2, 3.... (d) represents the distance between crystal planes and (θ) represents the diffraction angle of X-ray radiation. It is observed in figure (2) which belongs to Bauxite-urea complex the occurrence of displacement or expansion of the crystal plane (110) of Gibbsite mineral by 0.09 \AA , this displacement also exists in high order diffractions of this plane (220) and (330) this displacement did not take place in the case of Bauxite-melamine complex as shown in figure (2) which may be explained by the small size of the urea molecule which can penetrate between the layers of this crystal plane, while melamine molecule cannot penetrate because of the large size of the molecule. The crystal planes (210) and (012) that belong to Gibbsite mineral incorporated into one crystal plane. The crystal displacements in Boehmite mineral were small in both complexes with urea and melamine, this can be explained by the fact that the Gibbsite mineral which has greater content of hydroxyl groups [10] has greater opportunity to interact with organic compounds through hydrogen bonding, as well as the hydroxyl groups gives more flexibility to the layers of the mineral to stretch and receive small molecules that can overlap [11]. In the formation of modified Bauxite with urea-melamine-formaldehyde copolymer complex the XRD pattern that shown in figure (4), it is observed the return most of the crystal planes especially for Gibbsite (110) plane and its higher order diffractions to their native locations with a decrease in intensity of the diffraction bands of these planes and increase the amorphous character of the sample which can be explained by the fact that urea molecules that have been penetrated between layers of crystal plane (110) in Gibbsite were unable to stabilize in these positions during polymer formation so the polymerization worked to pull out the urea molecules, hence the polymer formed outside the crystal planes of Bauxite minerals (i.e. around the microscopic crystals of Bauxite mineral), for this reason the polymer growth works to close the active sites on the surface of the crystals and to saturate them. AFM image of Bauxite figure (5) and table (2) show that the particle size distribution of the of the Bauxite granular size of less than $150 \mu\text{m}$ ranging from (75-130 nm) this distribution of the size represents the growth limit of Bauxite micro-crystals. The passage of these crystals from the sieve of $150 \mu\text{m}$ diameter does not necessarily mean that the growth of these crystals was reached the diameter of $150 \mu\text{m}$, indeed this diameter represents the accumulation diameter of the individual micro-crystals [12]. It is noted in the picture there are two types of varying sizes of crystals, the first type has large sizes with percent of 31.08% and has diameters ranging from (110-125nm) belonging to the Gibbsite mineral. The second type is of small sizes with percent of 37.82% and diameters ranging from (80-90nm) belonging to the Boehmite mineral. The reason behind the growth of Gibbsite crystals to large size with a few numbers is due to the presence of a large proportion of crystallization water, which works to connect the largest number of unit crystal cells to form large crystals with few numbers [13].

In the case of Boehmite mineral the possibility of accumulation is small because the crystallization water content is less than that in Gibbsite [14], therefore, Boehmite crystals do not grow to large volumes where the crystal growth diameter reach 85 nm , but the number of these units will be larger. The SEM images figures (7 and 8) prove that the orthorhombic crystals are smaller with large number, these belong to the Boehmite mineral, while the mono-clinic crystals which is the largest size but have least number belong to Boehmite mineral [7]. Figures (9), (10), (11), (12), (13) and (14) show FT-IR spectrums for Bauxite, urea, Bauxite-urea complex, melamine, Bauxite-melamine complex and modified

Bauxite respectively, table (2) shows the most important peaks for above materials. In Bauxite-urea complex (BU) there is a shift stretching vibration for NH_2 that belongs to the urea towards a higher frequency $3428\text{-}3441\text{ cm}^{-1}$, this means the force constant of this bond increases due to the appearing electronic positive charge on the N atom through the contribution of its lone pair by a some kind of bonding such as with acidic protons on the surface of Bauxite or coordination bonding with empty aluminum orbital exposed Al atom within the crystal lattice of Bauxite [15-16]. The appearance of the positive charge on the nitrogen atom works to consistently increase the strength of the bonds of NH through affinity electron density of the bond towards the positively charged nitrogen atom, leading to compression of the bond and thus its force constant increases its strength. This happens for both frequency symmetric and anti-symmetric of NH_2 group, this assumption supported by shifting the stretching frequency of OH group which existed on the surface of the Bauxite towards a lower frequency of $3620\text{-}3618\text{ cm}^{-1}$ which shows the contribution of the proton of OH with bonding led to the weakening of OH bond and thus increases the length of it. As well as the group AlOH this shifted toward the lower frequency of $3690\text{-}3680\text{ cm}^{-1}$. For the Al-O-Al group which belongs to structural core of Bauxite exhibit a split to two bands, the first one displaced to the lower frequency by 10 cm^{-1} , while the other displaced to a higher frequency by 20 cm^{-1} , it is clear that the part that displaced toward the lower frequency is due to Al-O-Al groups that have entered a kind of coordination bonding or hydrogen bonding with NH_2 group that belongs to NH_2 group of urea molecule where it played the role of the donor group lone pair while Al-O-Al played the role of the receptor for this lone pair. Note, Al-O-Al group can contain a proton linked to mediated oxygen atom. This acidic proton could become the center of the bonding with NH_2 group. The reason of displacement towards a higher frequency returns to the positioning of the acidic protons that exist on the Bauxite surface on a few number of AlOAl centers, this means that the positive charge spreads over a less number of centers which leads to the appearing of more dense positive charge on non-bonded Al-O-Al centers with urea resulting in increase in the strength of these bonds and shifting of their vibration toward a higher frequency [17-18]. For the same reason there is an increase of strength for the bonds force constant Al...OH which shifted toward a higher frequency. The above discussion was supported by shifting the vibration frequency for CN group of urea molecule towards lower frequency as a result of the contribution of N lone pair by bonding with functional groups on the surface of Bauxite instead of entering a resonance with neighboring carbonyl group, in addition there is no change in stretching vibration of the carbonyl group which indicates it did not interact with functional groups that exist on the surface of Bauxite. For the Bauxite complex with melamine BM, the general aspects of its complex with urea are similar, especially the terms of the behavior of NH_2 groups belonging to the melamine molecule, as well as the behavior of groups Al-O-Al, and AlOH and OH on the surface of Bauxite. The $\text{C} = \text{N}$ groups located within the melamine ring pushed towards a lower frequency of $1535\text{-}1512\text{ cm}^{-1}$, also the CN group shifted towards lower frequency of $1462\text{-}1450\text{ cm}^{-1}$ due to the contribution of N lone pair by bonding with Bauxite surface functional groups.

Finally in the complex of Bauxite-Urea-Melamine-Formaldehyde copolymer there are following points.

- 1- Return of vibration frequencies of the AlOH and OH belonging to the surface of Bauxite to their original locations.
- 2- The vibration frequencies of different kinds of NH_2 groups have changed their values but remained within the range of $3269\text{-}3522\text{ cm}^{-1}$.
- 3- The appearance of aliphatic CH groups stretching vibration that come from formaldehyde at 3092 cm^{-1} and 2903 cm^{-1} .
- 4- The appearance of aldehydic $\text{C} = \text{O}$ group belonging to formaldehyde at 1742 cm^{-1} .

- 5- For C = N melaminic group note that after the decrease of its frequency in a Bauxite-Melamine complex it returned to raise strongly after the formation of the polymer complex which means that the NH₂ lone pair that was engaged with the surface Bauxite functional groups became more free to incorporate by a resonance with aromatic ring this led to the increase C = N groups order so it appears at 1541 cm⁻¹.
- 6- In Al-O-Al groups note the disappearance of the fission to some extent, on the other hand there is increase of its rank even higher than in the Bauxite alone and this means that the protons that come from polymerization acidic environment were bonded with groups Al-O-Al belonging to the Bauxite surface more than they do with NH₂ groups returning to the polymer segments this due to their blocking by steric factor. On the other hand, the formation of the polymer, who has worked on break the bonding of basic amine groups with Bauxite surface active groups led to get the field to link Al-O-Al groups with the protons that come from the acid used in the polymerization and thus increasing the positive charge on the surface and appearing of their vibration in the highest frequency at 1011cm⁻¹.
- 7- The Al ... O-H groups return back to their original position before polymerization.

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Table (1) :XRD peaks and Miller indices of Bauxite minerals

Number of peak	Gibbsite				Boehmite			
	2θ	hkl	d-spacing	2d	2θ	hkl	d-spacing	2d
1	18.30	[010]	4.8384	9.6768	14.4	[020]	6.1412	12.2823
2	20.3	[110]	4.3677	8.7353	28.2	[120]	3.1595	6.3190
3	24.5	[012]	3.6276	7.2552	38.3	[031]	2.3464	4.6927
4	24.8	[210]	3.5844	7.1688	47.9	[131]	1.8961	3.7922
5	25.2	[201]	3.5284	7.0568	48.9	[051]	1.8597	3.7193
6	36.3	[120]	2.4709	4.9418	49.2	[200]	1.8490	3.6980
7	37.6	[121]	2.3884	4.7768	52.1	[220]	1.7527	3.5054
8	40.1	[022]	2.2451	4.4902	55.1	[151]	1.6642	3.3283
9	41.6	[220]	2.1675	4.3351	60.5	[080]	1.5279	3.0558
10	44.1	[410]	2.0503	4.1006	64	[231]	1.4525	2.9051
11	45.4	[402]	1.9945	3.9891	67.6	[171]	1.3837	2.7673
12	47.3	[320]	1.9188	3.8375				
13	50.5	[403]	1.8044	3.6089				
14	51.6	[500]	1.7685	3.5370				
15	54.3	[030]	1.6868	3.3736				
16	63.7	[330]	1.4586	2.9173				
17	64.9	[331]	1.4345	2.8691				
18	66.1	[233]	1.4114	2.8228				

Table (2): Characteristic bands of FT-IR spectra for Bauxite, urea, melamine, Bauxite-ureaBauxite-Melamineand modified Bauxite

Bauxite					
Assignment groups	Al...OH stretch	O-H stretch	H ₂ O bending	AlOAl stretch	Al...O-H stretch
Wave number (cm ⁻¹)	3690	3620	1655,1628	1009	914
Urea					
Assignment groups	-NH ₂ asy. stretch	-NH ₂ sym. stretch	-NH ₂ (H-bond)	C=O stretchig	C-N stretching
Wave number (cm ⁻¹)	3428	3329	3256	1676	1460
B-U complex					
Assignment groups	Al...OH stretch	O-H stretch	-NH ₂ asy. stretch	-NH ₂ asy. stretch	-NH ₂ sym. stretch
Wave number (cm ⁻¹)	3680	3618	3441	3441	3372
Assignment groups	C=O stretchig	C-N stretching	AlOAl stretch	Al...O-H stretch	
Wave number (cm ⁻¹)	1676	1458	1030,999	924	
Melamine					
Assignment groups	-NH ₂ stretch	C=N stretching	C-N stretch		
Wave number (cm ⁻¹)	3414,3327, 3120	1641,1535	1462		
B-M complex					
Assignment groups	Al...OH stretch	O-H stretch	-NH ₂ stretch	C-N stretch	AlOAl stretch
Wave number (cm ⁻¹)	3680	3618	3360	1450	1031,995
Assignment groups	Al...O-H stretch				
Wave number (cm ⁻¹)	925				
P-BUM complex					
Assignment groups	Al...OH stretch	O-H stretch	-NH ₂ stretch	C-H stretch	C=O stretchig
Wave number (cm ⁻¹)	3690	3620	3269-3522	2903	1741
Assignment groups	C=N stretching	AlOAl stretch	Al...O-H stretch		
Wave number (cm ⁻¹)	1541	1011	910		

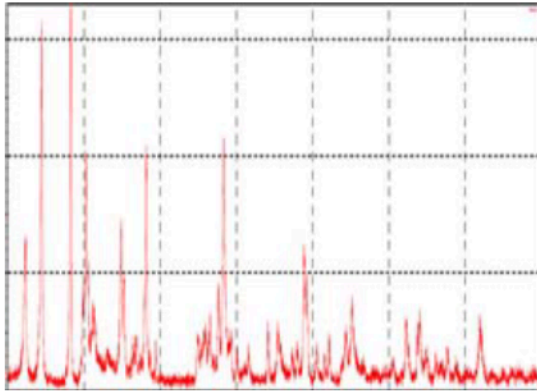


Figure (1): XRD pattern of the Bauxite

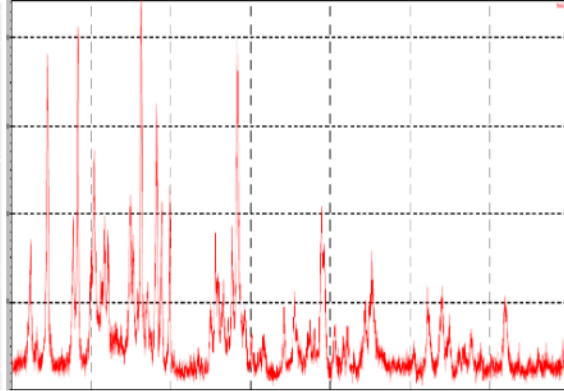


Figure (2): XRD complex scheme to Bauxite with melamine

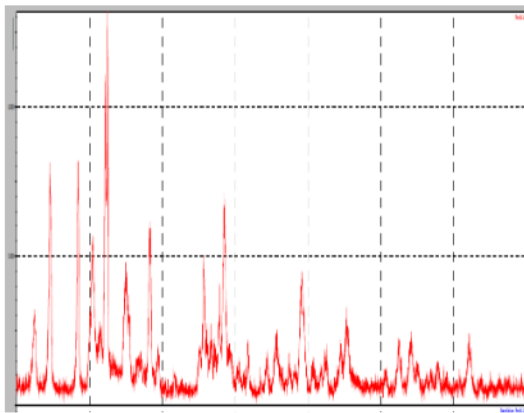


Figure (3) :XRD scheme for Bauxite complex with urea

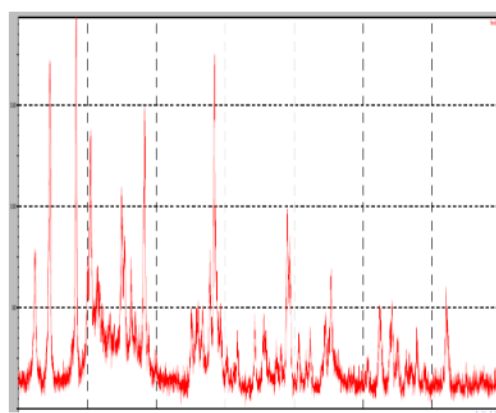


Figure (4): XRD scheme Bauxite average (polymer) before adsorption

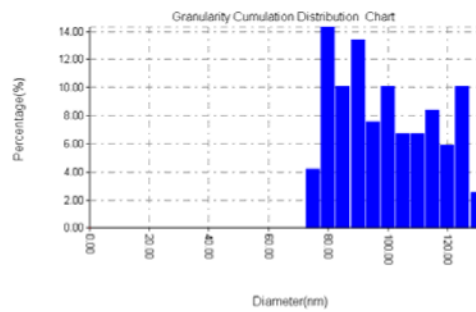
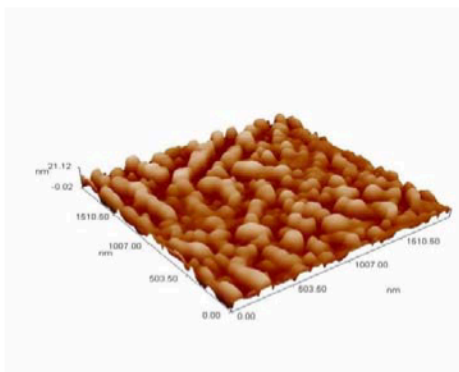


Figure (5): AFM image of the surface of Bauxite

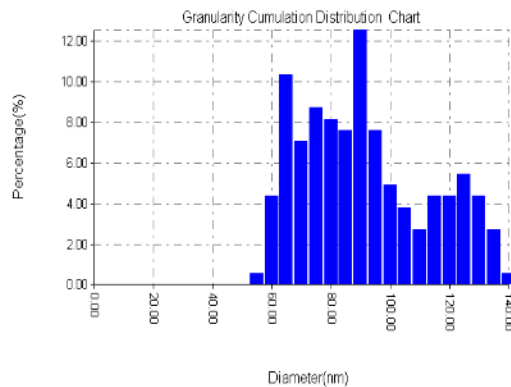
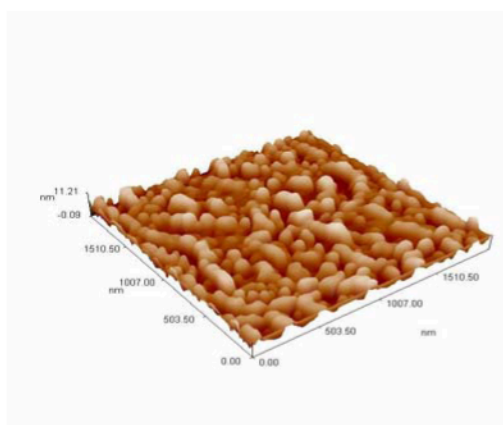


Figure (6): AFM image of the surface of the modified Bauxite

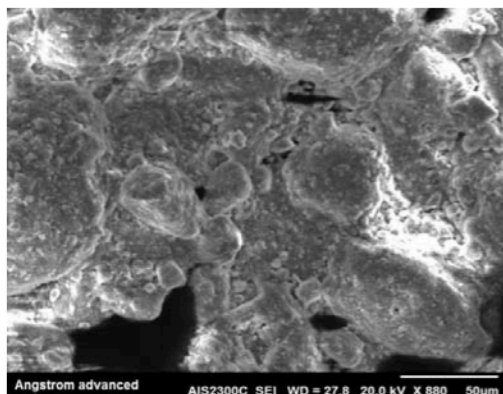


Figure (7): SEM image of the Bauxite surface

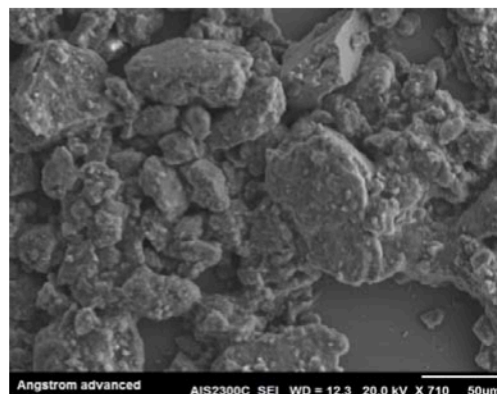


Figure (8): SEM image of the modified Bauxite surface

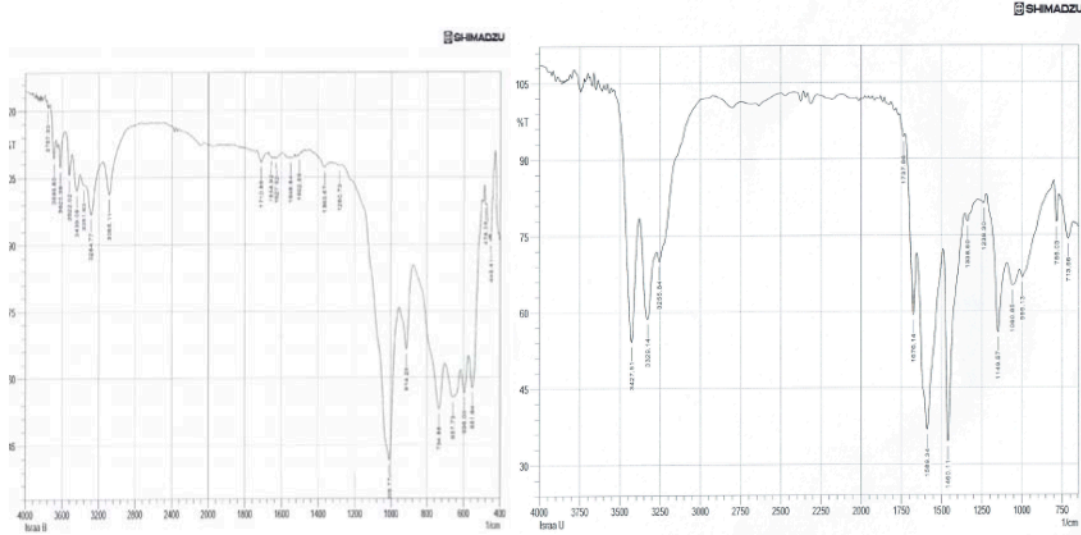


Figure (9): infrared spectroscopy(FT-IR)to the surface of the Bauxite

Figure (10): infrared spectroscopy(FT-IR) urea

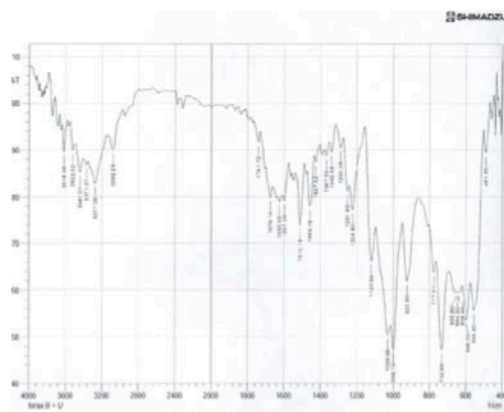


Figure (11): Infrared spectroscopy (FT-IR)of Bauxite-Urea

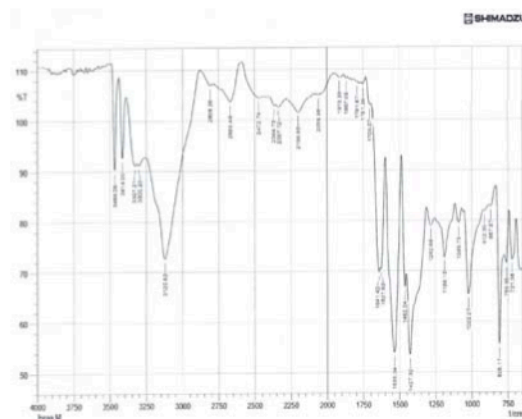
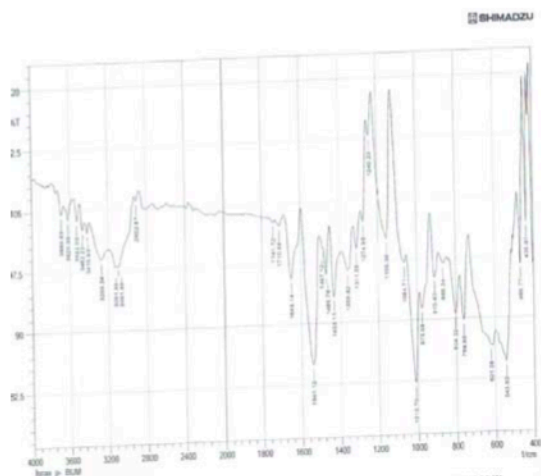


Figure (12): Infrared spectroscopy (FT-IR)of melamine



Figure(13): Infrared spectroscopy(FT-IR)ofBauxite–Melamine complex



**Figure (14) :Infrared spectroscopy(FT-IR)of Bauxite copolymerurea-Melamine-
Formaldehyde complex**

استقصاء التداخلات في مادة مركبة جديدة محضرة من البوكسايت مع البوليمر المشترك ميلامين-يوريا فورمالديهايد

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تقي الدين عبد الهادي حمدان
قسم الكيمياء/كلية التربية للعلوم الصرفة/ (ابن الهيثم) /جامعة بغداد

استلم في: 17/أيلول/2015، قبل في: 12/تشرين الأول/2015

الخلاصة

في هذه الدراسة تم تنشيط البوكسايت واستعماله لتحضير معقدي: البوكسايت-اليوريا والبوكسايت -الميلامين، تم دمج هذه المعقدات وبلمرتها مع الفورمالدهايد لإعداد معقد البوكسايت بوليمر-اليوريا-ميلامين-الفورمالديهايد(البوكسايت المعدل). في معقد البوكسايت-اليوريا بينت نتائج XRD إلى ان جزيئات اليوريا تتخلل بين طبقات المستوي البلوري (110) لمعدن الجبسايت بينما في معقد البوكسايت-الميلامين فقد اقتصر التداخل على السطح الخارجي للمعادن المكونة للبوكسايت بسبب الكبر النسبي لحجم جزيئة الميلامين. أظهرت نتائج FT-IR ان تداخل هذه القواعد مع البوكسايت استند أساسا على الرابطة الهيدروجينية و بدرجة أقل على التناسق بين المزوج الالكتروني لذرة النيتروجين مع الاوربتال الفارغ لذرة الألمنيوم في المعقدات المذكورة أعلاه. وأخيرا فان تكون البوليمر تم على حول البلورات المجهرية لمعادن البوكسايت.

الكلمات المفتاحية: البوكسايت , البوكسايت المضغوط , حيود الاشعة السينية , المجهر الالكتروني الماسح , مجهر القوى الذري , مطيافية الاشعة تحت الحمراء