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

Israa M. Radhi
Yousif I. Mohammed
Takialdin A. Himdan
Dept. of Chemistry/ College of Education for Pure Science (Ibn Al- Haitham)/
University of Baghdad

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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 usedthe followingdevices: 1-Double beam UV- visible spectrophotometer type Shimadzu.1800,Japan. 2- FT-IR spectrometertypeShimadzu. Iraffinity-1(8400 s).3-A water bath4.Balance(0.0001 g ±) type Sartorius Lab. BL 210 S, Germany.4-laboratoryoventypeDaihanLabtech Oven LDO - 060E. 5-X-ray diffraction device Shimaduz 6000. 6-AtomicforcemicroscopeAFM- SPM AA3000 USA 20089.7-scanning electronmicroscopeSEM. 8-microwavedevice.Thechemicalsused 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^{o} for four hours, then re-grinding again and sieved to particle size less than 150µm. 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 amortar with the addition of two drops of distilled water to the mixtureto complete the over lapprocess, the blending reached half an hour then left for10 daysinan 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^{o} 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 Å, b = 5.075 Å, c = 9.65 Å, and for Boehmite were. a = 3.71 Å, b = 12.2Å, c = 2.90 Å. The value of d (which represents the distance between the crystal planes) has been calculated from Bragg's Law [9]

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

Where (λ) representsthe 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 Å, 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-melamineformaldehyde 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 thier. 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 150μm 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 150μm diameter does not necessarily mean that the growth of these crystals was reached the diameter of 150 μm, 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 85nm, 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 complexand modified

Bauxiterespectively,table(2) shows themost importantpeaks for above materials.In Bauxite-ureacomplex (BU) there is a shiftstretching vibrationforNH_2 that belongs to theureatowardsa higher frequency 3428-3441 cm^{-1}, this means the force constant of this bond increases due to the appearingelectronicpositive chargeon the N atomthroughthe contribution of its loan pair by a some kind of bonding such as with acidic protons on the surface ofBauxiteorcoordination bondingwith emptyaluminum orbital exposed Al atomwithinthe crystal latticeofBauxite[15-16].The appearance ofthe positive chargeon thenitrogenatom worksto consistentincrease the strength ofthe bonds ofNHthroughaffinityelectron densityof thebondtowards thepositively charged nitrogenatom, leading to compression of the bondand thusits force constantincreasesits strength. This happensfor bothfrequenciessymmetricand anti-symmetric ofNH_2 group,this assumption supported by shifting the stretching frequency of OHgroupwhich existed on the surface of the Bauxite towards a lower frequency of 3620-3618 cm^{-1}which shows thecontribution of the protonofOHwith bondingledto the weakening ofOH bondand thus increasethe length of it. As well as thegroupAl ... .OHthis shifted toward the lower frequency of 3690-3680 cm^{-1}.For theAl-O-Algroup which belongs tostructuralcoreofBauxiteexhibit asplit to two bands, the first one displaced to thelower frequency by10 cm^{-1}, while the other displacedto a higherfrequencyby20 cm^{-1},it is clear thatthe part thatdisplacedtowardsthe lowerfrequencyis duetoAl-O-Algroupsthat have entereda kind ofcoordination bondingor hydrogen bondingwithNH_2group that belongs to NH_2 group of urea moleculewhere it playedthe role ofthe donorgrouploan pairwhileAl-O-Alplayedthe role ofthe receptorforthis loan pair. Note, Al-O-Algroup can contain a proton linked tomediatedoxygen atom. This acidic proton could become the center of the bondingwithNH_2group.The reason ofdisplacementtowards a higher frequencyreturns to thepositioning ofthe acidic protons that exist on the Bauxite surface on a few number ofAlOAlcenters,this meansthat thepositive chargespreads over a less number of centerswhich leadsto the appearing ofmore dense positive chargeonnon-bonded Al-O-Alcenterswithurearesultingincreaseinthe strength of thesebondsandshifting of their vibration toward a higher frequency[17-18].For the same reasonthere is anincrease ofstrength for the bonds force constant Al....OHwhichshiftedtowarda higher frequency.The above discussion wassupported by shifting the vibration frequency forCNgroupof ureamoleculetowardslowerfrequency as a result of the contribution of N loan pairby 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 existon the surface ofBauxite.For theBauxitecomplexwithmelamineBM, the general aspects ofitscomplex with urea are similar, especially the terms ofthe behavior ofNH_2groupsbelonging to themelaminemolecule, as well as the behavior ofgroups Al-O-Al, andAl ... .OHandOHon the surface ofBauxite.TheC = Ngroupslocated within themelamineringpushedtowards alowerfrequencyof1535-1512 cm^{-1}, alsotheCNGroupshiftedtowardslowerfrequencyof1462-1450 cm^{-1}due to thecontribution of N loan pairby bondingwithBauxite surface functional groups.

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

1- Return of vibration frequencies of the Al ... .OH and OH belonging to the surface of Bauxite to their original locations.
2- The vibration frequencies of different kinds ofNH_2 groups have changed their values but remained within the range of 3269-3522 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 C = 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 NH_2 loan 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 NH_2 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- TheAl ... O-H groups return backto their original positionbeforepolymerization.

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

Gibbsite					Boehmite			
Number of peak	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_2O 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		

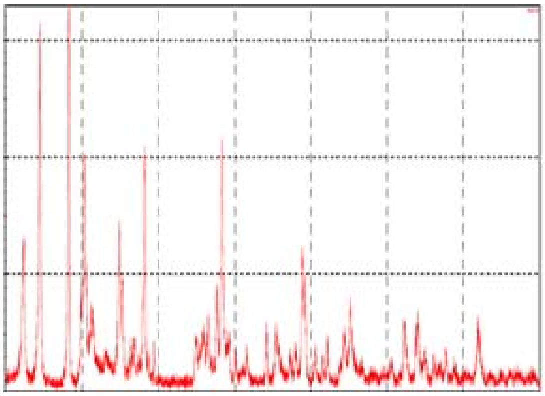


Figure (1): XRD pattern of the Bauxite

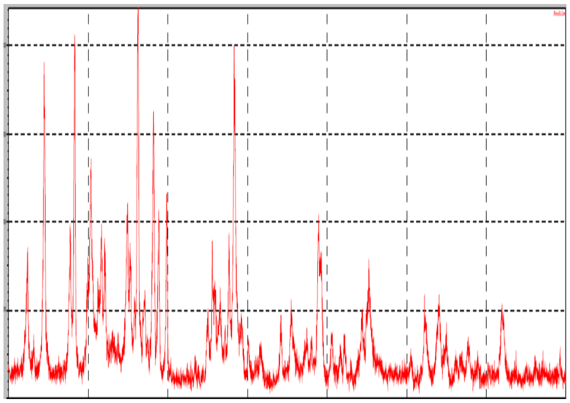


Figure (2): XRD complex scheme to Bauxitewith melamine

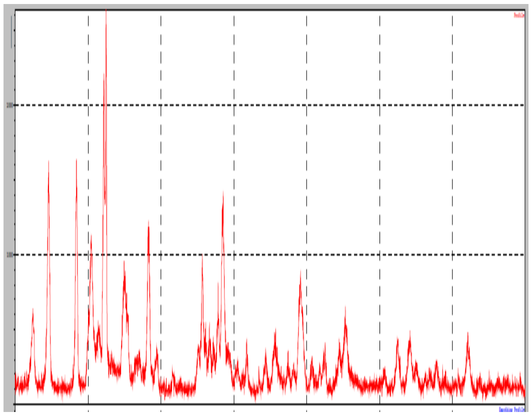


Figure (3) :XRD scheme for Bauxite complex with urea

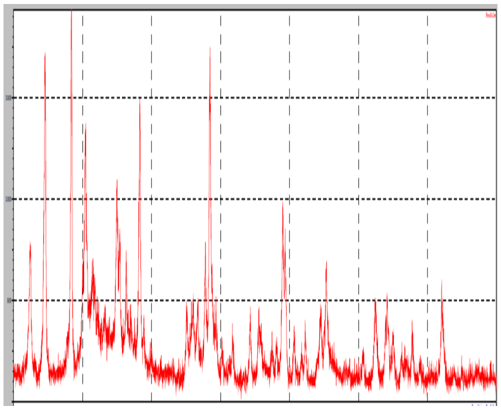


Figure (4): XRD scheme Bauxite average (polymer) before adsorption

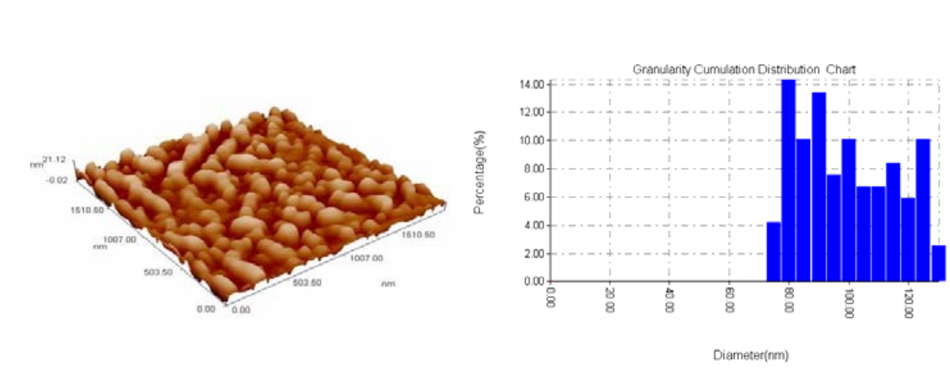


Figure (5): AFM image of the surface of Bauxite

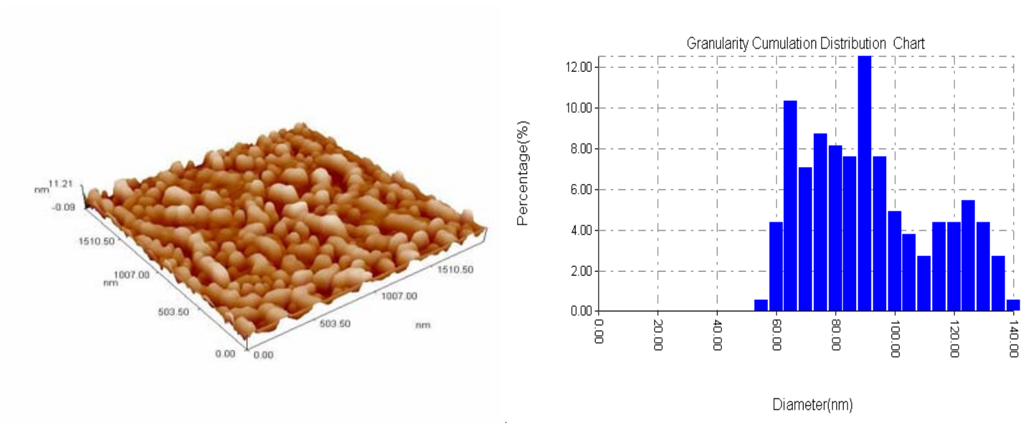


Figure (6): AFM image of the surface of the modified Bauxite

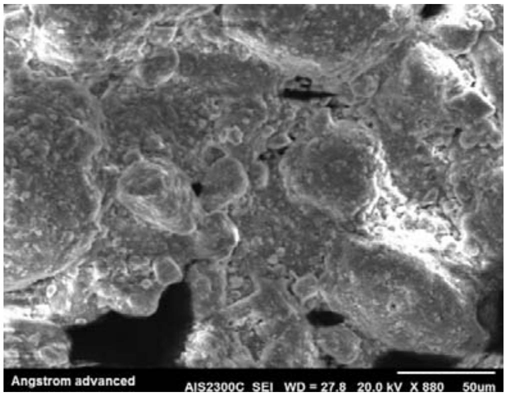


Figure (7): SEM image of the Bauxite surface

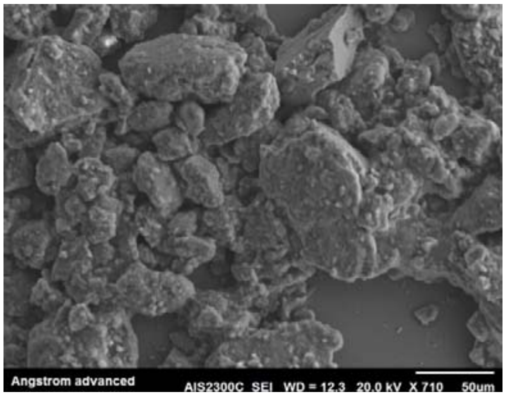
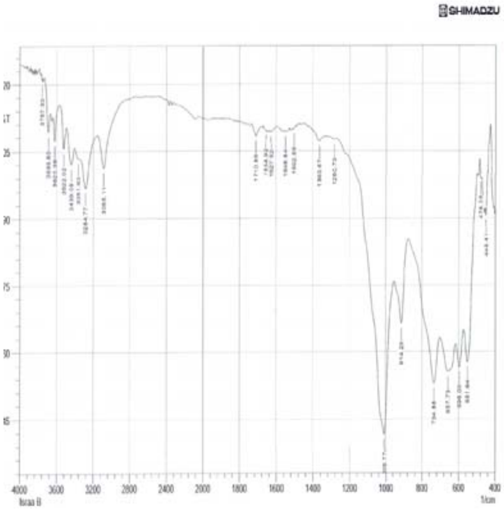


Figure (8): SEM image of the modified Bauxite surface



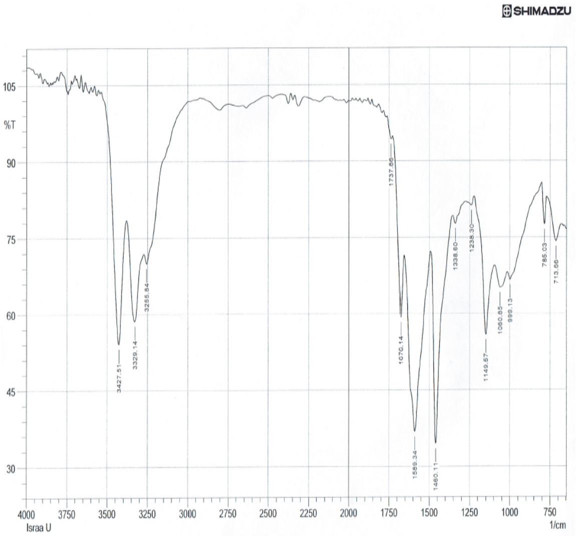


Figure (9): **infrared spectroscopy(FT-IR)to the surface of the Bauxite**

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

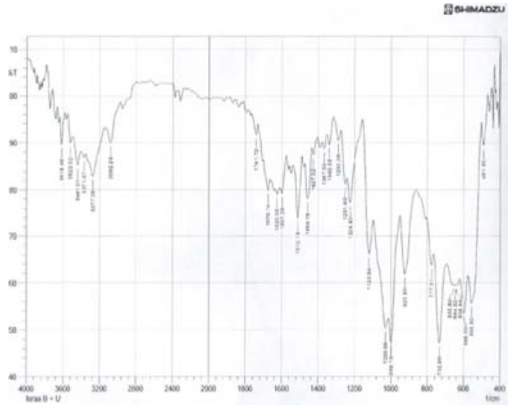


Figure (11): Infrared spectroscopy (FT-IR)of Bauxite–Urea

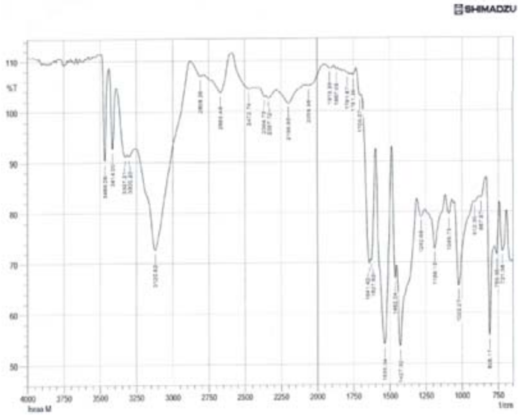
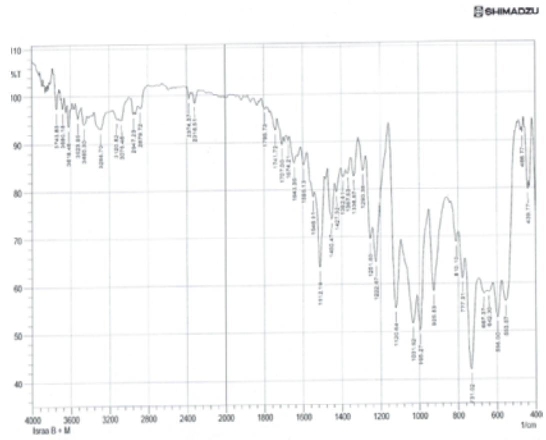


Figure (12): Infrared spectroscopy (FT-IR)of melamine



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

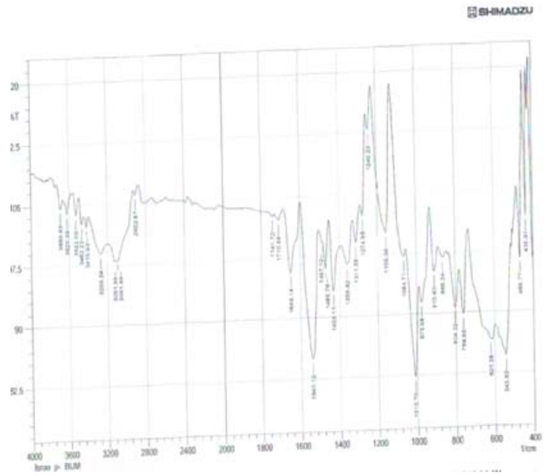


Figure (14) :Infrared spectroscopy(FT-IR)of Bauxite copolymerurea-Melamine–Formaldehyde complex

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

اسراء محمد راضي الفضلي
يوسف ابراهيم محمد ابو زيد
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 البوكاسيت واستعماله لتحضيرمعقدي: البوكاسيت-اليوريا والبوكاسيت -الميلامين، تم دمج هذه المعقدات وبلمرتها مع الفورمالدهايد لإعداد معقد البوكاسيت بوليمر-اليوريا-ميلامين-الفورمالديهايد(البوكسيت المعدل). في معقد البوكسيت-اليوريا بينت نتائجXRD إلى ان جزيئات اليوريا تتخلل بين طبقات المستوي البلوري(110) لمعدن الجبسايت بينما في معقد البوكسيت-الميلامين فقد اقتصر التداخل على السطح الخارجي للمعادن المكونة للبوكسيت بسبب الكبر النسبي لحجم جزيئة الميلامين. أظهرت نتائجFT-IR ان تداخل هذه القواعد مع البوكسيت استند أساسا على الرابطة الهيدروجينية و بدرجة أقل على التناسق بين المزدوج الالكتروني لذرة النيتروجين مع الاوربتال الفارغ لذرة الألمنيوم في المعقدات المذكورة أعلاه.
وأخيرا فان تكون البوليمر تم على حول البلورات المجهرية لمعادن البوكاسيت.

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