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Preparation and characterization of some retention water polymers for improvement of agricultural desert soil.

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ABSTRACT

A different types of retention water polymers were prepared in different methods (composite ,Graft, Copolymers) and different kinds of monomers were used, such as (acrylic Acid, Vinyl pyrrolidone and, Vinyl acetate)and Ammonium per sulfate (APS) used as initiator, while N,N/-Methylene –bis-acryl amide (MBA)as a cross-linking agent ,The reaction was carried out using nitrogen gas as inert atmosphere, furthermore, poly vinyl alcohol polymer was modified by the addition of polarity group to encourage its water absorbency to water, The water absorbency(WA)of the samples was varied from (448.8-3161.7)H2O/g from dry sample in (24 h)at room temperature, the structure of the samples were characterized using FTIR technique.

Introduction

Retention polymers or Super absorbent polymers (SAPs) are polymeric network compounds that can absorb water and swell into many times their original size and weight. They are lightly cross-linked networks of hydrophilic polymer chains. The network can swell in water and hold a large amount of water while maintaining the physical dimension structure . The factors that supply absorbing power to polymers are osmotic pressure, based on movable counter-ions, and affinity between the polymer electrolyte and water. The factor that suppresses absorbing power, in contrast, is found in the elasticity of the gel resulting from its network structure. Not only are they of high fluid absorbing capacity, but the absorbed fluid is hard to release, as they merely immobilize the fluid by entrapment rather than by holding it in the structure(1).

Presently, many natural polysaccharides such as starch, cellulose, chitosan, and alginate, etc. and their derivatives have been adopted to prepare new type of superabsorbent(2).

The material's biodegradability is an important focus of the research in this field because of the renewed attention towards environmental protection issues ,The half life is in general in the range 5 - 7 years, and they degrade into ammonium, carbon dioxide and water, SAPs are widely used in personal hygiene products. Recent research is focused in other application areas of SAPs, viz., bio sensing, soft actuators/valves, catalysis, concentration of viruses, vitamin, bovine serum albumin and controlled drug Delivery, The surface substitution of SAPs by cationic and anionic groups results in transformation of SAPs into selective and effective sorbents (3). The steps of hydrogel formation essentially involve (i) monomer polymerization in the presence of various amounts of a bifunctional co-monomer or (ii) crosslinking of preformed polymers, Hydroxyl radicals, a highly reactive species, have been used as initiators for

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crosslinking reactions. If favorably positioned, these radicals may undergo recombination leading to a covalent crosslink. For this purpose, hydroxyl radicals have been produced by water radiolysis or by alternative methods that use UV radiation and hydrogen peroxide(4),retention polymers or SAPs can be classified into two types: based on charge-nonionic and ionic ,and based on its affinity towards water –hydrophobic and hydrophilic. Ionic SAPs are further classified into cationic and anionic.(5)

The objective of this study is to prepare some of retention water polymers(composite, copolymer , grafting)and preparing of modified polymers develop the absorption of water in high quantities and improving the texture of agriculture soil in deserts.

Experimental and material

Materials:

Acrylic Acid monomer was obtained from Sigma-Aldrich,and distilled under redused pressure before use,Bentonite powder was from natural sources, Ammonium persulfate was obtained from Hopkin and Williams ,(Cobalt acetate ,Methanol, ثthanol, Benzoyl peroxide) were obtained from BDH chemical LTD pool ,England,(poly vinyl alcohol,vinyl pyrrolidone, N,N-Methylene bis- acrylamide) were obtained from Sigma-Aldrich, vinyl acetate was obtained from Alfa Aesar.

Instrumental analysis:

Samples were characterized as KBr pellets using a Shimadzu (PRESTIGE) JAPAN ,FTIR spectrophotometer.

Preparation of polymers:

a-Modification of Poly vinyl alcohol (PVA):

(1 gm) of PVA was dissolved in 25 ml of distilled water in a hot plate with temperature of (40-45 c), after dissolving ,(15 ml) of (0.5 % NaOH) Was added to the solution ,after 20 min of stirring (15 ml) of (0.9% CLCH2COOH) chloroaceticacid was added and stirred for another 20 min then it was left for about 24 hr , then was filtered and dried in an oven at 80 c for 2 hr .the dried gel was ground and it was put in a dissicator .

b-preparation of PVA /vinylpyrrolidon graft polymer:

PVA was modified as mentioned earlier (adding 0.5%NaOH +0.9% Chloro acetic Acid), (30 g)of vinyl pyrrolidon monomer was added into a 250 ml in three- necked flask equipped with a mechanical stirrer, a thermometer and a nitrogen line. The monomer was heated to 80 c using a water bath ,with stirring in nitrogen for about 30 min ,then (3 gm) of modified PVA was added to the monomer and after a while ammonium per sulfate(0.9 g) ,after stirring for about 20 min (0.04 g) of N,N-Methylene bis-acrylamide (MBA) Was added, the mixture solution was stirred for another 3 hr ,after the reaction was complete the solution was immersed in ethanol for 24 hr and then was dried in an oven at 80 c for 3 hr .the dried gel was ground and it was put in a dissicator .

c-preparation of poly(sodium acrylate)/Bentonite composite:

The polymer was synthesized with aqueous solution polymerization method, an Acrylic acid monomer (30 g) was neutralized at ambient temperature with a predetermined sodium hydroxide solution sufficient to achieve the desired neutralization degrees of the sample. A monomer /Bentonite mixture solution was prepared by mixing bentonite powder(3 g)in the monomer solution mentioned earlier. A radical initiator ammonium per sulfate (0. 9 g)was added to the mixture solution Under a nitrogen atmosphere. The crosslinking agent N,N-Methylene bis-acrylamide(0.04 g)was dissolved in the monomer/ bentonite mixture solution before it was degassed for about 30 min. The above –mentioned mixture system was stirred and heated to 60-70 c in a water bath for 2 hrs. After completion of the polymerization reaction, ethanol was added to the mixture and left for about 24 hr and then it was filtered and dried in an oven at 80 c for about 8 hrs. Until the weight of the specimen was constant.

d-preparation of PAAc-co-PVAc Copolymer:

(1 ml) of acrylic acid monomer was mixed with (1 ml) of vinyl acetate monomer along with (0.02 g)of APS initiator and (0.005 g) of MBA as across linking agent in a tube of Pyrex, the solution was mixed using the shaker for about (4-5 min), then it was put in to a water bath with Temperature of 80 c and using nitrogen atmosphere ,after shaking in the water bath for about 20 min the gel was observed, then we added 5ml of 4% NaOH for 20 min to neutralize the acrylic polymer ,then it was get rid off the base and ethanol was added to the gel, and was left for 24 hr and then it was filtered and cut into a small pices and dried in an oven for at 80 c for about 10 hr and was put into the dissicator.

measurement of water absorbency :

The weighted dry samples were immersed in excessive distilled water at room temperature for 24 hr to reach swelling equilibrium, then the swollen samples were filtered ,the water absorption of the hydrogels was derived from the mass change before and after swelling, the water absorbency was calculated according to the following equation:

$$Q = \frac{W' - W}{W} \times 100\%$$

were Q = water Absorbency

W',W = weight of wet and dry samples respectively.

The following table shows the difference in water absorbency .

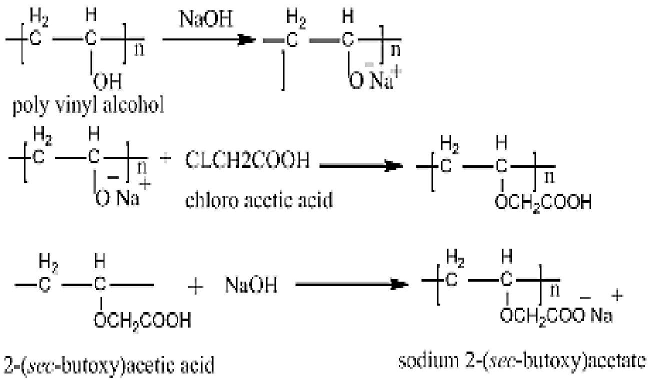
Table. 1. difference of water absorbency with polymers

NO.	Type of polymer	Wt. of dry sample (g)	Wt. of wet sample (g)	Absorbency Wt/wt%
2	Graft (PVA/vinylpyrrolidon)	0.3003	1.9668	554.9
3	poly(sodiumacrylate AAc) / Bentonite composite	0.3032	2.4378	704
4	AAc/ PVAc Copolymer	0.2231	7.2768	3161.7

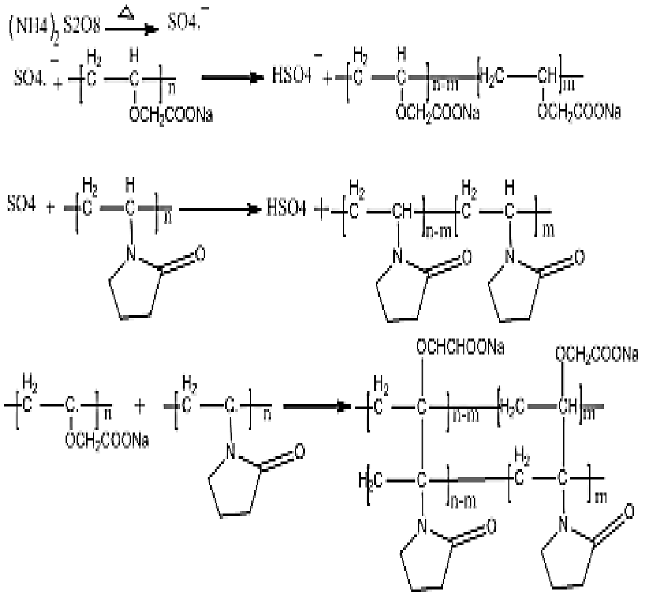
Result and Discussion

The polymerization process was carried out using inert atmosphere to ensure that the oxygen radical (O0) do not contribute during the polymerization .

modification of Poly vinyl alcohol was to increase the water absorbency by adding a hydrophilic group without affecting the base structure of the polymer, using chloroacetic acid that will lead to insert the carboxylic acid group, using NaOH will neutralize some of he carboxylic acid groups to the carboxylate groups, and that will lead to a better water absorbency, FTIR analysis Fig.(1- 2) shows a wide peak at 3565 cm-1 for stretching of the hydroxyl group, two peaks were observed at 1637 cm-1 and 1670 cm-1 due to the symmetrical and asymmetrical stretching of C= O\ groups. On the basis of this observations, the mechanism of this preparation may be proposed as:



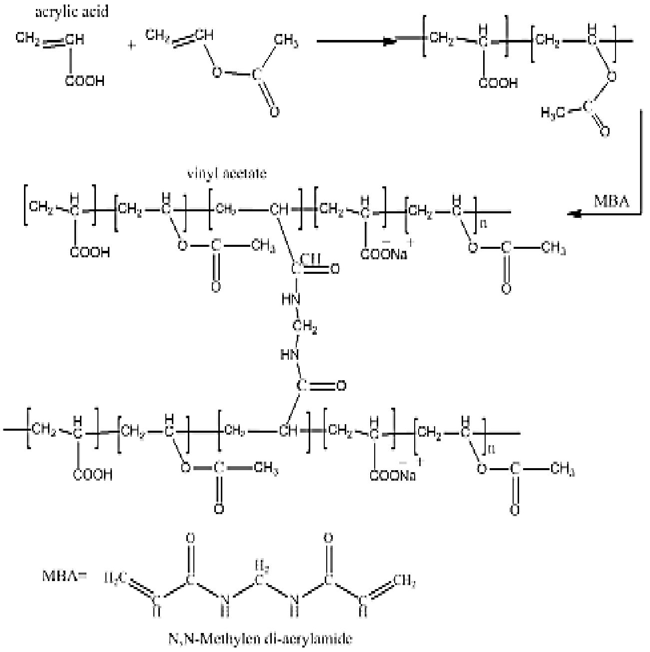
PVA /vinyl pyrrolidon graft polymer ,the preparation of this kind of retention polymer include the grafting of modified PVA as mentioned in such.(3.1 of the experimental).with vinyl pyrrolidone monomer, the concentration of the cross linking agent may have the higher effect on the water absorbency ,also, the concentration of vinyl pyrrolidon monomer may have the influence on the absorbency due to its an symmetrical structure and the hydrophility of its polymer, FTIR spectra Fig.(3-4) of the end hydrogel clearly mark the presence of hydroxyl group at 3475 cm-1(O-H stretching)a sharp peak at 1620 cm-1due to carbonyl group starching (C=O)the spectra also contain characteristic band at1203 cm-1of (C-O-C)(7) . on the basis of this observations, the mechanism of network formation may be proposed as:



poly(sodium acrylate)/Bentonite composite (AAc + Bentonite) : the swelling capability of this hydrogel mainly depend on the neutralization degree of the retention polymer, in this procedure we used a neutralization degree reaches to 60%,The swelling value of the hydrogel increase with increase of the neutralization degree from 0 to 60%, the retention polymer composite is a mixture of poly(sodium acrylate)/Bentonite and poly (acrylic acid)/Bentonite, and the primary hydrophilic groups are carboxylate and carboxylic acid groups. Higher neutralization degree means higher content of poly(sodium acrylate)/Bentonite and larger amount of carboxylate group on the retention polymer. Science the carboxylate group is electronegative in water, higher carboxylate concentration will lead to repulsion among these groups and a decrease of water absorbency, although carboxylate group have a better water absorbency than carboxylic group does. On the other hand, the carboxylic acid group is charge neutral .Therefore, when carboxylate and carboxylic acid groups on the retention polymer composite cooperate in a suitable ratio, the polymer composite will have higher water absorbency(6).FTIR spectra Fig (6 – 8) of the initial bentonite shows that the band at 1041 cm-1could be attributed to the stretching of siloxane (Si-O-Si) group, and this was confirmed by the –Si-o-Si- bending vibration at 495.7 cm-1.The band at 790 cm-1 was attributed to SiO-H vibration, in the spectrum of the resulting polymer composite a peak at 1639 cm-1due to symmetrical and asymmetrical stretching of COO_groups. A peak at 3622 cm-1 for the hydroxyl group(8).

AAc/PVAc Copolymer ,the preparation of this retention polymer include the synthesis of highly absorbency gel that can absorb and retain the water in amounts reached 3163 g/g which is the highest result so far. This high absorbency may have resulted from different variables such as the structure of the polymer and the amount of hydrophilic groups in this structure, also the type and the concentration of the initiator. The concentration of the crosslinking agent can also effect on the absorbency by affecting on the degree of network formation.(9) FTIR spectra Fig.(8 – 9) shows a peak at 3500 cm-1 for the hydroxyl group of carboxylic acid, a sharp peak at 1600 cm-1due to carbonyl group starching (C=O)the spectra also contain characteristic band at1220 cm-1of (C-O-C),a peak at 3600 cm-1a stretching band for (N-H) group.

on the basis of this observations, the mechanism of network formation may be proposed as:



Conclusions

From the results of water absorbency of the produced polymers, we can observed that there were differences in the capability of the hydrogel to swell and retain that water ,those differences caused from other variables such as: molecular polarity, molecular volume, ionic intensity, and on the neutralization degree of the retention polymer. The change on the neutralization degree of the resulting polymer during the sample preparation process will lead to the change of the hydrophilic groups on retention polymer and turn to the swelling capability of the hydrogel. With the increase of neutralization degree of the retention polymer the polarity of solute(retention polymer) increases, which means that the swelling value increase in polarity solvents(water) and decrease in non-polarity solvents (such as: methanol).

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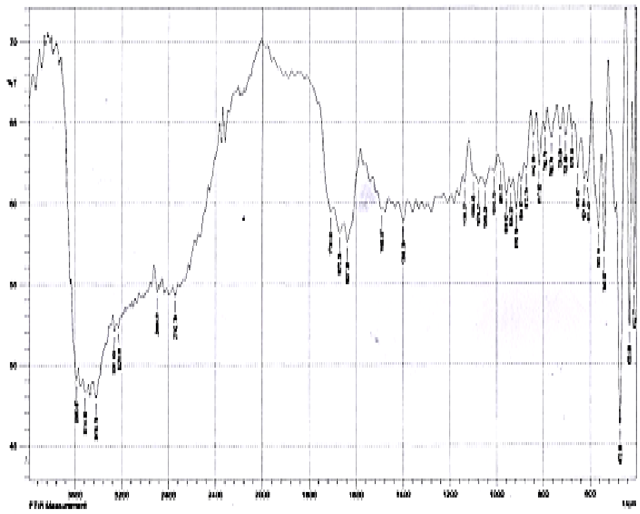

Fig.1. FT-IR of modified Poly vinyl alcohol (mPVA).

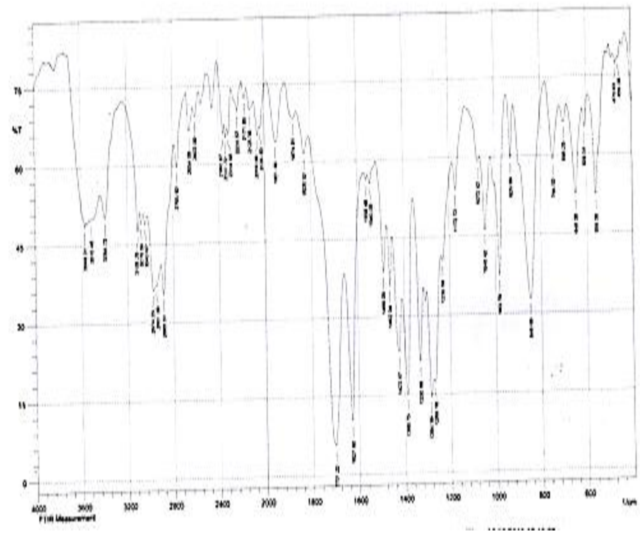

Fig.4. FT-IR of vinyl pyrrolidon (PVPy

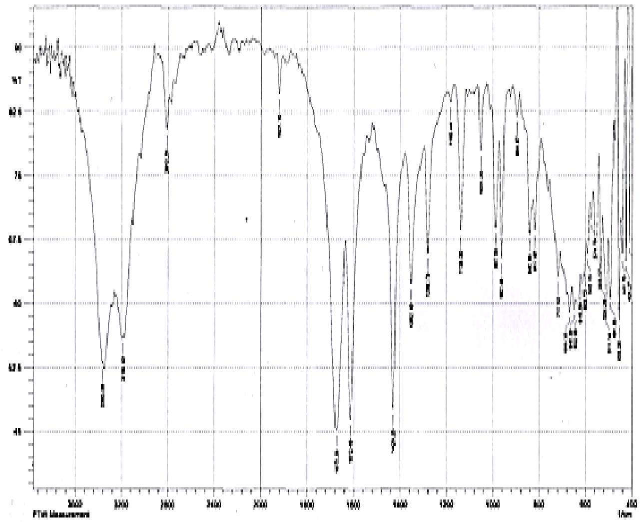

Fig.2. FT-IR of Poly vinyl alcohol (PVA).

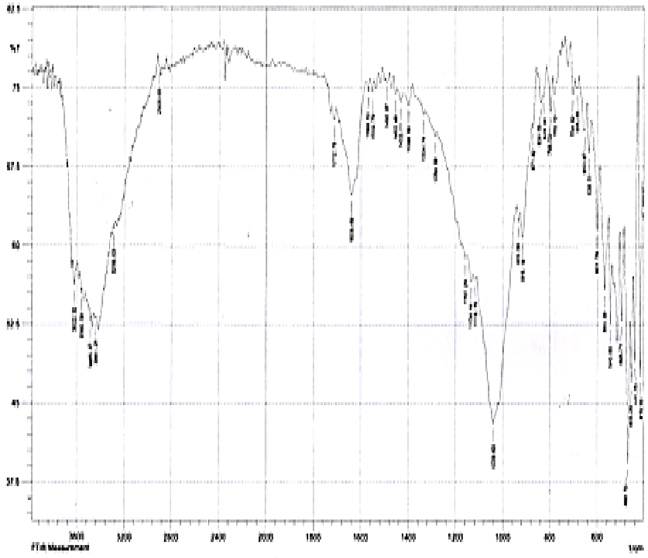

Fig.5. FT-IR of Composite AAc on Bentoniet

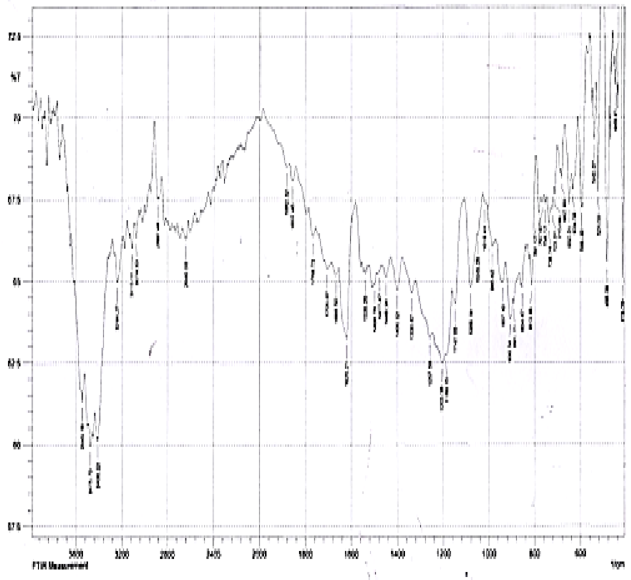

Fig.3. FT-IR of Graft Poly (PVPy – G - PVA)

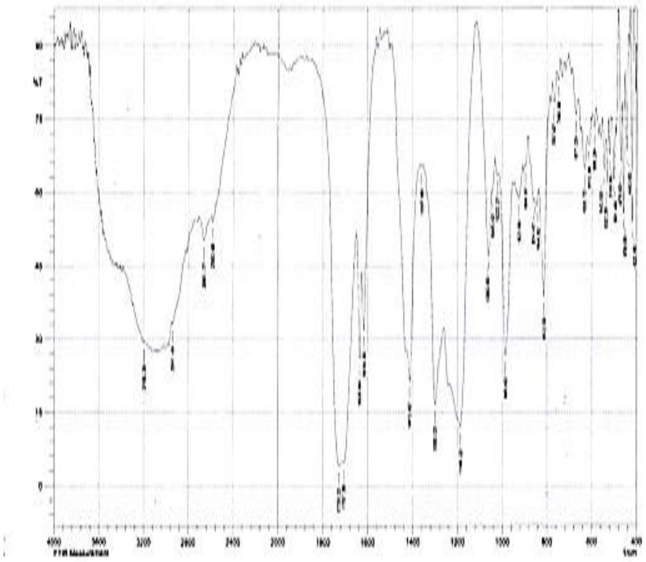

Fig.6. FT-IR of Acrylic Acid AAc

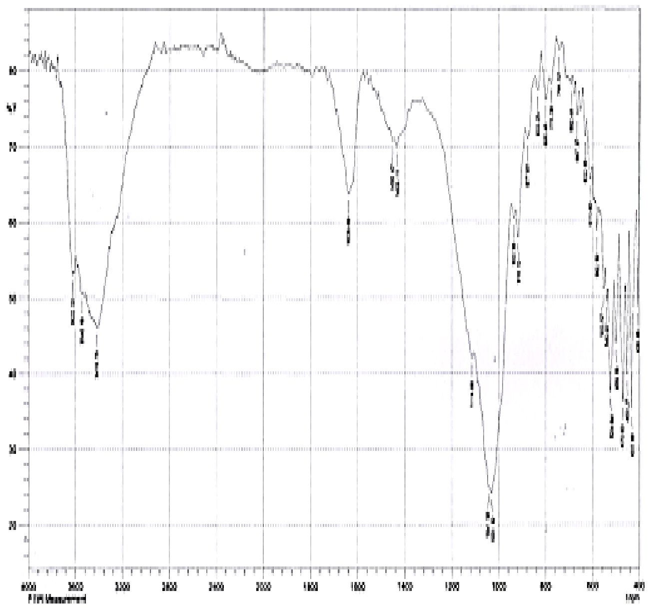

Fig.6. FT-IR of Composite AAc on Bentoniet

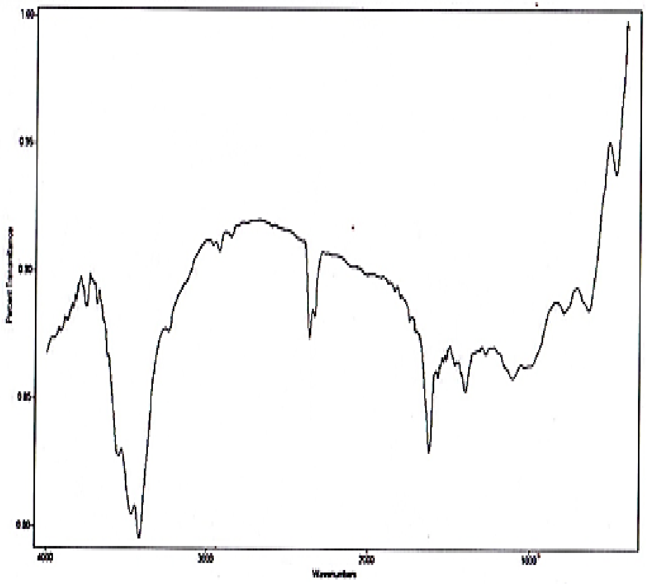

Fig.7. FT-IR of Bentoniet

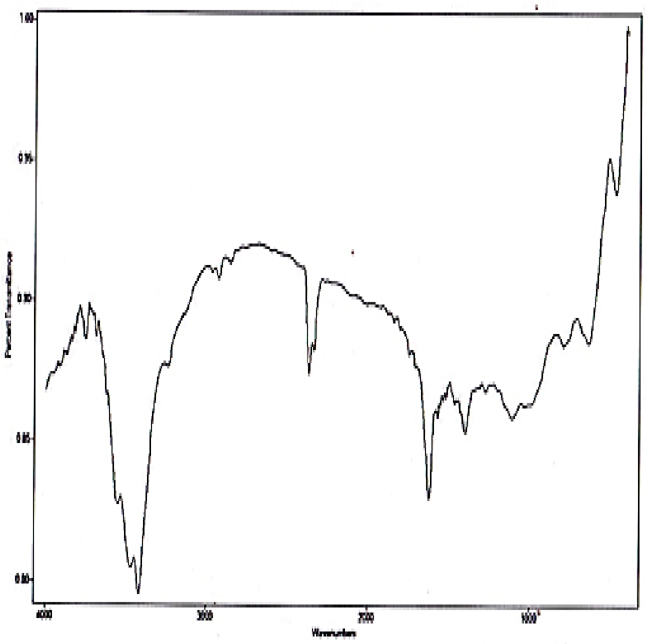

Fig.8. FT-IR Copolymer of (AAc – co – VAc)

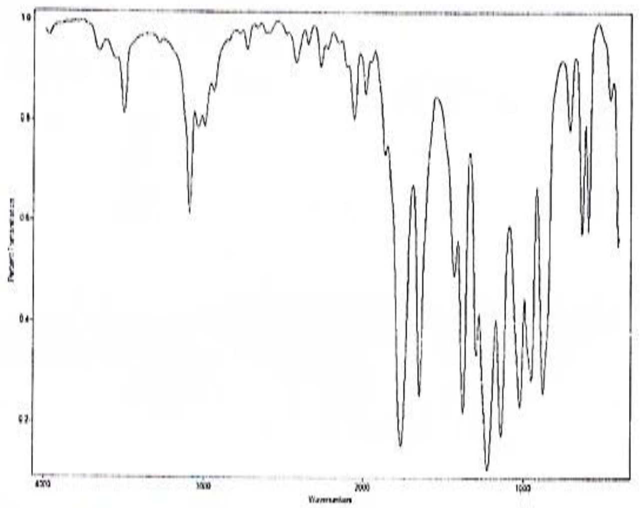

Fig.9. FT-IR of vinyl acetate VAc.

تحضير وتشخيص بوليمرات الاحتجاز المائي لتحسين زراعة التربة الصحراوية.

تمارا عبدالله السلماني **طارق عبدالجليل منديل**

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الخلاصة

تم في هذه الدراسة تحضير ثلاثة أنواع من بوليمرات الاحتجاز المائي (بوليمر متراكب composite، بوليمر مطعمgraft وبوليمر مشتركcopolymer) وباستخدام انواع مختلفة من المونومرات اساس للتحضير:(حامض الاكريليك،الفينايل بايروليدون،والفينايل اسيتيت) وبوجود الامونيوم بيرسلفات (APS) كمادة بادئة واستخدام مادة (MBA) كمادة رابطة، تم اجراء التفاعل بوجود النتروجين كوسط خامل للتفاعل ، كذلك تم تحوير البولي فينايل الكحول بإضافة مجموعة قطبية لزيادة قابليتها على امتصاص الماء وتم قياس كمية الامتصاص للبوليمرات الناتجة(WA). وجد ان كميات الامتصاص لها تتراوح بين H2O/g (448.8-3161.7) وزن ماء/ وزن العينة الجافة، بعد امتصاصها للماء خلال 24 ساعة وبدرجة حرارة الغرفة وتم اجراء فحص تركيب البوليمر الناتج باستخدام تقنية ال FTIR .