Synthesis and characterization of methacrylamide-itaconic acid hydrogel

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ABSTRACT

In this research, methacrylamide-itaconic acid hydrogel was synthesized using 4, 4-azobis-4-cyanovaleric acid radical initiator and ethylene glycol dimethacrylate as crosslinker. Then, the role of various factors such as the weight percentage of monomers in the mixture - the concentration of the initiator - the effect of temperature and reaction time and the concentration of the cross-linker were determined. The best conditions for hydrogel synthesis were recorded (time = 120 min, (EGDMA) = 0.025 mol/L, monomer = 0.5 mol/L (75% itaconic acid and 25% methacrylamide) (wt %), ACV = 0.04 mol/L and Temperature = 70 °C). The hydrogel structure was confirmed using scanning electron microscope (SEM), X-ray energy diffraction (EDX) and Fourier transform infrared spectroscopy (FT-IR).

Keywords: **Hydrogel, methacrylamide, itaconic acid, initiator**

1. *Introduction*

Hydrogels are cross-linked polymer networks that have the ability to absorb large amounts of water or biological fluids even under pressure. These compounds can absorb a lot of water without dissolving. Hydrogels are cross-linked by chemical or physical methods. Hydrogels are cross-linked by chemical or physical methods. Increasing attention is paid to physical

hydrogels due to the relative ease of the process and the absence of crosslinks in their synthesis, while the chemical types are of interest due to their good mechanical strength. Compared to synthetic hydrogels, natural hydrogels are very interesting due to their diversity, abundance, cheapness, renewable, non-toxicity, biodegradability and biocompatibility. In recent years, hydrogels have been used in various industries such as food, packaging, medicine, agriculture, biomedical applications, bio engineering, making electronic devices, and also as adsorbents to remove environmental pollutants. Also, significant progress has been made in the use of water-swellable biomedical hydrogels as targeted carriers for the release of drugs and proteins. In this regard, the nature, size of the holes, their stability and responsiveness to external stimuli are one of the most important behaviors of these networks.[1-10]

1.1 Materials and methods

In this research, high purity methacrylamide and itaconic acid monomers were obtained from Merck.co (Germany). Methacrylamide was purified by recrystallization in pure ethanol and itaconic acid was consumed as purchased. 4, 4-Azobis 4-cyanovaleric acid (ACV) was prepared as an initiator. For this purpose, it was first made into a suspension with double distilled water, then sodium bicarbonate and hydrochloric acid (1mol/L) were added. The resulting solid was used after filtration and washing with ice water and drying at room temperature and under vacuum. During the experiments, initiator and monomers were stored in the dark and in the refrigerator. Ethylene glycol dimethacrylate (EGDMA) crosslinker and high purity standard solvents were used as purchased. The structure of the hydrogel were investigated by FTIR (Thermo Nicolet IR100 spectrophotometer with KBr disks), SEM (Philips CM120) and EDX.

1.2 Hydrogel synthesis

Inside a 50ml Pyrex tube, a mixture of methacrylamide (MAm) and itaconic acid (IA) monomers (0.5 mol/L) along with ($4.0x10^{-2}$ mol/L) initiator 4 and 4-Azobis 4-cyanovaleric acid (ACV) and ($2.5x10^{-2}$ mol/L) crosslinker ethylene glycol dimethacrylate (EGDMA) and 25 ml of doubly distilled water were added, then the tube was placed in a water bath with a constant temperature of 80 ℃ for two hours. After the specified time, filtration was done with Whatman paper. Then the samples were carefully washed with distilled water and acetone to remove unreacted homopolymers. It was dried for 24 hours in the oven at 30℃. Finally after complete dehumidification in a desiccator, next to $CaCl_2$, it was weighed. Based on the obtained sample weight, the best conditions of weight percentage of monomers - initiator concentration - crosslinker concentration and optimal time and temperature were determined.

2. *Results and discussion*

2.1 Characterization of the hydrogel

In the best hydrogel synthesis conditions and in the presence of 25% methacrylamide and 75% itaconic acid (wt), EDX results showed acceptable percentages of N, O, and C in the hydrogel.Fig1 and Tacle1. As shown in the SEM figure, the hydrogel surfaces provide suitable bonds between monomers and there is a possibility of absorption due to the presence of holes, and in the existing conditions, this hydrogel can be used as a suitable adsorbent and there are no impurities on the hydrogel surfaces.Fig2. The FTIR results showed the following peaks:

1. The sharp peak in the 3500-3700 cm^{-1} is related to the stretching N-H of the amide group.

2. The broad peak related to the stretching O-H hydrogen bond of the carboxylic acid group was observed at 2400-3400 cm^{-1}.

3. The sharp peak in the range of 1450-1350 cm^{-1} corresponds to C-H.

4. A sharp peak related to C=O strong stretching related to acidic or amide group was observed at 1650-1800 cm^{-1}.Fig3.

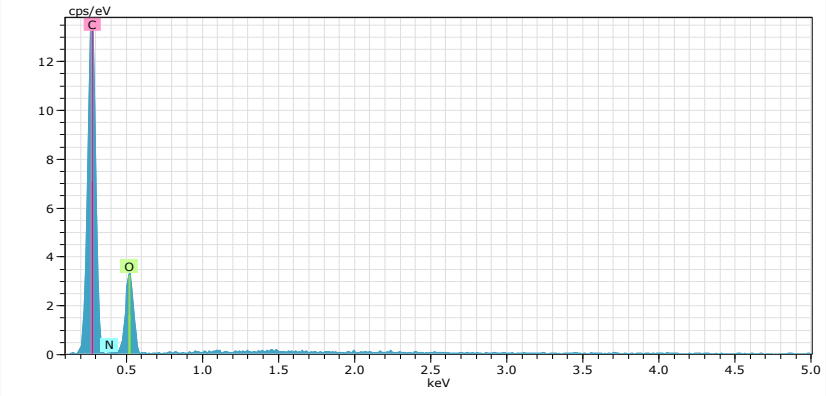
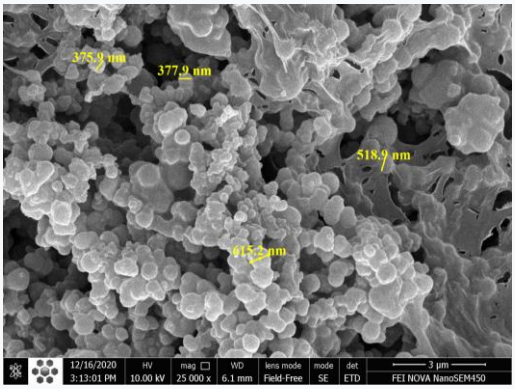


Fig1. *EDX analysis*

Table1.*EDX results*

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	63.64	63.64	69.81	8.58
O	8	K-series	34.22	34.22	28.18	5.83
N	7	K-series	2.13	2.13	2.01	1.23



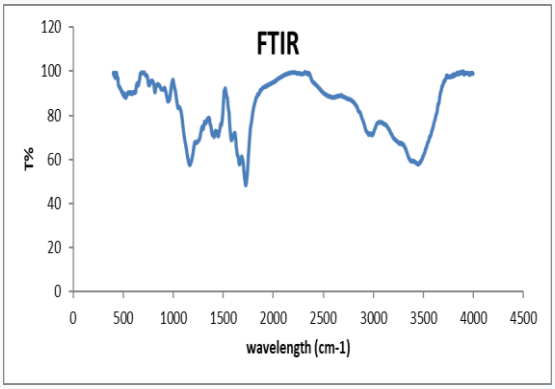


Fig2. *SEM image of the hydrogel (magnification 25k)*

Fig3.*FTIR of the hydrogel*

2.2 Water absorption capacity

For this purpose, it was used in different pH, acidic, neutral and alkaline:

1. HCI (1M) +Sodium acetate (1M) →pH=0.5-3.5

2. Sodium acetate (1M) +Acetic acid (0.2M) →pH=4.0-7.0

3. Ammonium chloride (2M) +NH4OH (1M) →pH=7.5-10.0

First, weigh 0.2 grams of the obtained hydrogel and place it in 5 ml of the above solutions for 24 hours, then dry it in an oven at 30°C for 24 hours, weigh the desired hydrogel, and calculate the final weight. The percentage of hydrogel water absorption was calculated with the following equation.

Water absorption %= final weight – initial weight/ initial weight X 100

$$pH: 3.2 \rightarrow water\ absorption\ \% = \frac{0.26 - 0.2}{0.2} X100 = 30$$

$$pH: 6.5 \rightarrow water\ absorbtion\ \% = \frac{0.23 - 0.2}{0.2} X100 = 15$$

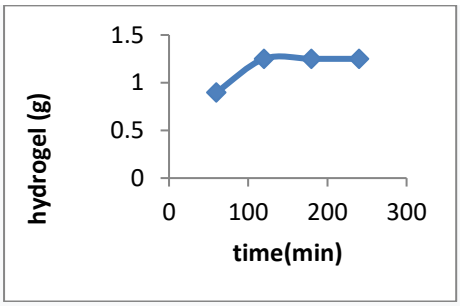
$$pH: 9.0 \rightarrow water\ absorption\ \% = \frac{0.34 - 0.2}{0.2} X100 = 70$$

According to the above results, the water absorption percentage of the desired hydrogel is higher in alkaline pH. This is related to the presence of more acidic groups of itaconic acid in the hydrogel structure.

2.3 Effect of time and temperature

Experiments were performed at different times of 1, 2, 3, 4 hours and in constant conditions of other variables mentioned in the above synthesis method. The best time was 2 hours. Fig4.

Meanwhile, by changing the temperature in the range of 60-90°C, the maximum product was obtained at 70°C. Fig5.



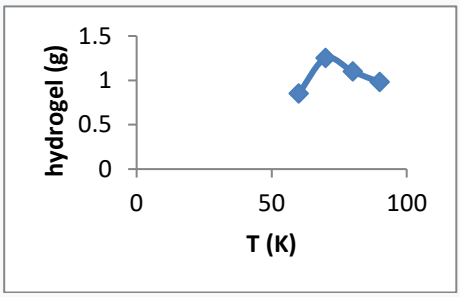


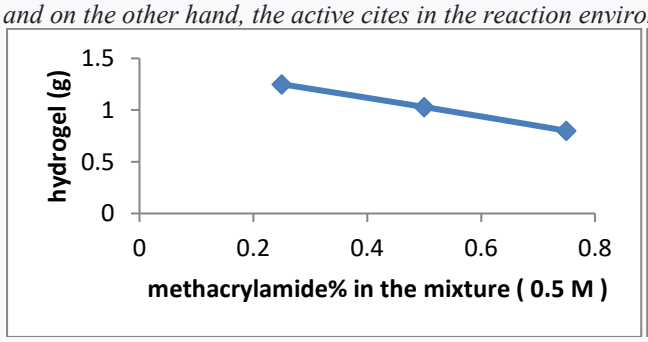
Fig4.*Effect of time* **Fig5**.*Effect of temperature*

2.4 Optimizing the percentage of monomers and concentration of initiator and cross linker

Experiments were performed in different weight ratios of IA/MAm monomers (50:50, 25:75 and 75:25) .The highest quantity of hydrogel was obtained in the ratio (75%IA: 25%MAm). It is probably due to the creation of more and stronger hydrogen bonds of itaconic acid, its higher molecular mass and higher reactivity.Fig6.

By changing the concentration of the initiator from 0.01-0.06 M and changing the concentration of the cross-linker from 0.01-0.06 M, the best conditions were observed at 0.04 M of the initiator and 0.025 M of the cross-linker, respectively.Fig7, 8.

By further increasing the initiator from 0.04 M to 0.06 M, the possibility of forming homopolymers increases and on the other hand, the active cites in the reaction environment are exhausted.



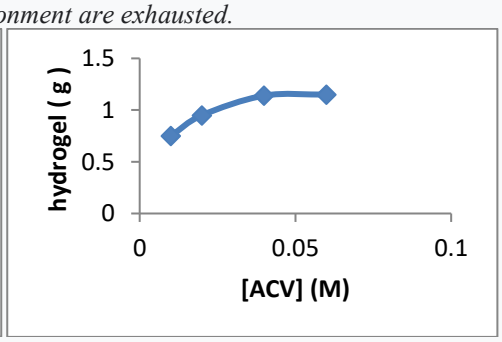


Fig6.*Effect of the monomers (wt %)* **Fig7**.*Effect of initiator*

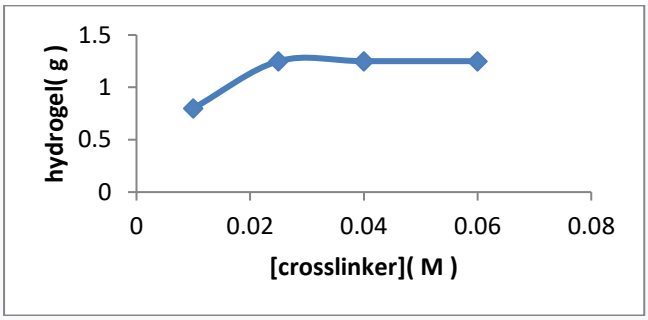


Fig8.*Effect of crosslinker*

3. Conclusion

In this research, MAm-IA hydrogel was successfully synthesized using radical initiator ACV and EGDMA as a cross-linker. The best conditions for hydrogel synthesis were recorded ([EGDMA] = 0.025 M, [monomer] =0.5 M (IA = 75%), (MAm = 25%), [ACV] = 0.04 M, optimum temperature = 70 ℃ and time = 120 min). The water absorbtion capacity showed the highest value in alkaline environment. Hydrogel characterization was confirmed by FTIR, SEM and EDX.

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