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Acrylonitrile-Containing Copolymer Synthesis and Magnesium Ions Adsorption of the Copolymer

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Abstract

Poly(acrylonitrile-co-methyl methacrylate) [P(AN-MMA)] copolymer was obtained in the presence of 2,2'-azobisisobutyronitrile by using acrylonitrile and methyl methacrylate monomers via free radical polymerization. The surface of the synthesized copolymer was hydrolyzed in sodium hydroxide solution. Nitrile groups ($-C\equiv N$) on the P(AN-MMA) copolymer surface were converted into conjugated imine groups ($-C=N-$). Hydrolyzed poly(acrylonitrile-co-methyl methacrylate) [HP(AN-MMA)] copolymer was used in the adsorption of magnesium ions. Magnesium ion was determined with ethylenediaminetetraacetic acid in a water solution containing $Mg(NO_3)_2.6H_2O$ before and after adsorption. The adsorption capacity of the HP(AN-MMA) copolymer against Mg^{2+} ions was found to be 1.27 mmol.g^{-1} (pH=4.5). After isolation and drying of the product, its structural and thermal characterization was determined by ^{1}H-nuclear magnetic resonance spectroscopy, Fourier transform-infrared spectroscopy and thermogravimetric analysis, which are the basic polymer characterization methods. The average surface roughness (*Ra*) values developed after magnesium ion adsorption were investigated by atomic force microscopy analysis. With magnesium ion adsorption, the Ra value increased from 136 nm to 354 nm.

Keywords: Magnesium Ion Adsorption, Hydrolyzed Poly(Acrylonitrile-co-Methyl Methacrylate) Copolymer, Atomic Force Microscopy, Free Radical Polymerization.

Akrilonitril İçeren Kopolimer Sentezi ve Kopolimerin Magnezyum İyonları Adsorpsiyonu

Öz

Serbest radikal polimerizasyonu yoluyla akrilonitril ve metil metakrilat monomerleri kullanılarak 2,2'-azobisizobütironitril varlığında poli(akrilonitril-ko-metil metakrilat) [P(AN-MMA)] kopolimeri elde edildi. Sentezlenen kopolimerin yüzeyi sodyum hidroksit çözeltisinde hidrolize edildi. P(AN-MMA) kopolimer yüzeyindeki nitril grupları ($-C\equiv N$), konjuge imin gruplarına ($-C=N-$) dönüştürüldü. Magnezyum iyonlarının adsorpsiyonunda hidrolize poli(akrilonitril-ko-metil metakrilat) [HP(AN-MMA)] kopolimeri kullanıldı. Magnezyum iyonu, adsorpsiyondan önce ve sonra $Mg(NO_3)_2.6H_2O$ içeren sulu bir çözelti içerisinde etilendiamintetraasetik asit ile belirlendi. HP(AN-MMA) kopolimerinin Mg^{2+} iyonlarına karşı adsorpsiyon kapasitesi 1,27 mmol.g^{-1} (pH=4,5) olarak bulunmuştur. Ürünün izolasyonu ve kurutulmasının ardından temel polimer karakterizasyon yöntemlerinden olan ^{1}H-nükleer manyetik rezonans spektroskopisi, Fourier transform-kızılötesi spektroskopisi ve termogravimetrik analiz ile yapısal ve termal karakterizasyonu belirlendi. Magnezyum iyonu adsorpsiyonu sonrasında gelişen ortalama yüzey pürüzlülüğü (Ra) değerleri atomik kuvvet mikroskobu analizi ile incelenmiştir. Magnezyum iyonu adsorpsiyonu ile Ra değeri 136 nm'den 354 nm'ye çıkmıştır.

Anahtar Kelimeler: Magnezyum İyon Adsorpsiyonu, Hidrolize Poli(Akrilonitril-ko-Metil Metakrilat) Kopolimeri, Atomik Kuvvet Mikroskobu, Serbest Radikal Polimerizasyonu.

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1. Introduction

In recent years, polymers with different structures and architectures have been synthesized and reported using new-generation techniques (Meyvacı et al., 2023; Öztürk and Meyvacı, 2017; Öztürk et al., 2013; Meyvacı, 2023; Tunca et al., 2002; Altintas et al., 2011; Öztürk et al., 2020; Savaş et al., 2020; Dag et al., 2008; Öztürk and Hazer, 2010). Polymer structures containing polyacrylonitrile groups have been modified with tetrazine (Meyvacı and Öztürk, 2022; Kara et al., 2019). Polyacrylonitrile has been used as an adsorbent for the removal of metal ions due to its replaceable cyano groups (Sruthi and Anas, 2020). Polyacrylonitrile-based resins have attracted much attention thanks to their high chemical resistance and thermal stability (Bagheri et al., 2010). Amine-containing resins have been modified on polyacrylonitrile, especially to prevent pollution caused by nickel ions (Arsalani et al., 2009; Dąbrowski et al., 2004).

Magnesium ions are among the most abundant ions in water. Polystyrene sulfonamides cross-linked with chelating groups such as ethylenediaminetetraacetic acid (EDTA) have been very effective in removing heavy metal ions (Şenkal and Biçak, 2001; Biçak et al., 2000). New magnetic EDTA-modified adsorbent structures were designed by surface modification to remove heavy metal ions from aqueous solution (Ren et al., 2013). An attractive polymer composite adsorbent has been developed by cross-linking EDTA onto chitosan for the adsorptive removal of heavy metals (Verma et al., 2022). EDTA has amine groups and metal it is a widely used agent due to its chelating properties. Cloud point with EDTA is a suitable method for the extraction of Mg^{2+} ions. *Prunus Dulcis L.* barks modified with EDTA were found to have high biosorption capacity (Canlıdinç, 2022; Jawad, et al., 2017). Examples of modification of polyacrylonitrile have been reported (Arsalani and Hosseinzadeh, 2005). Amine and hydroxyl functional structures were formed by reacting polyacrylonitrile with ethylenediamine and monoethanolamine. Metal sorption capacities of various metal ions were measured (Arsalani and Hosseinzadeh, 2005). In the literature, -C≡N groups found in the polymer structure were converted into imine (-C=N-) groups by a simple hydrolysis process (Bagheri et al., 2010; Deng et al., 2003).

In this study, poly(acrylonitrile-co-methyl methacrylate) [P(AN-MMA)] copolymer was synthesized by free radical polymerization. The surface of the copolymer was hydrolyzed in sodium hydroxide solution to convert nitrile groups (-C≡N) to imine groups (-C=N-). In accordance with the literature (Deng et al., 2003), the adsorption was performed based on the electrostatic interaction between hydrolyzed P(AN-MMA) [HP(AN-MMA)] copolymer and magnesium ion. The products were characterized using various characterization methods.

2. Materials and Methods

2.1. Materials

2,2'-azobisisobutyronitrile (AIBN) (Sigma-Aldrich, 98%), methyl methacrylate (Sigma-Aldrich, 99%, an alumina column was used to remove the inhibitor), acrylonitrile (Sigma-Aldrich, $\geq$ 99%), N,N-dimethylformamide (anhydrous, Sigma-Aldrich, 99.8 %), methanol (anhydrous, Kimetsan 99.8 %), magnesium nitrate hexahydrate (Merck, $Mg(NO_3)_2.6H_2O$), sodium hydroxide (anhydrous, Sigma-Aldrich, $\geq$ 98 %), hydrochloric acid (Kimetsan, 37 %), ethylenedinitrilotetraacetic acid disodium salt dehydrate (Merck, $C_{10}H_{14}N_2O_8.2Na.2H_2O$) were used.

2.2. Instrumentation

^{1}H-NMR spectra were recorded using Bruker Ultra Shield Plus, ultra-long hold time 400 NMR spectrometer in deuterated DMSO. FT-IR/ATR spectra were detected using Jasco FT/IR 6600 spectrometer in the range of 600-4000 cm^{-1}. TGA measurements were conducted using a Seiko II Exstar 6000 model instrument (10 $°C.min^{-1}$ from 25 °C to 600 °C under N_2). The surface morphologies of the polymers were examined with the NT-MDT Ntegra-Solaris brand atomic force microscope (AFM) instrument before and after magnesium ion adsorption. Two different types have been tried (Tapping/Intermittent contact). Resonant Frequency: 240-440 kHz, Force Constant: 22-100 $N.m^{-1}$ & Resonant Frequency: 47-150 kHz, Force Constant: 0.35-6.06 $N.m^{-1}$. Surface images were taken with dimensions of 25x25 µm.

2.3. Synthesis of Poly(acrylonitrile-co-methyl methacrylate) [P(AN-MMA)] Copolymer by Free Radical Polymerization

Poly(acrylonitrile-co-methyl methacrylate) [P(AN-MMA)] copolymer was synthesized using acrylonitrile and methyl methacrylate by free radical polymerization. 0.180 g (0.001 mol) AIBN, 8.100 g (0.152 mol) acrylonitrile, 2.808 g (0.028 mol) methyl methacrylate [acrylonitrile:methyl methacrylate=(5.4):(1) (mol:mol)] and 10 ml of N,N-dimethylformamide were put separately into a glass balloon followed by N_2 flux for 5 minutes. The balloon was placed in an oil bath equipped with a magnetic stirrer. The polymerization was conducted at 70 °C for 20 hours. The precipitation of the copolymer was achieved by pouring the reaction mixtures into excess cold methanol. Therefore, the unreacted monomers were dissolved in methanol. After being kept in the freezer for 1 day, P(AN-

MMA) copolymer was isolated by decantation and dried at ambient temperature under vacuum for 4 days.

2.4. Synthesis of Hydrolyzed Poly(acrylonitrile-co-methyl methacrylate) [HP(AN-MMA)] Copolymer

A similar hydrolyze method was present in the literature (Bagheri et al., 2010; Deng et al., 2003). For the synthesis of hydrolyzed poly(acrylonitrile-co-methyl methacrylate) [HP(AN-MMA)] copolymer, 100 mL of ethanol:water (0.7 mol:3.3 mol) solution containing 5.035 g of NaOH was added into a 250 mL glass balloon. 1.625 g of P(AN-MMA) copolymer was added into the balloon and mixed at 75 °C. After 30 minutes, the reaction was terminated and the HP(AN-MMA) copolymer was collected with ordinary filter paper. It was washed with deionized water and dried in a vacuum oven at 40 °C.

2.5. Adsorption of Hydrolyzed Poly(acrylonitrile-co-methyl methacrylate) [HP(AN-MMA)] Copolymer

A similar method for polymer adsorption was present in the literature (Sruthi and Anas, 2020). 50 mL of deionized water solution containing 0.120 g of $Mg(NO_3)_2.6H_2O$ was added into a 100 mL glass balloon. The pH value of the solution was adjusted to 4.5 (pH=4.5). The optimum pH value at which the polymer-metal complex is 4.5 (Deng et al., 2003). 0.184 g of HP(AN-MMA) copolymer was added to the aqueous solution containing the metal ion. The polymer-metal complex was formed by mixing until adsorption equilibrium was reached at room temperature. The complex was then separated from the solution by filtration. Mg^{2+} concentrations in the solution before and after adsorption were calculated. At the end of the adsorption experiment, the adsorbent was separated from the aqueous solution, and the amount of Mg^{2+} in the remaining solution was found by titration with 0.01 mol ethylenedinitrilotetraacetic acid disodium salt dehydrates at pH=10 using NH_3/NH_4Cl buffer system.

3. Findings and Discussion

3.1. Synthesis of P(AN-MMA) Copolymer

The product was weighed as 9.966 g [yield: 91.36% (wt)]. The reaction step is shown in Scheme 1.
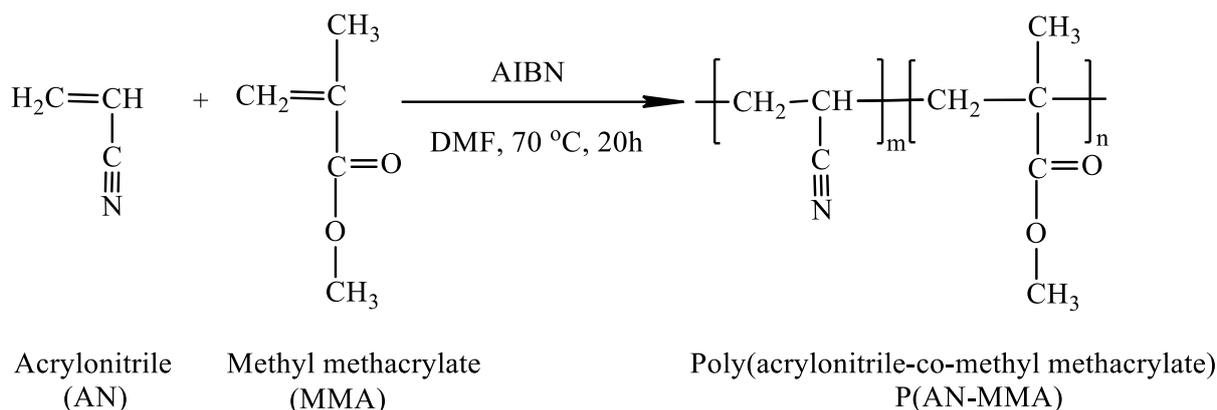
Scheme 1. Reaction pathway in the synthesis of P(AN-MMA) copolymer.

FT-IR spectrum of P(AN-MMA) copolymer given in Figure 1 shows the bands at 3426 cm^{-1} and 2947 cm^{-1} for asymmetric aliphatic -CH stretching, 2878 cm^{-1} for symmetric aliphatic -CH stretching, 2245 cm^{-1} for -C≡N stretching, 1728 cm^{-1} for asymmetric -C=O stretching, 1667 cm^{-1} for symmetric -C=O stretching and 1095-1211 cm^{-1} for -CO stretching. The ^{1}H-NMR spectrum of P(AN-MMA) copolymer in Figure 2 displayed signals at; (δ, ppm): 3.66 (-OC<u>H</u>$_3$ of polymethyl methacrylate block), 3.14 (-C<u>H</u> of polyacrylonitrile block), 2.05 (-C<u>H</u>$_2$ of polyacrylonitrile and polymethyl methacrylate blocks) and 1.33 (-C<u>H</u>$_3$ of polymethyl methacrylate block). The signals that -C<u>H</u> of the polyacrylonitrile group and -OC<u>H</u>$_3$ of polymethyl methacrylate trace in the spectrum were indisputable evidence of the synthesis of the copolymer (Vargun et al., 2014).
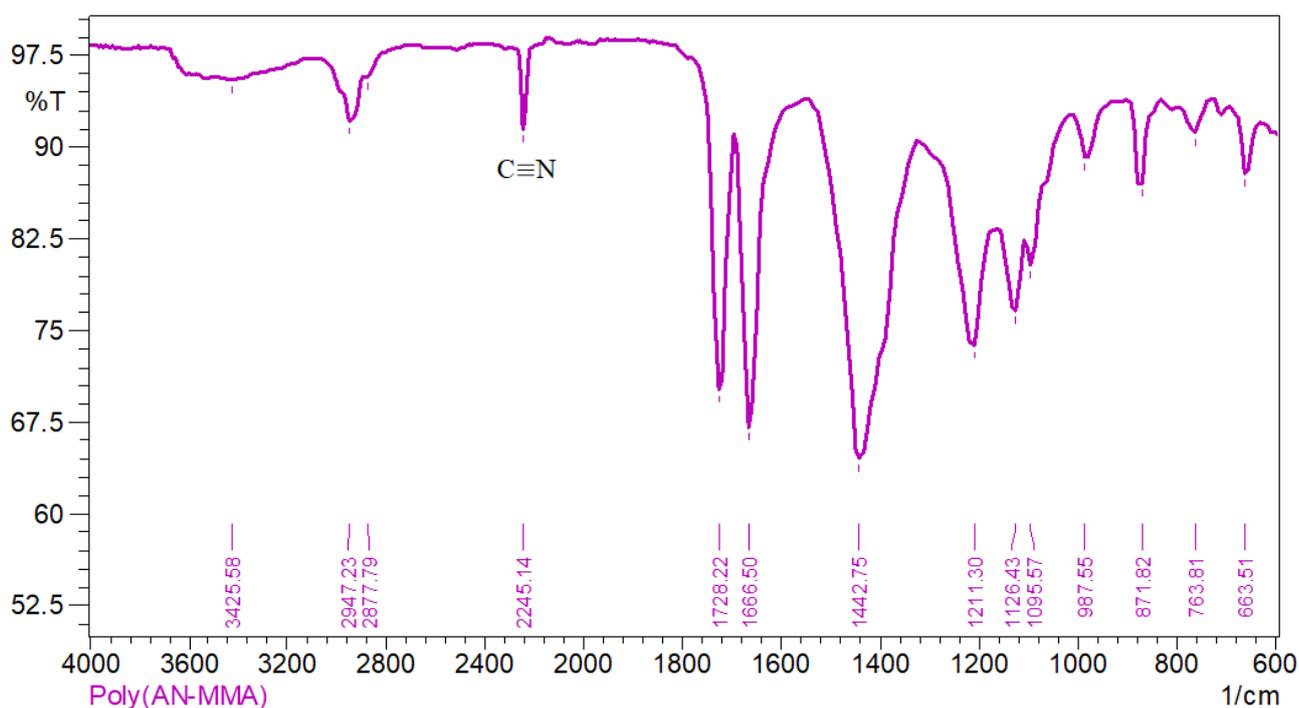

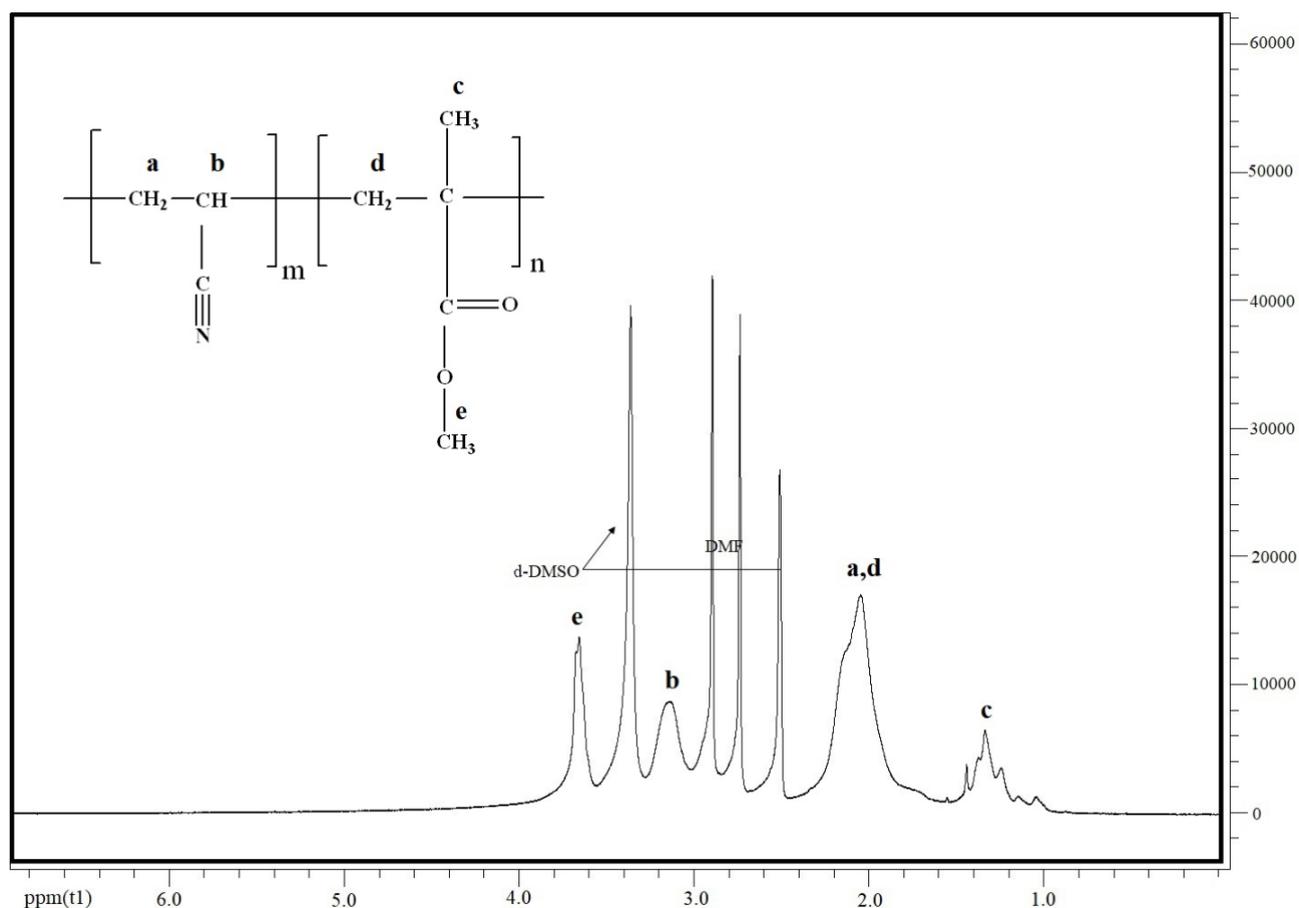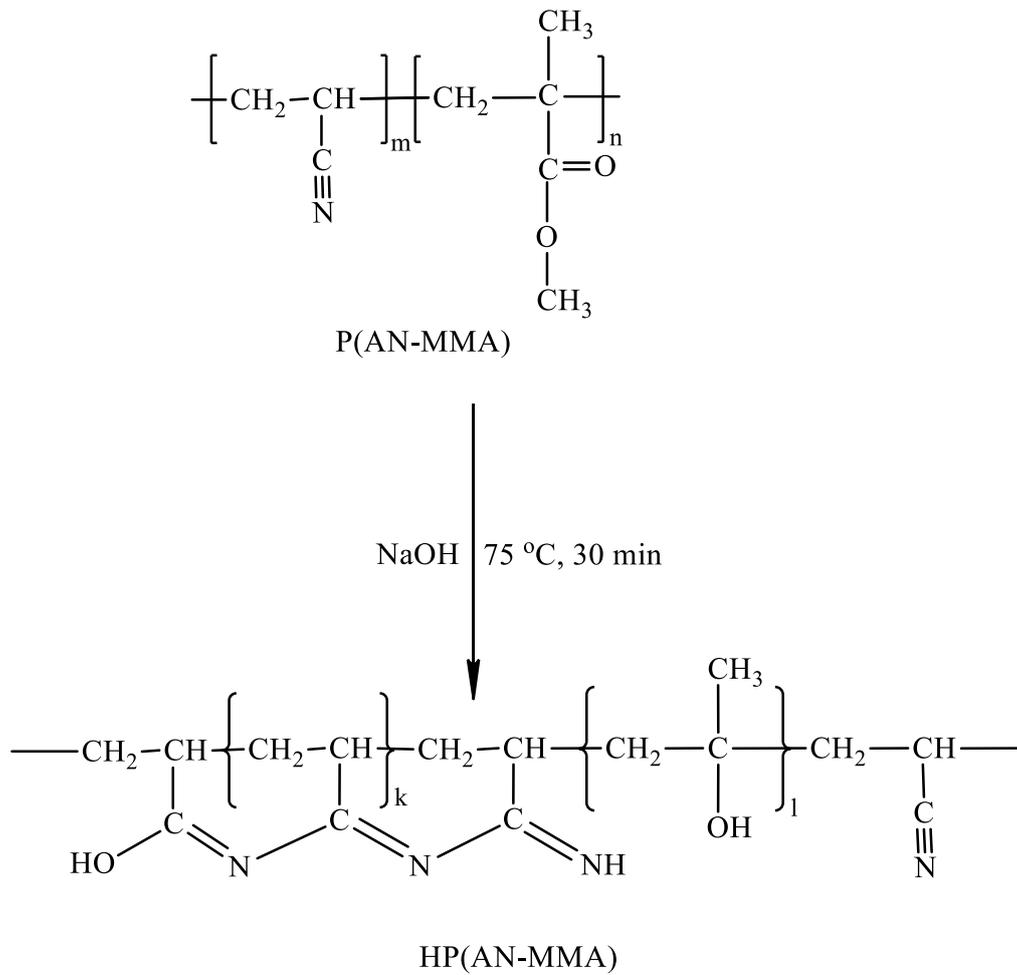**Figure 1**. FT-IR spectrum of P(AN-MMA) copolymer.

Figure 2. ^{1}H-NMR spectrum of P(AN-MMA) copolymer.

3.2. Hydrolysis of P(AN-MMA) Copolymer

The reaction outline is shown in Scheme 2. FT-IR spectrum of HP(AN-MMA) copolymer given in Figure 3 shows the bands at 3287 cm^{-1} for -OH stretching, 2245 cm^{-1} for -C≡N stretching, 1558 cm^{-1}, 1404 cm^{-1} and 1350 cm^{-1} for -C=N stretching vibration of the imine group. These new peaks formed in Figure 3 indicate the formed conjugated imine -C=N peaks. Since the -C≡N groups in the P(AN-MMA) copolymer turned into -C=N groups, the density of -C≡N groups in the HP(AN-MMA) copolymer decreased in Figure 3 compared to Figure 2. Additionally, the presence of -OH groups in Figure 3 is another proof that the synthesis was successful.

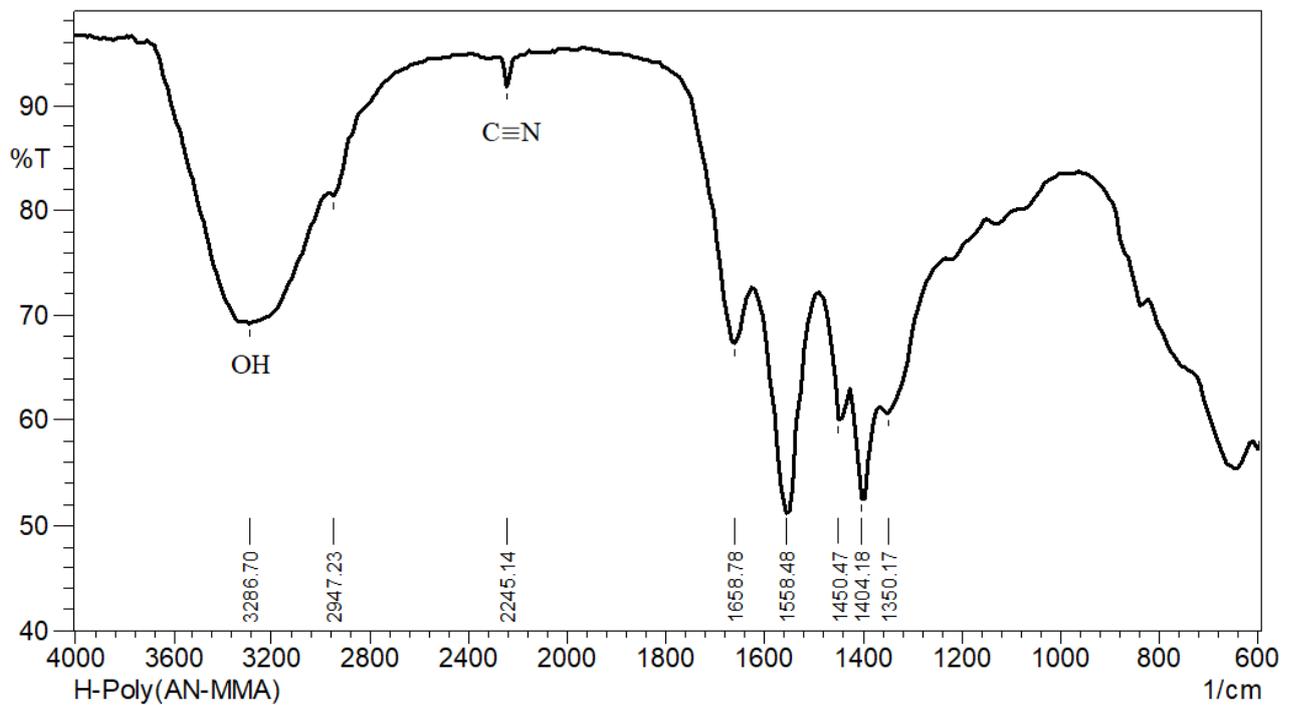**Scheme 2.** Reaction outline in the synthesis of HP(AN-MMA) copolymer.

Figure 3. FT-IR spectrum of HP(AN-MMA) copolymer.

3.3. Adsorption of HP(AN-MMA) Copolymer

The adsorption of the magnesium ion onto HP(AN-MMA) copolymer is illustrated in Figure 4. The amount of Mg^{2+} in the remaining solution was found to be 115 mg.L^{-1} at pH=10 by titration. The performance of the adsorbent was calculated to be approximately 50% for Mg^{2+}. The 3D image of the surface topography was visualized with an AFM instrument. Images of HP(AN-MMA) copolymer and magnesium-adsorbed HP(AN-MMA) copolymer are given in Figure 5. Average roughness (*Ra*) values were calculated from AFM images. The *Ra* value of HP(AN-MMA) copolymer was found to be 136 nm, and the *Ra* value of the magnesium-absorbed HP(AN-MMA) copolymer was found to be 354 nm. Magnesium ion adsorption made the surface rough. The increase in the roughness ratio proves that absorption has occurred.
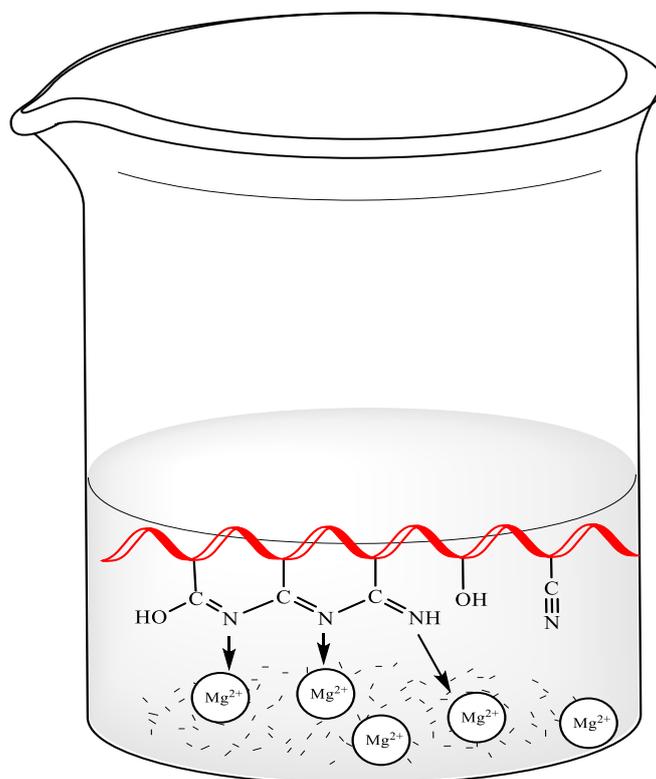

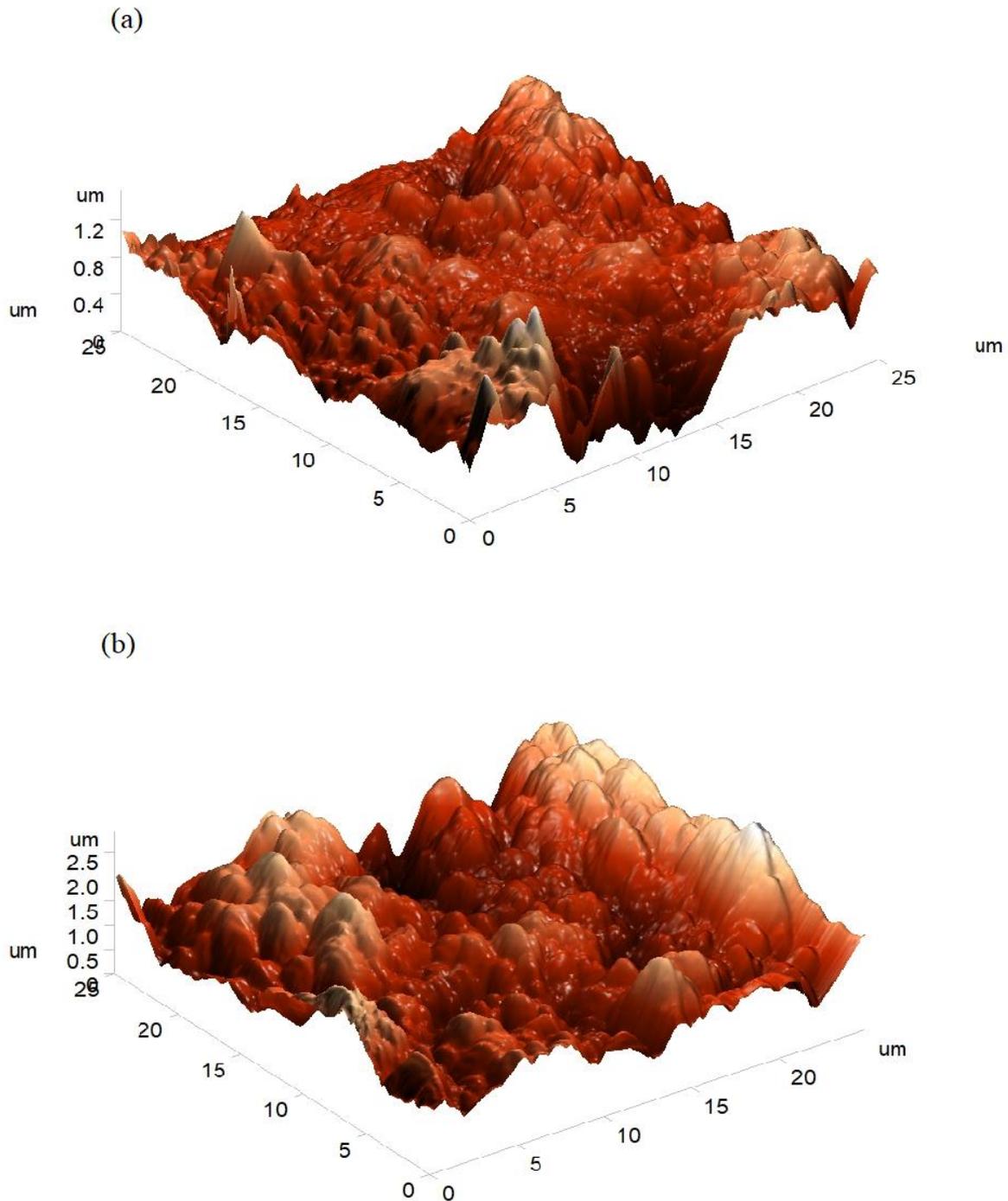**Figure 4.** Adsorption of magnesium ion onto HP(AN-MMA) copolymer.

Figure 5. Tridimensional AFM images of (a) hydrolyzed poly(acrylonitrile-co-methyl methacrylate) and (b) hydrolyzed poly(acrylonitrile-co-methyl methacrylate) with magnesium ion adsorption.

TGA results of P(AN-MMA) copolymer and HP(AN-MMA) copolymer with magnesium ion adsorption are shown in Figure 6. Initial weight losses in the TGA thermogram are due to the dissociation of residual solvent. P(AN-MMA) copolymer has two main decomposition temperatures (Td). The first weight loss occurred between 277 °C and 322 °C, with a maximum of 7.8% (wt) decomposing at 303 °C. According to the literature, this decomposition temperature is attributed to the decomposition of the polyacrylonitrile unit in the copolymer structure (Liu et al., 2019). The second weight loss occurred between 328 °C and 476 °C, with a maximum of 40% (wt) decomposing

at 385 °C. According to the literature, this decomposition temperature is attributed to the decomposition of the polymethyl methacrylate unit in the copolymer structure (Balci et al., 2002). TGA curve shows that the magnesium-adsorbed HP(AN-MMA) copolymer has a lower % weight loss than the P(AN-MMA) copolymer. It was observed less weight loss in the TGA curve due to the magnesium in the structure of the magnesium-adsorbed HP(AN-MMA) copolymer. It shows that the stability of the copolymers depends on the components in the copolymer (Çankaya and Besci, 2018).
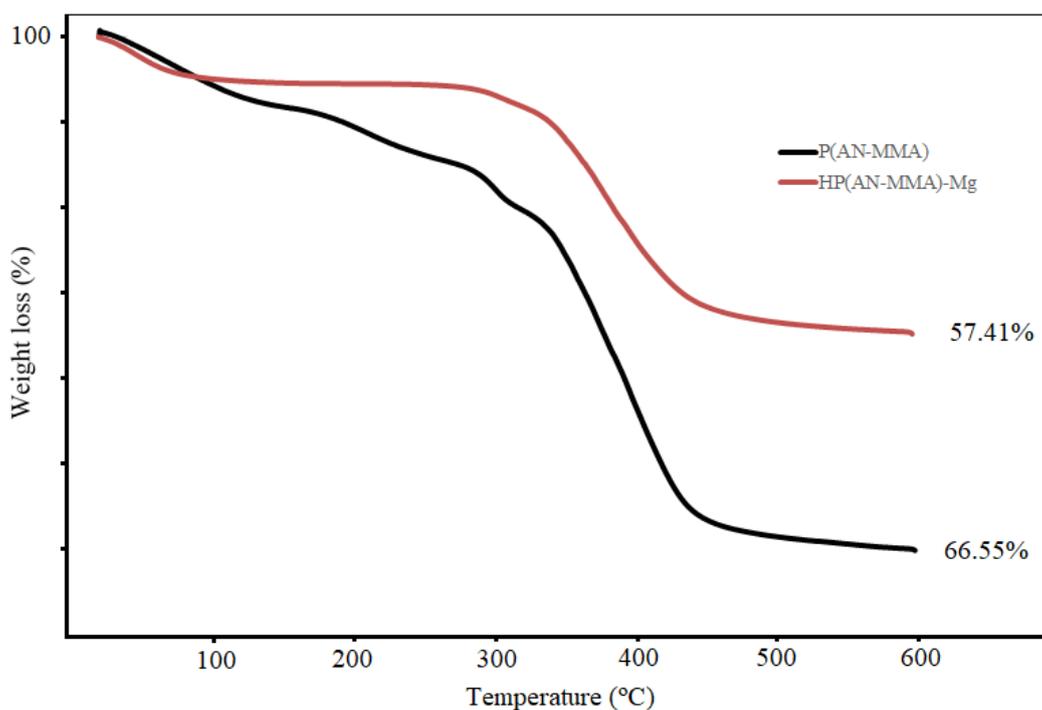

Figure 6. TGA results obtained for P(AN-MMA) and HP(AN-MMA)-Mg showing thermal degradation.

4. Conclusions and Recommendations

FT-IR, ^{1}H-NMR, AFM, and TGA were carried out for the product characterizations. These characterization methods prove that product syntheses have occurred. The *Ra* value of HP(AN-MMA) copolymer calculated from AFM images was found to be 136 nm, and the *Ra* value of the magnesium-absorbed HP(AN-MMA) copolymer was found to be 354 nm. The increase in the roughness ratio at AFM image and lower % weight loss at TGA of magnesium-adsorbed HP(AN-MMA) copolymer confirmed that absorption occurred. Hydrolyzed P(AN-MMA) copolymer can be used to obtain softened hard water.

Authors' Contributions

All authors contributed equally to the study.

Statement of Conflicts of Interest

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The author declares that this study complies with Research and Publication Ethics.

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