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Naringine Filtration By Polyacrylonitrile-co-poly(2-ethylhexyl acrylate) Copolymers

Poliakrilonitril-ko-poli(2-etilhegzil akrilat) Kopolimerleri İle Narinjin Filtrasyonu

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ABSTRACT

Polyacrylonitrile-co-poly(2-ethylhexyl acrylate) copolymers with different acrylonitrile/2-ethylhexyl acrylate ratios were synthesized and tested in terms of filtration performance for naringine removal. The flux increased with poly(2-ethylhexyl acrylate) content of the copolymer membrane. Moreover, the filtration performance increased with increasing polyacrylonitrile content of the copolymer membrane. The percent removal of naringin was found as 53.5%, 74.9% and 92.6% for PAN(84)-co-P2EHA(16), PAN(88)-co-P2EHA(12) and PAN(92)-co-P2EHA(8), respectively. Also, copolymer membranes could preserve its 83% of its initial performance after the fifth use.

ÖZET

Farklı akrilonitril/2-etilhegzil akrilat oranlarına sahip poliakrilonitril-ko-poli(2-etilhegzil akrilat) kopolimerleri sentezlenmiş ve narinjin filtrasyonu performansları test edilmiştir. Akış hızı kopolimer zardaki poli(2-etilhegzil akrilat) miktarıyla artmıştır. Filtrasyon performansı ise kopolimer zardaki artan poliakrilonitril miktarıyla artmıştır. Narinjinin yüzde filtrasyon değerleri PAN(84)-ko-P2EHA(16), PAN(88)-ko-P2EHA(12) ve PAN(92)-ko-P2EHA(8) kopolimerleri için sırasıyla %53.5, %74.9 ve %92.6 olarak bulunmuştur. Ayrıca kopolimer zarlar beşinci kullanımdan sonra başlangıç performanslarının %83'ünü korumuşlardır.

1. Introduction

Naringine is a flavonoid having a bitter taste that gives bitternes to various citrus juices such as mandarin and grapefruit (Figure 1) [1]. Also it has applications depending on its antioxidant, anti-ulcer and anti-inflammatory features. [2-5]. For the filtration of this flavonoid, various filtration methods have been used. They can be named as adsorption, solvent extraction, filtration, supercritical carbon dioxide, chemical processes, enzymatic and biological processes [1, 6-10]. In this study, filtration method with a membrane was used for its removal from aqueous solution. Membranes used in this study were obtained by the copolymerization of aniline with 2-ethylhexyl acrylate. Aniline ratio in the copolymer was varied from 84 to 92 mole percent while 2-ethylhexyl acrylate ratio was varied from 16 to 8 mole percent. The copolymer having acrylonitrile/2-ethylhexyl acrylate ratio of 84/16 was denoted as PAN(84)-co-P2EHA(16). Similarly, copolymers having acrylonitrile/2-ethylhexyl acrylate ratios of 88/12 and 92/8 were defined as PAN(88)-co-P2EHA(12) and PAN(92)-co-P2EHA(8), respectively.

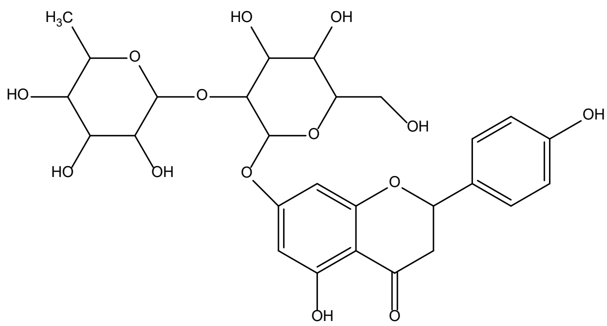

Figure 1. The chemical formula of naringine

2. Experimental

2.1. Materials

Acrylonitrile (Sigma-Aldrich, 99%) and 2-ethylhexylacrylate (Sigma-Aldrich, 98%) monomers were used for copolymerization. They were distilled before usage. Sulfuric acid (Sigma-Aldrich, 95-97%), isopropyl alcohol (Sigma-Aldrich, 99.9%) and ammonium persulfate (Sigma-Aldrich, 98+%) were directly used. 1-dodecanethiol (Sigma-Aldrich, 98+%) was used for chain transfer. DMF (Sigma-Aldrich, 99+%), NMP (Sigma-Aldrich, 99+%), magnesium sulfate (Sigma-Aldrich, 99+%) and DOWFAX 8390 (Dow Chemical Company) surfactant were used directly.

2.2. Copolymer Synthesis

Copolymers were synthesized via emulsion polymerization method. Polymerization was performed as follows:

20% of total 2-ethylhexylacrylate/acrylonitrile mixture, chain transfer agent, ammonium persulfate (65%), water and DOWFAX 8390 were mixed in a flask with three nakes. The flask contained thermocouple, dropping funnel, stirrer and condenser. Before and during the polymerization process, nitrogen gas was fed to the solution. The temperature was set at 66°C. The rest of 2-ethylhexylacrylate/acrylonitrile mixture was provided in 2 hours. When the monomer addition was finished, the remaining of DOWFAX 8390 was provided via dropping funnel. The solution was kept at 66°C for extra 40 min. Then the produced copolymer was obtained by precipitation in a 10% (w/w) aqueous solution of $MgSO_4$. Then, it was washed with distilled water and kept at 60°C in a vacuum oven for a day.

Aniline ratio in the copolymer was varied from 84 to 92 mole percent while 2-ethylhexyl acrylate ratio was varied from 16 to 8 mole percent. The amount of compounds in the copolymerization process is listed in Table 1.

Table 1. The amount of compounds for copolymerization process

Polymer	**Aniline** *(g)*	**2-ethylhexyl acrylate** *(g)*	**Surfactant** *(g)*	**Initiator** *(g)*	**Chain transfer agent** *(g)*	**Water** *(ml)*
PAN(84)-co-P2EHA(16)	3.39	2.25	0.45	0.006	0.11	7.1
PAN(88)-co-P2EHA(12)	3.42	1.61	0.40	0.005	0.09	7.1
PAN(92)-co-P2EHA(8)	3.38	1.02	0.35	0.004	0.08	7.1

2.3. Membrane Preparation

Synthesized copolymers (1.4 g) were added to DMF (9.0 g) and stirred for a day. After they were completely dissolved and obtaining homogeneous solution, the solution was poured on glass plate. Then, it was immersed in an IPA for 1 h and put in water for a day.

2.4. Characterization

FTIR of copoylmers was obtained by Spectrum100 FTIR spectrometer (Perkin Elmer). Flux and filtration measurements were conducted via a dead end filtration instrument under 2 bar pressure. The initial concentration of naringin solution was 7.5 ppm. The removal percent of naringine was obtained by UV-Vis spectrophotometer (Perkin Elmer Lambda 35). The area of membranes was 8.0 cm^2. Flux was calculated by Eq. 1;

$$J = \frac{V}{At} \tag{1}$$

where V, A and t are volume (L) of the solution passed through the membrane, membrane area (m^2) and filtration time (h), respectively.

The removal of naringine (R) was calculated by Eq. 2;

$$R = \left(1 - \frac{C_f}{C_i}\right) x100 \tag{2}$$

where C_f and C_i are the final and initial concentrations of naringine solutions before and after the filtration process, respectively.

3. Results and Discussions

The copolymers' chemical structure is seen in Figure 2.

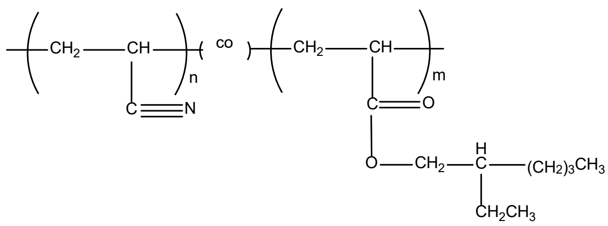

Figure 2. The chemical formula of polyacrylonitrile-co-poly(2-ethylhexylacrylate)

The FTIR analysis of copolymers were in Figure 3. CN and CH (aliphatic) stretchings were observed at 2241 and 2932 cm^{-1}, respectively. The CH bending was seen at 1453 cm^{-1}. Moreover, 2-ethyl acrylate ester group's C=O and C-C-O/O-C-C signals were found at 1726 and between 1064-1268 cm^{-1}, respectively.

As shown in Table 2, both water and filtrate fluxes were increased with increasing 2-ethylhexyl acrylate amount in the copolymer membranes. Water fluxes were found as 38.7, 94.4 and 116.8 L m^{-2} h^{-1} for PAN(92)-co-P2EHA(8), PAN(88)-co-P2EHA(12) and PAN(84)-co-P2EHA(16), respectively. Also, filtrate fluxes were calculated as 29.9 for PAN(92)-co-P2EHA(8), 61.8 for PAN(88)-co-P2EHA(12) and 78.3 L m^{-2} h^{-1} PAN(84)-co-P2EHA(16). This behaviour may arise from the increase in the amount of branching group 2-ethlyhexyl acrylate. As the branching group amount increases, pore diamaters of membranes may increase also. Thus, water and filtrate can pass through membrane more easily.

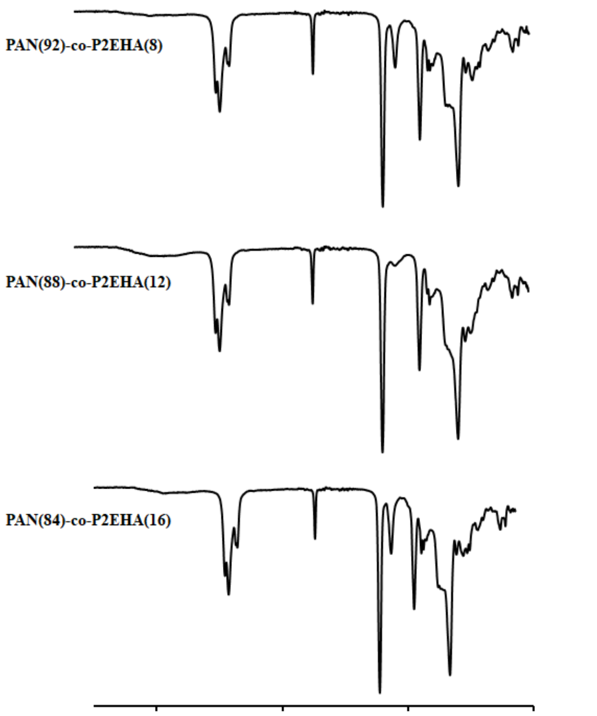

Figure 3. The FTIR spectra of PAN(92)-co-P2EHA(8), PAN(88)-co-P2EHA(12) and PAN(84)-co-P2EHA(16)

Table 2. Flux of membranes and permeates.

Membrane	Thickness (*µm*)	Pure water flux (*L/m²h*)	Filtrate Flux (*L/m²h*)
PAN(84)-co-P2EHA(16)	549	116.8	78.3
PAN(88)-co-P2EHA(12)	553	94.4	61.8
PAN(92)-co-P2EHA(8)	550	38.7	29.9

On the other hand, as the 2-ethylhexyl acrylate amount and the flux of filtrate decreased, the filtration performance increased. The decrease in flux shows that membranes get denser. Thus, the filtrate passed through membranes slower since its passing got more difficult. This led to that more naringin was prevented from passing through membrane without filtration. Hence naringine could be filtered more effectively with denser membrane and this increased the filtration performance. Removal percents of naringine was found as 92.6%, 74.9% and 53.5%, for PAN(92)-co-P2EHA(8), PAN(88)-co-P2EHA(12) and PAN(84)-co-P2EHA(16), respectively (Figure 4).

When reusage of membranes was tested, it was found that filtration performance of PAN(92)-co-P2EHA(8) membrane decreased from 92.6% to 76.6% (Figure 5). In other words, the membrane conserved 83% of its initial performance after the fifth use. Thus, it can be deduced that the membrane had reasonable durability upon reusage.

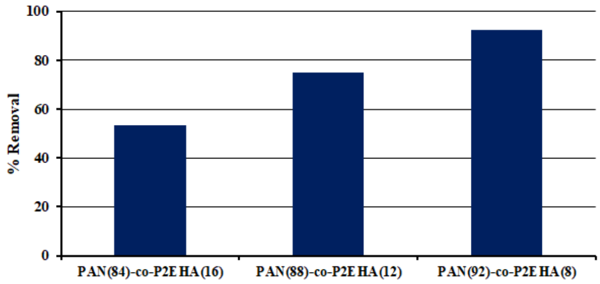

Figure 4. Filtration performances of PAN(92)-co-P2EHA(8), PAN(88)-co-P2EHA(12) and PAN(84)-co-P2EHA(16)

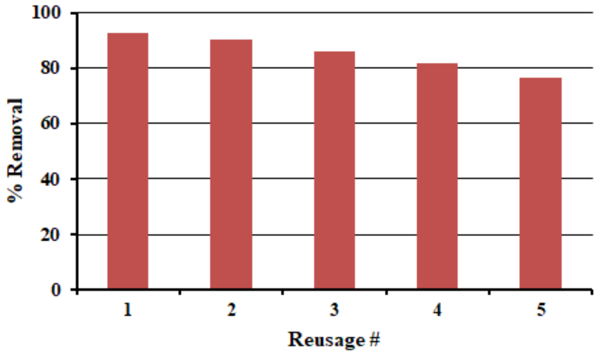

Figure 5. Reusage performance of PAN(92)-co-P2EHA(8) membrane

4. Conclusion

Naringine containing solution (7.5 ppm) was filtered by PAN(92)-co-P2EHA(8), PAN(88)-co-P2EHA(12) and PAN(84)-co-P2EHA(16) membranes. Fluxes increased with increasing poly(2-ethylhexyl acrylate) amount in the copolymer structure. On the other hand, filtration performance of membranes increased in the order of PAN(84)-co-P2EHA(16), PAN(88)-co-P2EHA(12) and PAN(92)-co-P2EHA(8). The highest naringin removal is obtained as 92.6% with PAN(92)-co-P2EHA(8). Also, this membrane preserved 83% of its initial performance after the fifth use. As a result, PAN(92)-co-P2EHA(8) copolymer membranes can be considered as a candidate for naringine filtration.

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Author Contributions: The authors confirm their responsibilities for the design of the study, data collection, analysis and interpretation of the results, and preparation of the manuscript.

Data Availability Statement: The data generated and/or analyzed during this study are not publicly available but can be provided by the corresponding author upon reasonable request.

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