

DIBENZO-18-CROWN-6/POLYCAPROLACTONE COMPOSITE NANOFIBERS FOR SELECTIVE ADSORPTION OF CATIONS

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Abstract: Electrospun nanofibers are attractive alternatives to traditional adsorbents due to their high surface-to-volume ratio, porosity, and loading capacity. Functionalization of nanofibers with macrocycles can contribute to further enhancement in selective adsorption of ions. In this study, polycaprolactone (PCL) nanofibers were functionalized with a crown ether, namely dibenzo-18-crown-6 (DB18C6), and the potential of the resultant electrospun PCL/DB18C6 nanofibers for selective ion adsorption, particularly the selective recovery for K^+ , was investigated. The morphology, chemical structure and thermal properties of PCL/DB18C6 nanofibers were characterized by scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The average diameter of PCL/DB18C6 nanofibers was 529 ± 196 nm. Single-ion adsorption experiments indicated that the adsorption capacity for K^+ ion was $137 \text{ mg} \cdot \text{g}^{-1}$ and the selectivity sequence was found as $K^+ > Ca^{2+} > Na^+$. The adsorption selectivity coefficients of K^+/Ca^{2+} and K^+/Na^+ were calculated respectively as 1.37 and 4.28 for single ion experiments and as 1.13 and 5.11 for mixed ion adsorptions which illustrate that the difference between the adsorption capacities of K^+ and Ca^{2+} decreased in mixed ion adsorption experiments. Overall results demonstrate that the electrospun PCL/DB18C6 nanofibers are amenable for use as polymer adsorbents for the selective ion recovery.

Keywords: Electrospinning, Nanofibers, Dibenzo-18-crown-6, Polycaprolactone, Adsorbent

Seçici Katyon Adsorpsiyonu için Dibenzo-18-Taç-6/Polikaprolakton Kompozit Nanolifleri

Öz: Elektroçirme yöntemi ile elde edilen nanolif yüzeyler yüksek yüzey alanı, gözeneklilik ve yükleme kapasitesi gibi özellikleri sayesinde geleneksel adsorban malzemelere karşı alternatif olarak dikkat çekmektedirler. Özellikle halkalı makromoleküller ile işlevselleştirilmiş nanolifler, iyonların seçici adsorpsiyonunun daha da geliştirilmesine katkıda bulunabilir. Bu çalışmada, polikaprolakton (PCL) ve dibenzo-18-taç-6 taç eteri (DB18C6) kullanılarak elektroçirme yöntemi ile PCL/DB18C6 kompozit nanolifleri elde edilmiş ve potasyum başta olmak üzere seçici iyon adsorpsiyonu için potansiyelleri incelenmiştir. PCL/DB18C6 nanoliflerinin morfolojileri, kimyasal yapıları ve ısı özellikleri taramalı elektron mikroskobu (SEM), Fourier dönüşümlü kızılötesi spektroskopisi (FTIR), X-ışını fotoelektron spektroskopisi (XPS), termogravimetrik analiz (TGA) ve diferansiyel taramalı kalorimetre (DSC) yöntemleriyle analiz edilmiştir. PCL/DB18C6 nanoliflerinin ortalama çapı 529 ± 196 nm olarak hesaplanmıştır. Tek iyon adsorpsiyon deneylerinde K^+ için adsorpsiyon kapasitesinin $137 \text{ mg} \cdot \text{g}^{-1}$, seçicilik sıralamasının ise $K^+ > Ca^{2+} > Na^+$ olduğu bulunmuştur. K^+/Ca^{2+} ve K^+/Na^+ adsorpsiyon seçicilik katsayıları tek iyon adsorpsiyon deneylerinde sırasıyla 1.37 ve 4.28, çoklu iyon adsorpsiyonlarında sırasıyla 1.13 ve 5.11 olarak hesaplanmıştır. Bu durum K^+ ve Ca^{2+} iyonlarının adsorpsiyon kapasiteleri arasındaki farkın çoklu iyon sistemlerinde azaldığını işaret etmektedir. Elde edilen sonuçlar, elektroçirme yöntemiyle üretilen PCL/DB18C6 nanoliflerinin seçici iyon kazanımı için adsorban malzeme olarak kullanımının uygun olduğunu göstermektedir.

Anahtar Kelimeler: Elektroçirme, Nanolif, Dibenzo-18-taç-6, Polikaprolakton, Adsorban

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1. INTRODUCTION

Macrocylic hosts such as crown ethers, cyclodextrins, calixarenes, pillararenes, and cucurbiturils are among the most widely used building blocks for the production of host–guest interaction-based supramolecular polymers (Chen et al., 2018; Fang et al., 2020; Liu et al., 2020; Ullah et al., 2022). They can be synthesized in high yields and versatility, and allow dynamic molecular activity, selectivity, reversibility, and responsiveness to external stimuli upon the introduction of a complementary guest molecule, pointing out their importance for the production of smart nanomaterials with controllable characteristics.

Crown-ethers are macrocyclic polyethers which are able to selectively bind specific cationic species through host-guest complexes. The complexation is due to the ion-dipole interaction between the positively charged metal ion and the negatively polarized oxygen atoms in the crown ether ring. The selectivity of the complexation is based on size-match, as crown ethers tend to form the most stable complexes with ions having similar diameters to that of the open cavity of the crown ether (Alexandratos and Stine, 2004; Limjuco et al., 2017; Nicoli et al., 2021). The interactions between cations, crown ethers, and solvents also play a role on the selectivity of the crown ethers. Crown ether incorporated polymers have been used as adsorbents in applications such as capillary chromatography, chemical sensor devices, ion transport membranes, phase-transfer catalysis, and ion-selective electrode (Stergiou et al., 2021; Yang et al., 2021; Jackson et al., 2021; Wang et al., 2022; Hu et al., 2022). Particularly, 18-crown-6 (18C6) and DB18C6 show the strongest binding affinity toward potassium cation (K^+) among alkali metal cations, although some reports pointed out that K^+ bound tightly to all crown ethers (12-crown-4 to 24-crown-8) regardless of the ring size (Pedersen, 1967; Gokel et al., 1983; Choi et al., 2012). Some experimental and computational studies revealed that the binding affinity of 18C6 or DB18C6 is stronger for smaller metal cations such as Li^+ or Na^+ compared to K^+ in the gas phase, unbarring the effect of solvation on the binding selectivity of crown ethers (Maleknia and Brodbelt, 1992; Anderson et al., 2003). DB18C6 also exhibits strong and selective binding for alkaline earth metal divalent cations. Buschmann et al. (1997) reported the order of selectivity for complexation of DB18C6 with divalent cations as $Ba^{2+}>Sr^{2+}>Ca^{2+}$ in aqueous solution. Rounaghi and Mofazzeli (2005) gave the order of selectivity as $Ba^{2+}>Sr^{2+}>Ca^{2+}>Mg^{2+}$ in methanol-water binary solvent system, while the theoretical order of selectivity was demonstrated as $Mg^{2+}>Ca^{2+}>Sr^{2+}>Ba^{2+}$ in the gas phase (Glendening and Feller, 1996; Heo, 2012). Heo (2012) also investigated that the strongest binding toward DB18C6 was that of Mg^{2+} among other alkaline dications, both in gas phase and aqueous solution.

Electrospinning is a widely used method for producing nanofibers due to its versatility, easy operation and low-cost (Bhardwaj and Kundu, 2010; Xue et al., 2019). This technique is based on the use of electrostatic forces to produce nanofibers from a wide range of polymers. A basic electrospinning set-up is composed of a syringe pump, a syringe connected to a spinneret, a high voltage supply and a grounded collector. The polymer solution is held by surface tension at the tip of the spinneret. When the applied voltage overcomes the surface tension, a jet is ejected from the spinneret with a whipping motion towards the grounded collector. The solvent evaporates during the travel of the jet, leaving the nanofibers on the collector. Nanofibers are one-dimensional nanomaterials which possess unique properties such as high surface area, high porosity, diversity in composition, high loading efficiency and easy functionalization with potential applications such as membranes, tissue engineering, wound dressings, drug delivery, energy applications, optics, catalysis, composites and biosensors (Barhoum et al., 2019; Islam et al., 2019; Yang et al., 2020).

Various methods have been used for the recovery of contaminants from water, including ion exchange, adsorption, chemical precipitation, coagulation–flocculation, filtration, reverse osmosis and solvent extraction. Among these techniques, adsorption becomes prominent as it is a simple, effective and low-cost method. Conventional adsorbents can suffer from low selectivity

and low efficiency in dilute aqueous solutions (Pereao et al., 2019). Nanofibers prepared by electrospinning are promising candidates as adsorbents because they can contribute to overcome such drawbacks. Nanofibers can decrease the necessary volume of both the solid phase and desorption solvent due to their high surface area, while the small diameter of the nanofibers can reduce the diffusion paths of the cations which will increase the adsorption kinetics (Salehi et al., 2021). Additionally, the porous structure of the nanofibrous membranes also enhances the convective delivery of cations on the fiber surface. Nanofibers provide enhanced sorption capacity due to their high surface area and active surface sites (Zhang et al., 2021). They also offer compositional flexibility and functionalizability with various fillers. Therefore, electrospinning will allow the design and synthesis of crown ether-containing composite nanofibers with ion recognition properties to be used as adsorption, enrichment and separation of ions. Cheng et al. (2021) introduced 2-(hydroxymethyl)-12-crown-4 ether/chitosan nanofiber composite membranes while Nisola et al. (2020) used azidated electrospun polyglycidyl methacrylate nanofibers functionalized with alkyne-ended DB14C4 for efficient Li^+ recovery from aqueous sources. DB18C6/PAN nanofibers were reported with good adsorptive selectivity for metal ions with a sequence of $\text{K}^+ > \text{Na}^+ > \text{Cs}^+ > \text{Li}^+$ and as $\text{K}^+ > \text{Ba}^{2+} > \text{Na}^+ \sim \text{Li}^+$ for single ion experiments (Tas et al., 2016; Shu et al., 2022). Polymeric crown ether/polystyrene composite nanofibers were used for selective extraction of catecholamines (Chen et al., 2015; Chen et al., 2017). The 14- to 16-membered crown ether diols and poly vinyl alcohol were electrospun, followed by aerosol glutaraldehyde crosslinking, leading to water-stable Li^+ adsorbent microfibrils (Limjuca et al., 2017). Ahmed et al. (2021) impregnated polyethylene terephthalate nanofibers with DB18C6 for the removal of methylene blue from aqueous solutions.

In this work, the selectivity of a crown ether, namely DB18C6, towards specific ions was investigated using electrospun PCL-based nanofibrous membranes with high surface area (Figure 1). PCL was chosen as the polymer for electrospinning process because of its high mechanical strength, low toxicity and low cost for the fabrication of nanofibrous adsorbents. The produced PCL/DB18C6 nanofibers were characterized by SEM, FTIR, DSC, TGA and XPS. The adsorption capacity of PCL/DB18C6 nanofibers was examined for both single and mixed ion solutions of Na^+ , K^+ and Ca^{2+} . The introduction of DB18C6 enhances the ion selectivity, making PCL/DB18C6 nanofibers promising materials for adsorption and filtration applications.

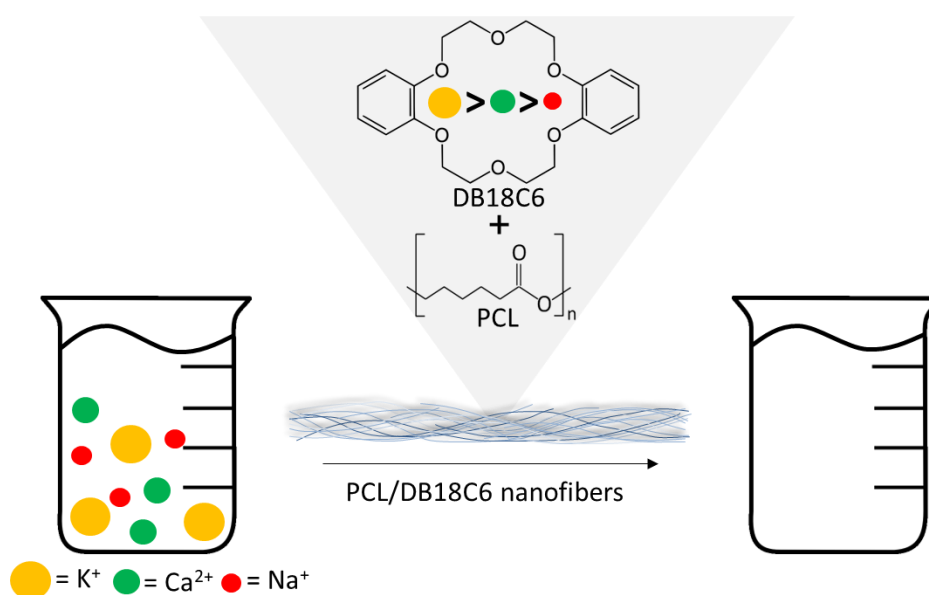


Figure 1:
Schematic illustration of the PCL/DB18C6 nanofibers for selective adsorption of cations

2. EXPERIMENTAL

2.1. Materials

Polycaprolactone (PCL, $M_n=70000-90000$ g/mol) and dibenzo-18-crown-6 (DB18C6, 98%) were purchased from Sigma. Dichloromethane and ethanol were purchased from Merck and used as received. NaCl, KCl and CaCl₂ were obtained from Merck.

2.2. Electrospinning of PCL and PCL/DB18C6 nanofibers

PCL solution was prepared in a dichloromethane/ethanol (4:1, v:v) solvent mixture with a concentration of 12 wt% and the solution was stirred for 4 h with a magnetic stirrer. The homogenous solution was placed in a syringe connected to a needle and a flow rate of 1 ml/h was applied to the solution. The applied voltage was 13 kV and nanofibers were collected on a grounded flat aluminum collector with a distance of 15 cm from the needle.

For PCL/DB18C6 nanofibers, DB18C6 was purified via washing with 1 M HCl. The dried DB18C6 was added to the PCL solution with an amount of 15% with respect to the polymer amount and stirred with a magnetic stirrer for a homogenous solution. The resultant PCL/DB18C6 solution was also electrospun with a feed rate of 1 ml/h, a voltage of 13 kV and tip-to-collector distance of 15 cm. Both PCL and PCL/DB18C6 electrospinning were performed at a relative humidity of 35±5% and a temperature of 23±3°C. The average diameters of the nanofibers were calculated by measuring 100 fibers using ImageJ.

2.3. Instrumentation

Scanning electron microscope (SEM, Tescan Vega3) was used to investigate the morphology of the fibers. Prior to analysis, samples were sputter-coated with 4 nm-thick gold/palladium layer. Nanofibers were analyzed by Fourier transform infrared-attenuated total reflectance spectroscopy (FTIR-ATR) using Perkin Elmer UATR Two for which 32 scans were recorded for each sample in the range of 500–4000 cm⁻¹. Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer DSC 4000 with a heating rate of 10°C/min and the scanning temperature range between 0 and 150°C with three cycles as heating, cooling and heating. Thermogravimetric analysis (TGA) measurements were carried out using a Hitachi STA7300 with a 15°C/min heating rate over a 25 to 800°C temperature range heated under N₂ atmosphere. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed on a Spectro SpectroBlue. X-ray photoelectron spectroscopy (XPS) measurements were taken by Specs-Flex XPS. The water contact angles (WCA) were detected by Theta Lite optical tensiometer TL 101. 5 µL of water was used to test WCA and the test procedure was monitored via a digital camera.

2.4. Single and mixed ion adsorption

Batch single ion adsorption experiments were performed by adding 15 mg of nanofibers in 15 mL of 10mM solutions of KCl, NaCl and CaCl₂ in ultrapure water at room temperature for 24h. For the mixed ion adsorption experiments, 15 mg of nanofibers were placed in 15 mL of a mixture of 10 mM KCl, 10 mM NaCl and 10 mM CaCl₂ in ultrapure water for 24 h at room temperature.

The adsorption quantities of metal ions onto PCL/DB18C6 nanofibers were calculated by testing the residual metal ions concentration with SpectroBlue ICP-OES. The equilibrium adsorption quantity of metal ions, q_e (mg·g⁻¹), is evaluated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

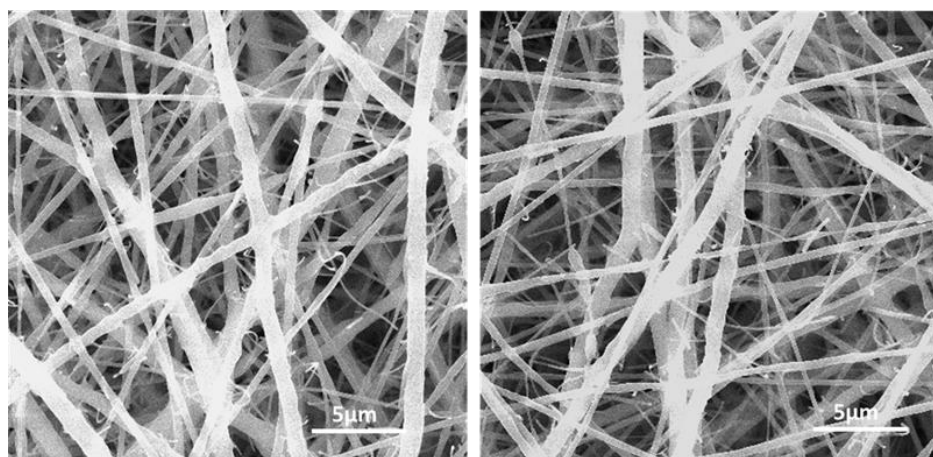
where c_0 ($\text{mg}\cdot\text{L}^{-1}$) is the initial concentration of metal ions, c_e ($\text{mg}\cdot\text{L}^{-1}$) is the equilibrium concentration of metal ions, V (L) is the volume of the solution, and W (g) is the mass of PCL/DB18C6 nanofibers. The selectivity coefficients were calculated using the equation:

$$S_{K^+/C^+} = q_e K^+ / q_e C^+ \quad (2)$$

where $q_e K^+$ and $q_e C^+$ are the adsorption capacities ($\text{mg}\cdot\text{g}^{-1}$) of K^+ and other cations (Na^+ or Ca^{2+}), respectively.

3. RESULTS AND DISCUSSIONS

Morphologies of neat PCL and PCL/DB18C6 nanofibers were investigated keeping the process parameters (applied voltage, tip-to-collector distance and feed rate) and ambient conditions (temperature, humidity) constant and were characterized by SEM. The micrographs of the nanofibers are shown in Figure 2a,b. The average diameters for PCL and PCL/DB18C6 nanofibers were calculated as 479 ± 278 nm and 529 ± 196 nm, respectively. The reason for the minor increase in the average diameter of PCL/DB18C6 nanofibers may be due to the possible decrease in the electrical conductivity and increase in shear viscosity of the electrospinning solution upon the addition of DB18C6. The incorporation of DB18C6 did not have a significant effect on the surface morphology of the PCL nanofibers. The slight roughness observed in the SEM images might be due to the difference in the boiling points of the solvents, causing phase separation and pores on the surfaces. Any variance in the electric field and shape of the Taylor cone during electrospinning can also cause unstable drawing which results in some deviations in the nanofiber diameters.



a.

b.

Figure 2:

- a.* SEM image of PCL nanofibers
- b.* SEM image of PCL/DB18C6 nanofibers

To confirm DB18C6 incorporation in the PCL nanofibers, PCL and PCL/DB18C6 nanofibers were characterized using FTIR spectrum (Figure 3). The characteristic peak of PCL due to the ester carbonyl stretching at 1734 cm^{-1} , as well as CH_2 stretching vibrations at 2942 cm^{-1} for asymmetric and at 2867 cm^{-1} for symmetric, were observed (Permyakova et al., 2019). The bands at 1016 cm^{-1} , 1150 cm^{-1} and 1294 cm^{-1} were respectively attributed to CO-O-CO , C-O and C-C stretching vibrations while C-C(=O)-O stretching was located at 1219 cm^{-1} for asymmetric and at 1149 cm^{-1} for symmetric. The presence of crown ether in the PCL nanofibers was confirmed by the absorption peaks at 1458 cm^{-1} , 1514 cm^{-1} and 1597 cm^{-1} corresponding to the aromatic skeleton of DB18C6. C-O-C and Ph-O-C stretching signals of the crown ethers were observed at around 1134 cm^{-1} and 1254 cm^{-1} , respectively (Chen et al., 2017; Guan et al., 2021). The band at 996 cm^{-1} corresponds to C-H in-plane bending vibration of the aromatic ring.

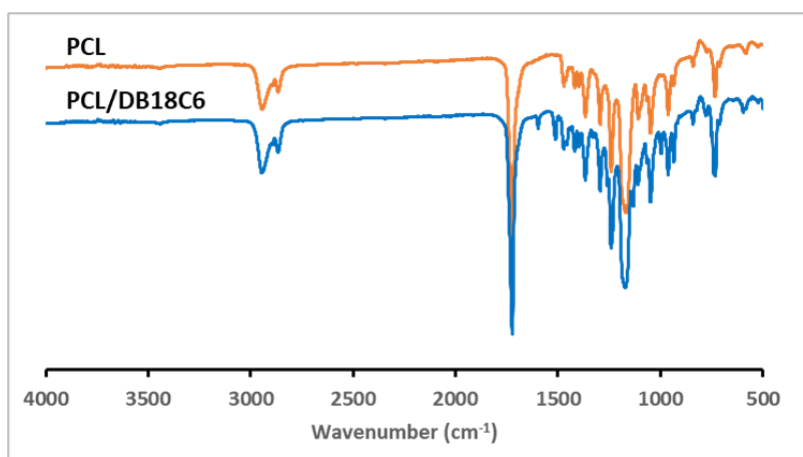


Figure 3:
FTIR spectra of PCL (orange) and PCL/DB18C6 (blue) nanofibers

The TGA curves in Figure 4 illustrate that PCL nanofibers show a single degradation step starting from 330°C to 417°C with a temperature of maximum decomposition at 401°C and a residue of 4.45%. These results agree with the values reported in the literature (Lozano-Sánchez et al., 2018). For PCL/DB18C6 nanofibers, the thermal degradation started at 295°C to 412°C as DB18C6 itself is more sensitive to thermal degradation, with a residue of 5.08 % (Figure 4). DB18C6 starts to decompose around 200°C and the decomposition completes around 375°C (Bhattacharyya and Goswami, 2009). As a result, the onset temperature shifted to lower temperature for PCL/DB18C6 nanofibers compared to neat PCL nanofibers and the introduction of DB18C6 did not bring any considerable changes on the thermal stability of PCL nanofibers.

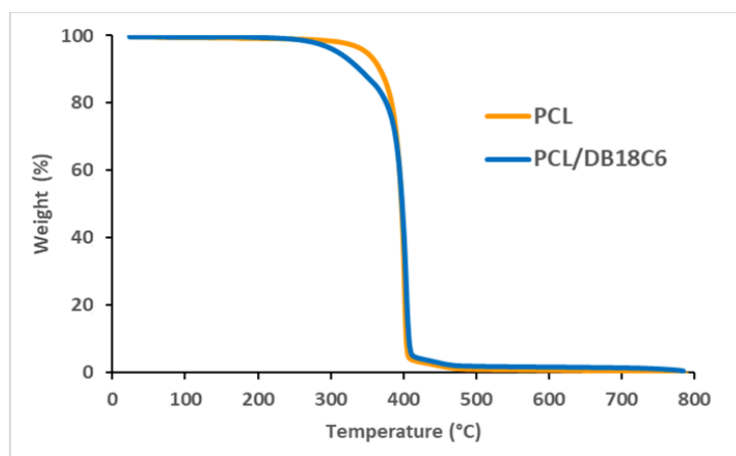


Figure 4:
TGA curves of PCL (orange) and PCL/DB18C6 (blue) nanofibers

DSC thermograms displayed a melting temperature of 56.87°C for PCL nanofibers and 55.60°C for PCL/DB18C6 nanofibers (Figure 5c,d). The crystallization temperature for PCL nanofibers was 25.06°C while it increased to 36.44°C for PCL/DB18C6 nanofibers with crystallization of DB18C6 at 82.96°C (Figure 5a,b). The increase in the crystallization temperature of PCL nanofibers might be due to the non-covalent interactions between PCL and DB18C6. The enthalpy of melting was 61.35 J/g and 54.18 J/g for PCL and PCL/DB18C6 nanofibers, respectively, while the enthalpy of crystallization was -62.34 J/g for PCL nanofibers and -52.38 J/g for PCL/DB18C6 nanofibers.

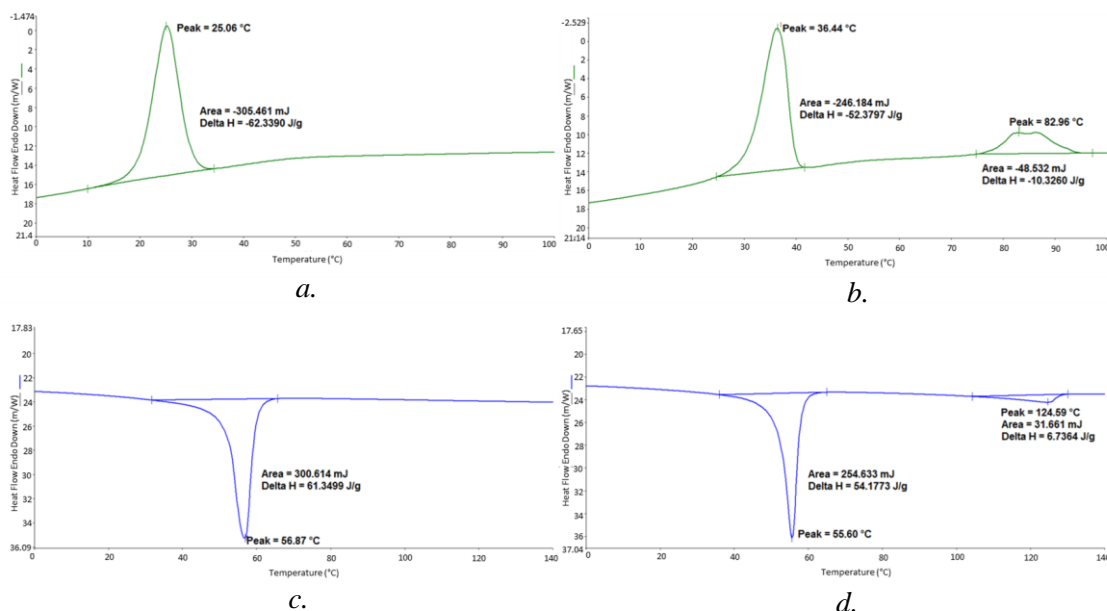


Figure 5:
a. Cooling thermogram of PCL nanofibers
b. Cooling thermogram of PCL/DB18C6 nanofibers
c. Second heating thermogram of PCL nanofibers
d. Second heating thermogram of PCL/DB18C6 nanofibers

Elemental analyses of PCL and PCL/DB18C6 nanofibers were characterized using XPS. The survey spectrum of PCL and PCL/DB18C6 nanofibers, as well as the PCL/DB18C6 nanofibers after K^+ adsorption were investigated. PCL and PCL/DB18C6 nanofibers showed a peak at 284.14 eV corresponding to C 1s and a peak at 532.16 eV corresponding to O 1s in the survey spectrum while the peaks shifted to 288.96 eV for C 1s and 536.98 eV for O 1s after K^+ adsorption (Figure 6a,d,g). The C 1s spectrum of PCL nanofibers can be curve-fitted to three peaks, including 284.91 eV, 287.16 eV and 290.76 eV which correspond to C–H, C–O and C=O, respectively. In PCL/DB18C6 nanofibers, the peak at 286.04 eV became more intense with crown ether addition and shifted to 286.57 eV upon K^+ adsorption (Figure 6i). There are two photoemission peaks in the O 1s spectrum of PCL nanofibers which are 533.62 eV and 531.17 eV for O=C–O and O=C–O ester oxygen environments. A third peak at 533.08 eV appeared in the O 1s spectrum of PCL/DB18C6 nanofibers which was attributed to the oxygen of crown ether and shifted to 532.09 eV after K^+ adsorption. The potassium ion amount on the PCL/DB18C6 nanofibers after K^+ adsorption was found as 17.25 at% from XPS analyses.

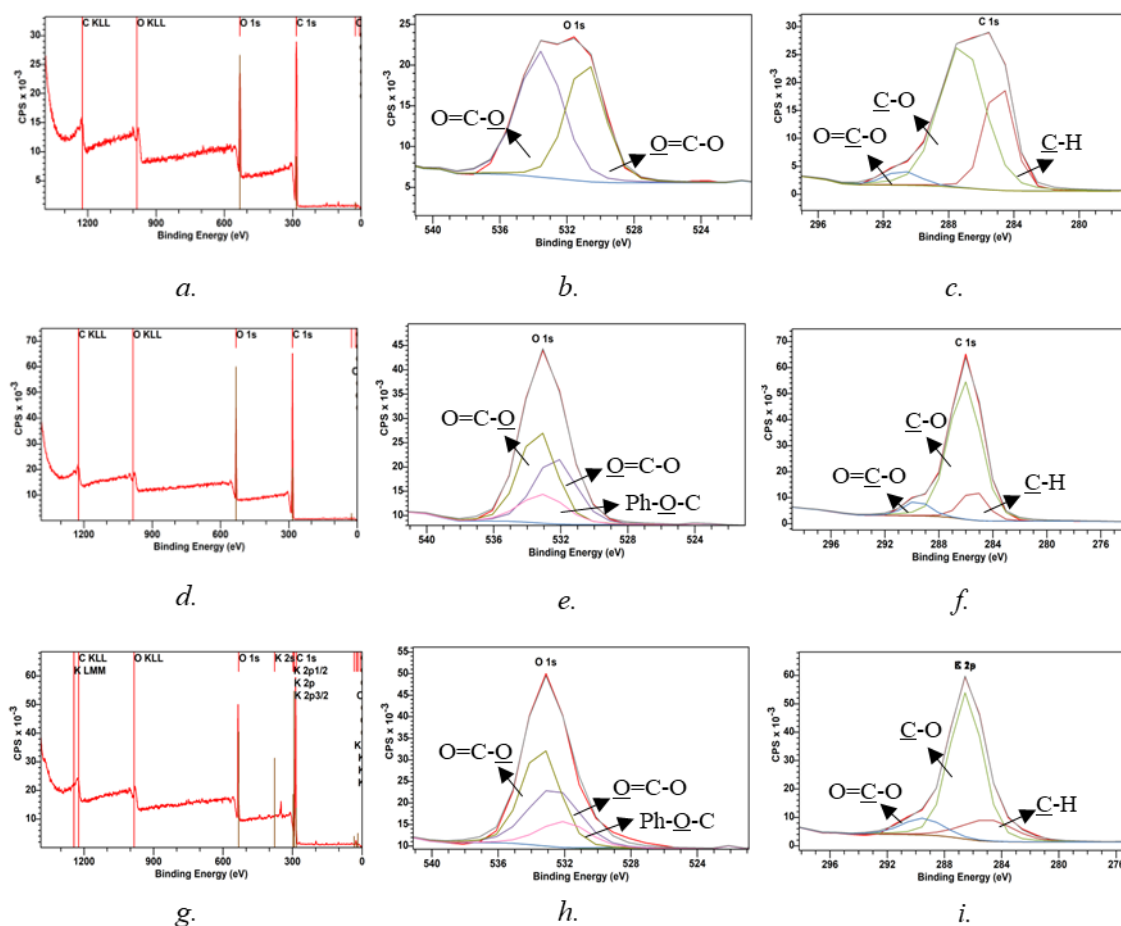


Figure 6:
a, b, c. Wide scan, O 1s, and C 1s XPS spectra of PCL nanofibers
d, e, f. Wide scan, O 1s, and C 1s XPS spectra of PCL/DB18C6 nanofibers
g, h, i. Wide scan, O 1s, and C 1s XPS spectra of PCL/DB18C6 nanofibers after K^+ adsorption

The ion adsorption capacities of the produced nanofibers were examined for both single and mixed aqueous ion solutions (Figure 7). Neat PCL nanofibers had a negligible adsorption capacity for Na^+ , K^+ and Ca^{2+} ions, whereas PCL/DB18C6 nanofibers displayed a tendency to Na^+ , K^+ and Ca^{2+} ion adsorption, pointing out that the adsorption ability of the PCL/DB18C6 nanofibers were due to the presence of the crown ether moieties. These nanofibers exhibited a K^+ adsorption capacity of $137 \text{ mg}\cdot\text{g}^{-1}$, which is higher than that of Ca^{2+} ($100 \text{ mg}\cdot\text{g}^{-1}$) and much higher than that of Na^+ ($32 \text{ mg}\cdot\text{g}^{-1}$). The Na^+ ion adsorption capacity was the lowest due to the weak interactions between Na^+ ions and DB18C6, which causes the formation of less stable complexes that can easily dissociate from the crown ether. Mixed ion adsorption experiments were performed in order to adjust the selective adsorption of the cations on the PCL/DB18C6 nanofibers. The adsorption capacities of Ca^{2+} and K^+ ions became closer to each other in mixed ion adsorption measurements. It can also be observed that both K^+ and Ca^{2+} adsorption capacities in mixed ion adsorption experiments decreased compared to single ion adsorption experiments, particularly that of K^+ at a higher extent. The adsorption selectivity coefficients of $\text{K}^+/\text{Ca}^{2+}$ and K^+/Na^+ were calculated respectively as 1.37 and 4.28 for single ion experiments and as 1.13 and 5.11 for mixed ion adsorptions, indicating that the K^+ adsorption reduced in the presence of Ca^{2+} ion in the solution.

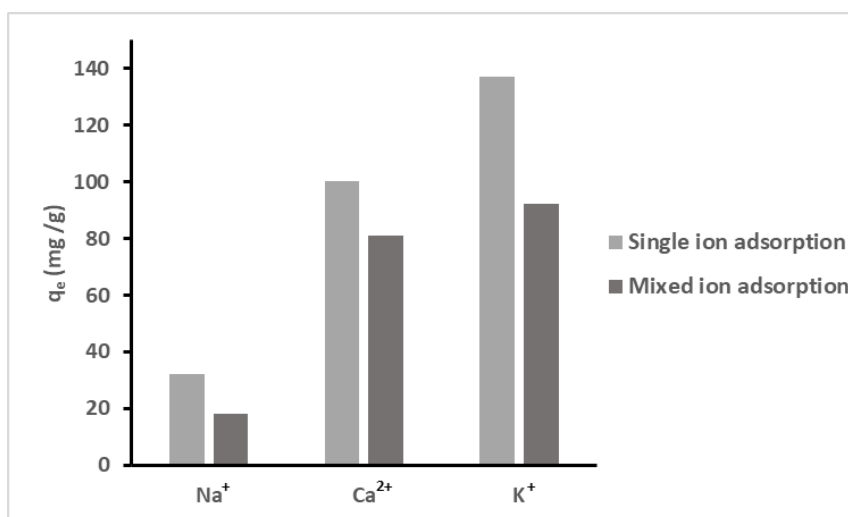


Figure 7:

Adsorption capacities of PCL/DB18C6 nanofibers for single and mixed ion systems

The surface wettability of the fabricated nanofibrous mats was investigated via measuring water contact angles. The WCA of neat PCL nanofibers was measured as $112.20 \pm 1.35^\circ$, while the WCA of PCL/DB18C6 nanofibers was $104.94 \pm 2.37^\circ$ before K^+ adsorption and $95.83 \pm 2.46^\circ$ after K^+ adsorption (Figure 8a-c). Taking into account that the surface properties of PCL and PCL/DB18C6 nanofibers investigated by morphological analyses were similar, the decrease in the WCA of PCL/DB18C6 nanofibers compared to the neat PCL nanofibers might be mainly due to the presence of DB18C6 on the surface of the nanofibers. DB18C6 is amphiphilic possessing hydrophobic aromatic rings and hydrophilic cavity, which can also interact with water and hydrated protons through non-covalent interactions (Kriz et al., 2008; Patel et al., 2018). The hydrophilic nature of DB18C6 is known to be improved with the adsorption of cations in the cavity (Sahu et al., 2014). As a result, the surface wettability of the PCL nanofibers was found to be enhanced upon incorporation of DB18C6, as well as K^+ adsorption.

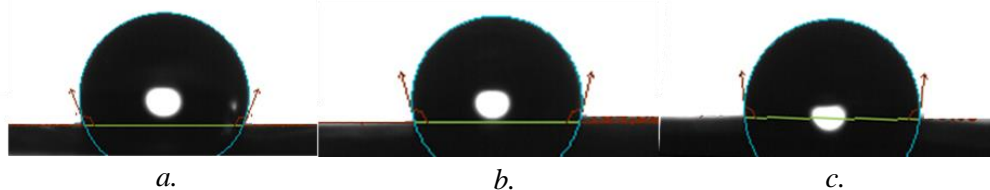


Figure 8.

- a. WCA of PCL nanofibers
- b. WCA of PCL/DB18C6 nanofibers
- c. WCA of PCL/DB18C6 nanofibers after K^+ adsorption

4. CONCLUSIONS

Uniform PCL/DB18C6 nanofibers were successfully prepared using electrospinning and the loading of DB18C6 was 15% of the PCL amount. The PCL/DB18C6 nanofibers were morphologically investigated using SEM and nanofibers with an average diameter of 529 ± 196 nm were observed. The composite nanofibers were characterized using FTIR, TGA, DSC and XPS. Both single ion and mixed ion adsorption experiments were performed on the nanofibers using K^+ , Na^+ and Ca^{2+} ions. In both cases, the adsorptivity sequence was found as $K^+ > Ca^{2+} > Na^+$ while the adsorption selectivity coefficients of K^+/Ca^{2+} decreased from 1.37 to 1.13 in the case of mixed ion adsorptions which pointed out that the K^+ adsorption reduced in the presence of Ca^{2+} ion in the solution. The maximum adsorption quantities of K^+ , Ca^{2+} and Na^+ were respectively $137 \text{ mg} \cdot \text{g}^{-1}$, $100 \text{ mg} \cdot \text{g}^{-1}$ and $32 \text{ mg} \cdot \text{g}^{-1}$ in single ion adsorption experiments and $92 \text{ mg} \cdot \text{g}^{-1}$, $81 \text{ mg} \cdot \text{g}^{-1}$ and $18 \text{ mg} \cdot \text{g}^{-1}$ for mixed ion adsorptions. The surface wettability of the PCL nanofibers was also found to be increased both with the incorporation of DB18C6 and adsorption of K^+ . Consequently, the PCL/DB18C6 nanofiber mats are suitable candidates for ion adsorption membrane applications.

CONFLICT OF INTEREST

The author acknowledges that there is no known conflict of interest or common interest with any institution/organization or person.

AUTHOR CONTRIBUTION

Özlem İpek Kalaoğlu-Altan contributed 100% at every stage of the study.

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