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Electrospun nanofiber membranes for adsorption of dye molecules from textile wastewater

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Abstract. The nanofiber membranes prepared by the electrospinning method have unique properties such as high specific surface area and high porosity with fine pores. These properties led electrospun nanofiber membranes to use for the removal of dye molecules from textile wastewater. In this study, a hydrophobic Thermoplastic Polyurethane (TPU) and a hydrophilic Poly (vinyl alcohol) (PVA) were selected for producing electrospun nanofibers and their sorption capacities were investigated. The largest sorption capacity reached to maximum 88.31 mg/g, belong to BTCA cross-linked PVA membranes due to hydrophilic character of PVA. Contrary to expectation, hydrophobic character of TPU was dominant and incorporation of CD to the TPU nanofibers did not affect the sorption of the TPU membranes, and showed very low adsorption capacity (14.48 mg/g).

1. Introduction

Dye wastewater discharge from the textile and dye industries has been one of the major environmental pollution concerns [1]. Dye's large and complex molecular structure, high degree of chemical and photolytic stability in order to fulfil the fastness requirements cause high recalcitrance to degradation which have posed a great challenge for color removal and complete mineralization [1-2]. With the growing awareness and environmental concerns, it is imperative that reduce, reuse and degrade be adopted and measures taken to remove color from the industrial discharges [3].

Thus, lots of researches have been undertaken in order to develop an effective treatment process for dye wastewater. For the removal of synthetic dyes from waters and wastewaters to decrease their impact on the environment, a wide range of methods have been developed. The technologies involve adsorption on inorganic or organic matrices, decolorization by photocatalysis, and/or by oxidation processes, microbiological or enzymatic decomposition, etc. [4]. Adsorption is one of the most effective, economically feasible techniques for the removal of textile dyes from wastewater [3].

The most important properties of any adsorbent are the surface area and structure. Furthermore, the chemical nature and polarity of the adsorbent surface can influence the attractive forces between the adsorbent and adsorbate [5]. The nanofiber membranes prepared by the electrospinning method have unique properties such as high specific surface area and high porosity with fine pores. These properties led electrospun nanofiber membranes to use for the removal of heavy metal ions [6-8] dye molecules from textile wastewater [9-11].



The electrospinning process simply uses a high voltage power source, a nozzle and a collector covered with aluminum foil. The potential difference between nozzle and collector leads to stretch of the solution and creates a thin jet from polymeric solution towards to the collector. During the stretch of the solution to the collector, the solvent evaporates and ultrafine nanofibers are collected [12, 13]. The electrospinning process has attracted a great deal of attention due to its relative ease of use, adaptability, ability to fabricate fibers with diameters on the nanometre scale [13,14], lots of possibilities for surface functionalization [15,16] with high surface area to volume or mass ratio, small inter-fibrous pore size and high porosity [13,17-18].

In the present study, a hydrophobic TPU and a hydrophilic PVA polymers were selected. TPU is chosen as a material for composing a nanoweb due to its chemical stability, mass transport, good mechanical properties, and also excellent nanofiber forming characteristic. On the other hand, PVA is a water-soluble synthetic polymer and because of its hydrophilic nature, PVA must be cross-linked to minimize swelling in water for water treatment applications. In this study polycarboxylic acids; 1,2,3,4 butanetetracarboxylic acid (BTCA) and citric acid (CA) were selected as cross-linking agents for PVA nanofibers. Cyclodextrins (CDs) were incorporated to the PVA and TPU nanofibers to alter the adsorption properties due to inclusion complex formation ability [19]. Neat TPU and PVA, cross-linked PVA, CD loaded TPU/CD and PVA/CD nanofiber membranes were prepared by the electrospinning method and its application for the removal of Reactive Red 141 (Figure 1) from aqueous solution was investigated. Then, the effects of contact time, incorporation of CD to the PVA and TPU nanofibers and cross-linking agents and their concentrations for PVA nanofibers have been investigated to obtain the optimum conditions for the maximum adsorption capacity of dye molecules.

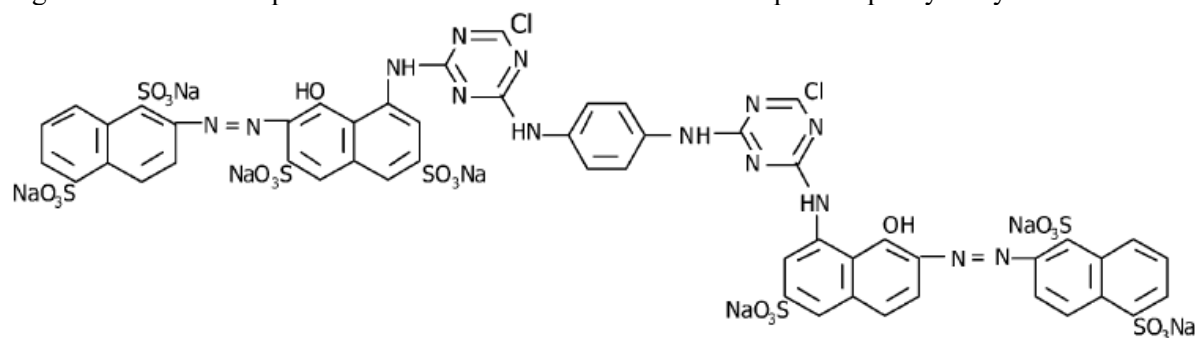


Figure 1. Reactive Red 141.

2. Experimental

Thermoplastic polyurethane (Pellethane 2103-80AE, based on 4,4-methylene bisphenylene isocyanate, polytetramethyleneoxide and 1,4 butanediol) was received from Velox (Lubrizol Advanced Materials). PVA with average molecular weight of $\sim 125,000$ g/mol, 1,2,3,4 butanetetracarboxylic acid (BTCA), citric acid (CA), cyanamide, sodium hypophosphite monohydrate ($\text{NaPO}_2\text{H}_2 \cdot \text{H}_2\text{O}$) and dimethylformamide (DMF) were purchased from Sigma Aldrich Chemical Company. β -CD was purchased from Wacker Chemie AG.

Homogeneous TPU solutions were prepared by dissolving 10% (w/w) of TPU plastic granulates in DMF. β -CD was added into the spinning solution followed by a further stirring. To examine the effects of the amounts of β -CD, 10%, 20% and 30% β -CD (w/w_{polymer}) concentrations were used for TPU and 30% β -CD (w/w_{polymer}) was used for PVA. A weighed amount of PVA was dissolved in distilled water at 100°C to prepare an aqueous PVA stock solution at a fixed concentration of 10% w/w. BTCA and CA as crosslinking agents were selected to be 5%, 10% and 20% (w/w_{polymer}) and were directly added into the spinning solution with cyanamide or sodium hypophosphite monohydrate as catalyst in ratio of 2:1 (w/w) followed by stirring for 10-15 min.

As a control, neat-TPU and neat-PVA nanofibers were prepared by electrospinning. Uniform TPU and PVA thin films were generated by a solvent-casting method.

Electrospinning of the polymer solutions was carried out by a set-up consisting of a syringe (10 mL) with a stainless steel needle (22 gauges, and flat tip), a ground electrode and a high voltage supply (Simco, MP Series CM5 30 P, Charging Generator Output 30 kV DC). A grounded stationary rectangular metal collector covered by a piece of aluminium foil was used for the nanofiber deposition. After electrospinning, PVA/BTCA and PVA/CA nanofiber and control groups of neat PVA nanofibers and PVA films were heat set. Heat set temperature were 110°C for cyanamide, 130°C for sodium hypophosphite monohydrate, for 20 min.

The nanofiber membranes and films used for the adsorption of reactive dye. The kinetic studies were carried out in 15 mL test tube containing 10 mL of the adsorption solution with 100 mg/L dye concentration and 10 mg adsorbent. These tubes were stirred on the orbital shaker (Nüve, ST 402) at 25°C over a time interval of 0-24 h. The residual dye concentration in the liquid was analyzed using a UV-Vis spectrophotometer (PerkinElmer Lambda 25) at 518 nm. The data were used to calculate the adsorption capacity (mg/g), q_e , of the adsorbent. The dye concentration on the adsorbent surface at equilibrium (1) was calculated by;

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

where C_0 , initial dye concentration in liquid phase (mg/L); C_e the equilibrium dye concentration (mg/L); V , total volume of dye solution used (L); m , mass of adsorbent used (g).

3. Results and Discussion

The surface morphology of electrospun nanofibers of neat TPU and PVA, BTCA and CA cross-linked PVA, TPU/CD and BTCA cross-linked PVA/CD nanofibers were investigated by scanning electron microscopy (SEM) imaging. Figure 2 shows the representative SEM images of TPU and PVA nanofibers.

Based on the SEM images bead free TPU and PVA nanofibers were produced. Table 1 lists the CD percentages, the crosslinker contents and the diameters of TPU and PVA nanofibers. TPU nanofibers were produced in the range of 506.12 nm and 762.92 nm, PVA nanofibers were produced in the range of 290.72 nm and 223.72 nm.

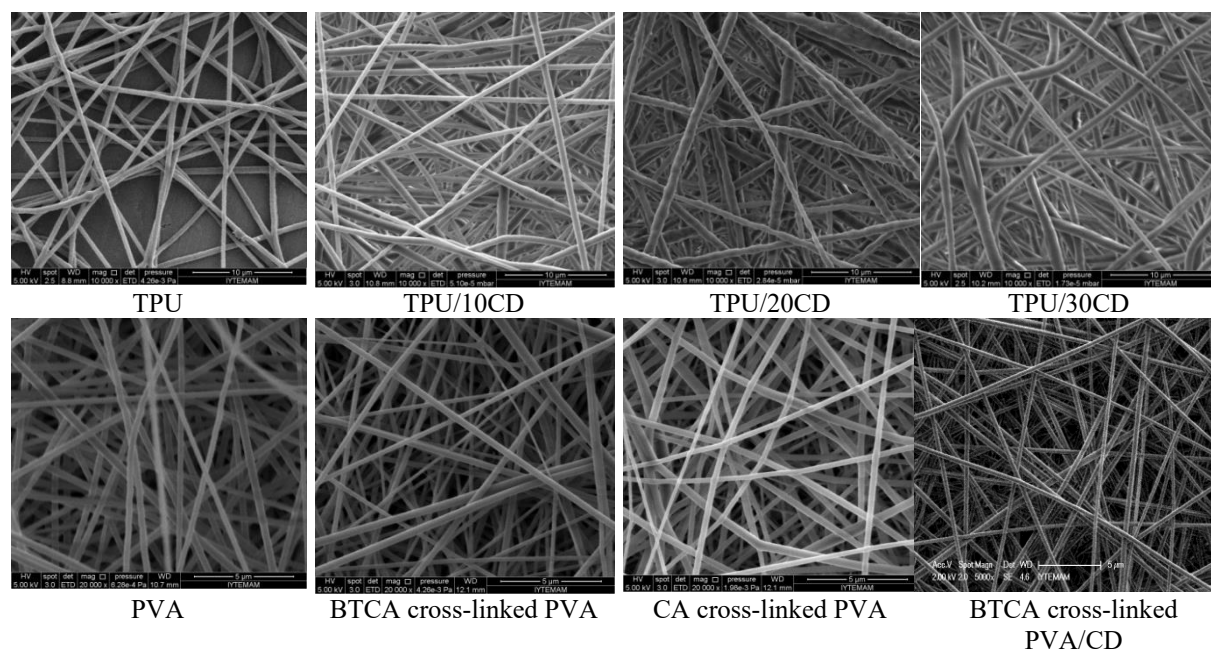


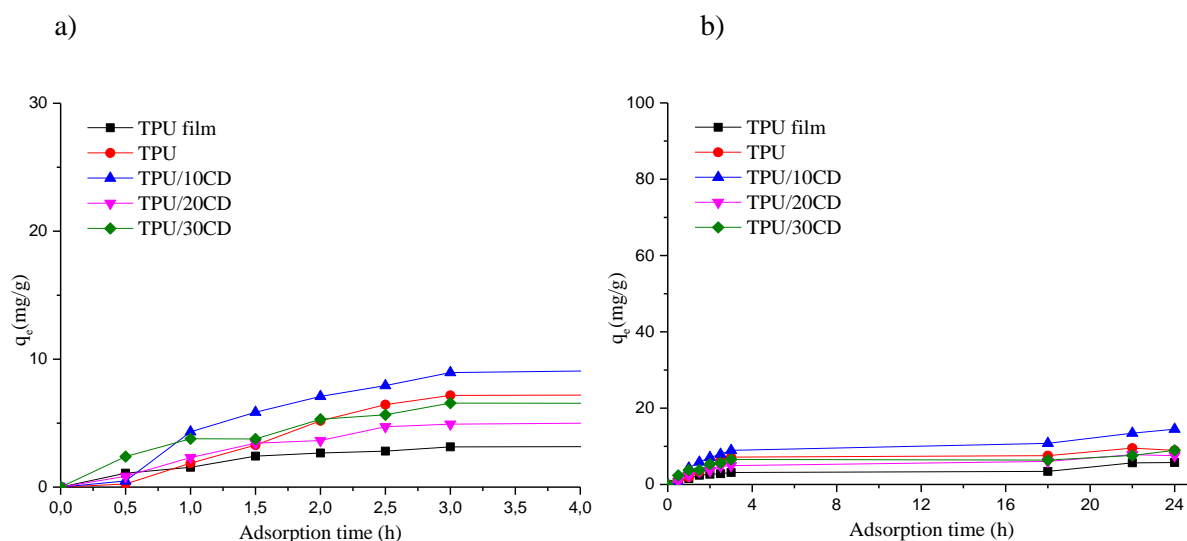
Figure 2. SEM images TPU, TPU/CD, PVA, cross-linked PVA and PVA/CD nanofibers.

Table 1. Diameters, CD percentages and crosslinker contents of TPU and PVA nanofibers.

	CD percentage (%)	Crosslinker content (%)	Nanofiber Diameter (nm) \pm SD
TPU	-	-	506.12 \pm 45.29
TPU/10CD	10	-	636.53 \pm 121.48
TPU/20CD	20	-	722.48 \pm 116.72
TPU/30CD	30	-	762.92 \pm 140.19
PVA	-	-	291.60 \pm 38.70
PVA/5BTCA	-	5 BTCA	290.72 \pm 47.11
PVA/10BTCA	-	10 BTCA	282.56 \pm 47.47
PVA/20BTCA	-	20 BTCA	235.92 \pm 64.41
PVA/5CA	-	5 CA	260.30 \pm 47.46
PVA/10CA	-	10 CA	253.37 \pm 58.15
PVA/20CA	-	20 CA	223.72 \pm 62.08
PVA/20BTCA-30CD	30	20 BTCA	278.23 \pm 51.33

In order to determine the adsorption rate, the adsorption of Reactive red 141 dyes onto the membranes was studied as a function of contact time. The contact time between the adsorbate and the adsorbent is of great importance in wastewater treatment by adsorption. A rapid uptake of adsorbents and the establishment of equilibrium in a short period signify the efficiency of an adsorbent for use in wastewater treatment [20].

Figure 3 presents the effect of contact time on the adsorption of Reactive red 141 dyes onto the TPU nanofibers. Contrary to expectation, the equilibrium sorption capacity of TPU film, TPU, TPU/10CD, TPU/20CD, TPU/30CD nanofiber membranes after 24h was equal to 5.74, 8.95, 14.48, 7.54 and 8.92 mg/g for initial concentration of 100 mg/L, respectively. It was possibly related with the hydrophobic character of TPU and incorporation of CD to the TPU nanofibers did not significantly affect the sorption of the membranes. For all TPU nanofiber membranes, sorption capacities were lower than 10 mg/g at the initial stage (0-4h) (Figure 3a).

**Figure 3.** Kinetics of Reactive Red 141 by TPU film, TPU, TPU/10CD, TPU/20CD, TPU/30CD nanofiber membranes at 100 mg/L initial dye concentrations, a)0-4h b)0-24h.

The inherent hydrophilicity of PVA makes it an attractive polymer for water treatment applications based on membranes [21]. However, PVA must be crosslinked to minimize its swelling in water for water treatment applications. Thus, BTCA and CA were added to the electrospinning solution of PVA and then electrospun PVA nanofibers were heat set after electrospinning process at 110 and 130°C. Sorption capacities of the PVA nanofibers were compared according to the crosslinker type and the crosslinker concentrations as well as different heat setting temperatures (110 and 130°C) in Figure 4 and Figure 5, respectively. As a control, one of the PVA films and neat-PVA nanofibers were also heat set at same temperatures and one of them were left untreated. In Figure 4, it was seen that the equilibrium sorption capacities of untreated PVA film and heat set PVA film were the lowest and reached to 17.50 and 17.60 mg/g after 24h. Beside, the equilibrium sorption capacities of untreated neat-PVA nanofibers and heat set neat-PVA nanofibers were 44.77 and 62.24 mg/g, respectively, which were higher than PVA films due to porous structure of nanofiber membranes, sorption capacity was higher. Heat setting also positively affected the sorption capacity because that provided a better preservation of nanofibrous structure for neat-PVA nanofibers. On the other hand, the initial adsorption and overall uptake rates, and the capacity q_e were increased with the increasing BTCA and CA addition. For 5, 10 and 20% of BTCA, q_e was 81.13, 85.35 and 88.13 mg/g, for 5, 10 and 20% of CA, q_e was 75.19, 76.70 and 80.86 mg/g, respectively. With the addition of BTCA and CA better crosslinking of PVA nanofibers were achieved and that affected the adsorption capacity of the nanofiber membranes. CD incorporation was also evaluated for PVA nanofibers and 30% of CD was added to the PVA/20BTCA polymer solution. However, sorption capacity of resulted nanofibers was 88.31 mg/g, and quite similar to PVA/20BTCA nanofibers. This might be the result of inconvenience size of the Reactive red 141 to the cavity of the β -CD molecule.

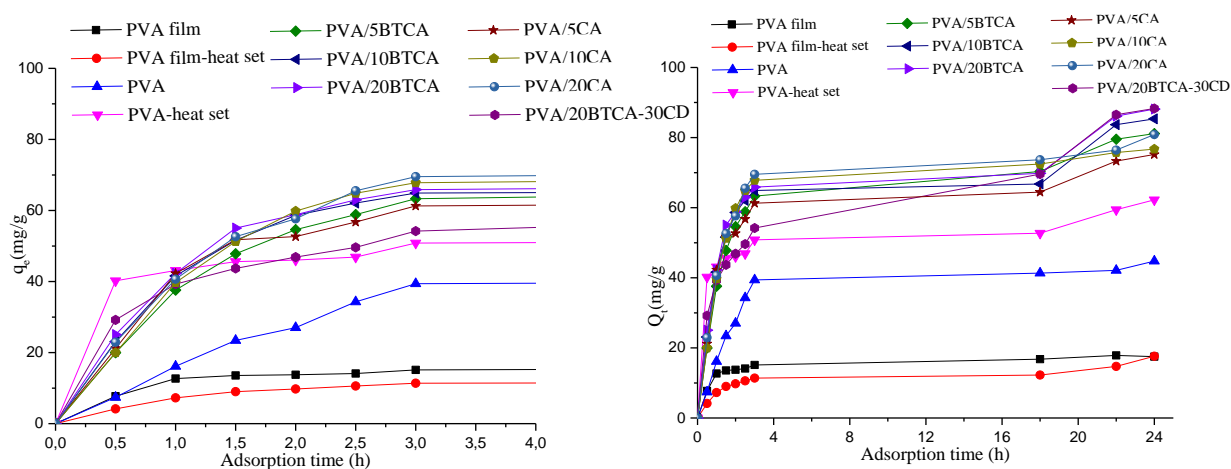


Figure 4. Kinetics of Reactive Red 141 by PVA film, PVA film-heat set, PVA, PVA-heat set, PVA/5BTCA, PVA/10BTCA, PVA/20BTCA, PVA/5CA, PVA/10CA, PVA/20CA and PVA/20BTCA-30CD nanofiber membranes (heat set at 110°C) at 100 mg/L initial dye concentrations, a)0-4h b)0-24h.

Figure 5 presents the adsorptions of the dye onto the PVA nanofiber membranes that were heat set at 130°C. The initial adsorption and overall uptake rates, and the capacity q_e were lower than PVA nanofiber membranes that were heat set at 110°C, except for neat-PVA nanofibers. Higher crosslinking temperature caused higher crystallinity [22, 23] of BTCA and CA crosslinked PVA nanofibers and that caused a decrease in hydrophilicity as some of the hydroxyl groups of PVA nanofibers are consumed by reaction with the crosslinking agent [21]. For 5, 10 and 20% of BTCA, q_e was 76.87, 71.94 and 46.45 mg/g, for 5, 10 and 20% of CA, q_e was 47.67, 38.00 and 44.33 mg/g, respectively which were significantly lower than PVA nanofibers which were heat set at 110°C. Increasing of the BTCA and CA concentration also decreased the sorption capacity. Higher temperatures are known to chemically bonded crosslinking for PVA [21]. Thus, neat-PVA nanofibers

showed better adsorption since heat setting at 130°C provided better self-crosslinking and durability than 110°C for neat-PVA nanofibers. However, excessive use of crosslinking agents at same temperature (130°C) led to decrease of adsorption.

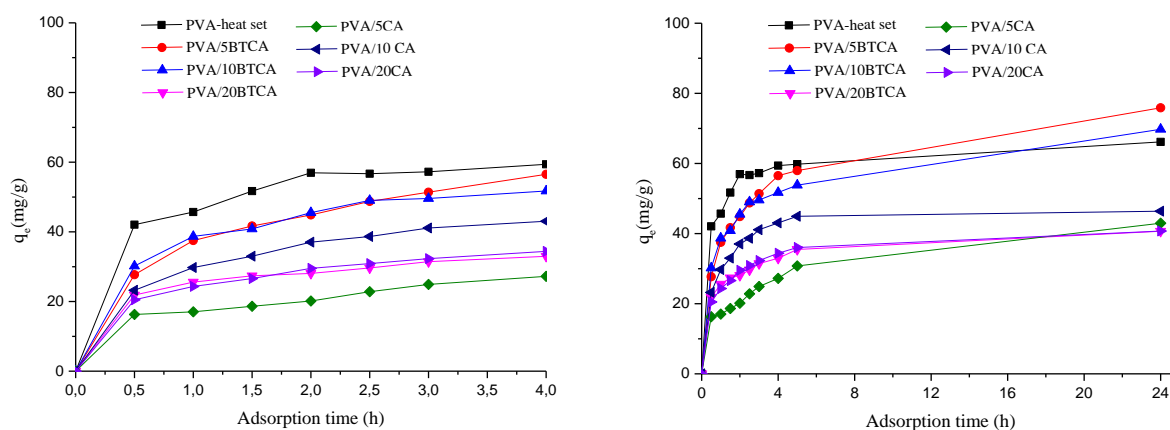


Figure 5. Kinetics of Reactive Red 141 by PVA film, PVA film-heat set, PVA, PVA-heat set, PVA/5BTCA, PVA/10BTCA, PVA/20BTCA, PVA/5CA, PVA/10CA, PVA/20CA and PVA/20BTCA-30CD nanofiber membranes (heat set at 130°C) at 100 mg/L initial dye concentrations, a)0-4h b)0-24h.

Figure 6 presents the initial and representative final color of the dye baths for TPU and PVA membranes. The largest adsorption capacity belongs to BTCA cross-linked PVA membranes, which were heat set at 110°C and reached to maximum 88.31 mg/g due to hydrophilic character of PVA. Heat setting at 130°C decreased the sorption capacity of the PVA nanofiber membranes. Beside, at 130°C increasing the crosslinking concentration also decreased the sorption capacity of the PVA nanofiber membranes due to consumption of hydroxyl groups by crosslinking agents. Contrary to expectation, hydrophobic character of TPU was dominant and incorporation of CD to the TPU nanofibers did not significantly increase the sorption of the TPU nanofiber membranes. They showed very low adsorptions and reached to maximum 14.48 mg/g.

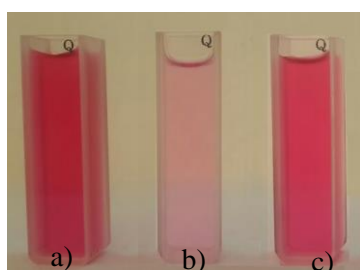


Figure 6. Dyebaths (a) before (b) after BTCA cross-linked PVA (c) after TPU/CD nanofiber membranes adsorption

4. Conclusion

In this study, the sorption capacity of electrospun TPU and PVA nanofiber membranes was investigated. Large surface areas per unit volume of those nanofiber membranes can very suitably remove specific materials by adsorption based on physical affinity. However, because of its hydrophobic structure of TPU nanofiber membranes, they showed quite low adsorptions. On the other hand, especially BTCA cross-linked PVA nanofiber membranes showed good performance in sorption of Reactive red 141 dye. The maximum sorption capacity reached to 88.31 mg/g. However, increase of the heat setting temperature from 110°C to the 130°C decreased the sorption capacity. Furthermore, the membranes become very small in volume after the adsorption process and complete drying. Thus, these materials could provide a new route for dye molecule removal from textile wastewater.

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