STUDY ON THE ACID DYE REMOVAL BY POLYAMIDE 6 NANOFIBROUS MEMBRANE

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Abstract

The aim of this study is to exam the acid dye removal by polyamide 6 nanofibrous membrane (PNM). An apparatus in the continual dead-end mode was applied to evaluate the efficiency of membranes. PNM with areal density 1.3 g/m^2 and C. I. Acid Blue 41 were used.. The surface morphology of PNM before and after filtration was observed by scanning electron microscope (SEM), the absorbance of dye solutions before and after filtration was tested by an UV-Vis spectroscopy. The dye removal capacity and dye removal kinetics of PNM were calculated based on the absorbance of solutions. The results showed that the dye removal rate of PNM was about 99% in the very beginning process. After 10 minutes, the filtration process reached the steady state, and the dye removal rate of PNM was less than 2%. The dye removal capacity of PNM increased as the increase of feed dye solution concentration and adding one more layer of PNM.

Keywords: Nanofibrous membrane; Polyamide; Acid dye; Filtration

1. INTRODUCTION

Dyestuff is widely used in many fields such as in textile industry, leather tanning industry, pulp and paper industry, agricultural research, hair coloring, food technology, and photoelectrochemical cells[1-6]. Release of dyes in water streams results in a serious environmental impact.

Many methods such as adsorption, coagulation, biodegradation, chemical degradation, photo degradation, and membrane filtration have been applied to remove the dyes from waters and wastewaters to decrease their impact on the environment. Membrane filtration was considered to be one of the most efficient methods for dyestuff removal and all the membrane separation processes are able to remove all types of dyes..

Other than four current crossflow, pressure-driven membrane separation processes which are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), electrospun nanofibrous membranes nowadays have aroused great attention for their special properties comparing with conventional fibrous mats such as a very large surface area to volume ratio, which for a nanofiber can be as large as 103 times that of a microfiber [7], tunable porosity, pore size, flexibility in surface functionalities, good mechanical performance, and malleability.

On the other hand, the concentrated sludge/pollutants would be produced in membrane separation process. Therefore, it is very important to understand the efficiency of membrane filtration regarding to time in order to apply the membrane efficiently in industry. In the work, a continual dead-end filtration process was assembled to investigate the efficiency of polyamide 6 nanofibrous membrane regarding to time. Moreover, the capacity of one layer and two layers PNM under three different feed concentrations of acid dye solution was evaluated.

2. MATERIALS AND METHOD

2.1 Nanofibrous membrane

Electrospun polyamide 6 nanofibrous membranes with area density 1.3 g/m^2 made by company ELMARCO s. r. o were used for the initial tests. The fiber diameter computed by picture analysis from SEM images was 113±16 nm and pore size analyzed by BET test was 11 nm.

2.2 Acid dye solution

C. I. Acid blue 41 (AB41) was used in this work, and its molecular structure is shown in Fig. 1. The molecular weight of AB41 is 487g/mol and its molecular formula is $C_{23}H_{18}N_3NaO_6S$. As a kind of water-soluble anionic dye, AB41 has good affinity for polyamide fibers.

AB41 solutions with three different concentrations of 0.01, 0.02, and 0.03 g/L were prepared for experiment. Firstly, 1 g/L AB41 solution was prepared, then the prepared solution was diluted with distilled water into the particular concentrations as mentioned above.

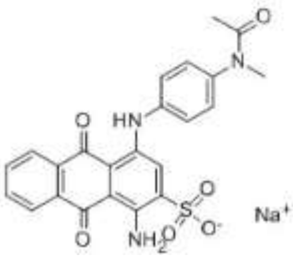


Fig. 1 The molecular structures of C. I. Acid blue 41.

2.3 Testing method

An apparatus for achieving continual dead-end filtration process was prepared in order to investigate the filtration property of membrane more flexibly and efficiently. This apparatus included two containers which were used for influent dye solution and effluent filtrate; a single piston pump with flow rate 0.01-9.99 mL/min under the standard configuration; an UV-Vis variable wavelength detector (Type: SAPPHIRE 600, company: ECOM, Country: Czech Republic) which is available for routine analytical chromatography as well as for preparative chromatography; a high pressure filter which used for supporting and fixing PNM between pipes without air leaking. All the parts of this apparatus were connected with pipes to make a circuit as shown in Fig. 2.

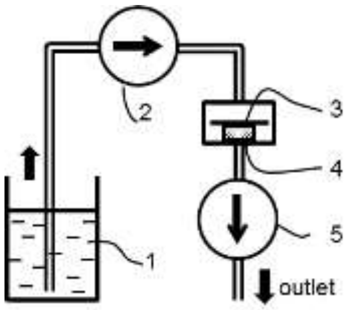


Fig. 2 The sketch of testing apparatus: (1) container with original dye solution; (2) single piston pump; (3) high pressure filter; (4) PNM; (5) UV-Vis variable wavelength detector.

In this study, the flow rate of piston pump was kept at 3 mL/min, the diameter of circular PNM used in experiment was 22 mm. The concentration of filtrate was examined on-line by UV-Vis variable wavelength detector, and the time interval between two tests was approximately 0.18 s.

2.4 Theory

The mass of dyes absorbed by the PNM can be calculated by Eq.1,

$$\Delta m = m_0 - m_f \quad (1)$$

Where Δm is the mass of dyes absorbed by the PNM (g); m_0 is the mass of dye in feed dye solution (g); m_f is the mass of dye in filtrate (g).

The masses of dye in feed dye solution and the filtrate can be obtained by,

$$m_0 = C_0 \cdot V = C_0 \cdot q \cdot t \qquad (2.a)$$

$$m_f = C_f \cdot V = C_f \cdot q \cdot t \qquad (2.b)$$

Where C_0 is the concentration of feed dye solution (g/L), C_f is the concentration of filtrate (g/L), V is the volume (L), q is the flow rate (L/min), and t is time (min).

According to Beer-Lambert law, the absorbance of solution is linear with the concentration of solution, which can be expressed by,

$$A = \alpha l C \qquad (3)$$

Where A is the absorbance of solution, α is the attenuation coefficient (L/(g·cm)), l is the path length (cm), and C is the concentration of solution (g/L).

Based on Eq. 3, the concentration of filtrate, C_f, can be derived,

$$C_f = C_0 \frac{A_f}{A_0} \qquad (4)$$

Where A_0 is the absorbance of feed dye solution, A_f is the absorbance of filtrate.

By substituting Eq. 2 and 4 into Eq. 1, the mass of dye absorbed by the PNM can be obtained by,

$$\Delta m = \left(C_0 - C_0 \frac{A_f}{A_0} \right) \cdot q \cdot t \qquad (5)$$

The accumulated mass, the sum of the mass of dye absorbed/blocked by PNM in a time period, can be calculated by,

$$\Delta m_a = \left(C_0 - C_0 \frac{\sum_1^n A_i}{A_0} \right) \cdot q \cdot t_i \qquad i = 1, 2, 3, \ldots, n \qquad (6)$$

Where Δm_a is the accumulated mass, A_i is the absorbance of fitrate after the ith filtration, t_i is the ith time interval.

The dye removal rate (%), ε, by PNM can be calculated by,

$$\varepsilon = \frac{A_0 - A_f}{A_0} \times 100 \qquad (7)$$

The dye removal capacity (*mg/g*), η, by PNM can be obtained by:,

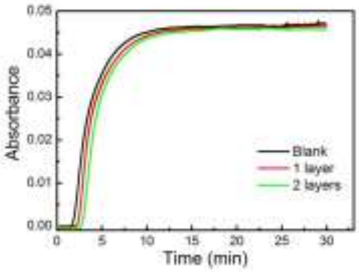
$$\eta = \frac{\Delta m_a}{m_m} \qquad (8)$$

Where , is the mass of the PNM sample used for filtration.

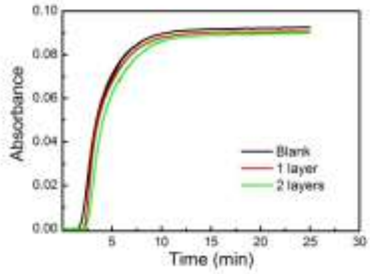
3. RESULTS AND DISCUSSIONS

3.1 The dye removal rate of nanofibrous membrane

In order to investigate the dye filtration efficiency of PNM, the absorbance of filtrates with and without PNM filtration was recorded. The absorbance curves of filtrates regarding to time are given in Fig. 3.



(a)



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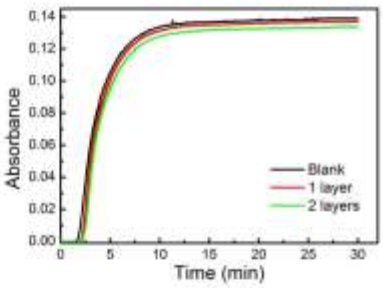


(c)

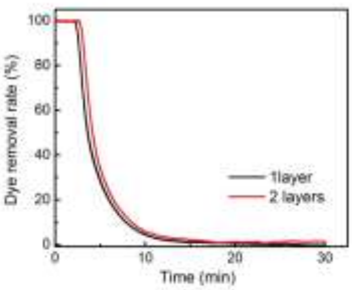
Fig. 3 Absorbance curves of filtrates regarding to time. (a) 0.01 g/L feed dye concentration; (b) 0.02 g/L feed dye concentration; (c) 0.03 g/L feed dye concentration

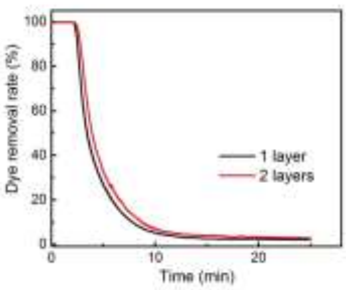
The absorbance curve can generally be divided into three zones. The first zone is from the very beginning to about 2 minutes, where the absorbance of solutions were very small which indicated the PNM absorbed and blocked most of the dyestuff. In other words, the PNM had the highest dye removal rate (shown in Fig. 4). The second zone is from 2 minutes to about 10 minutes, where the absorbance of filtrates was keeping increasing, which indicated the adsorption/blocking capacity of PNM was decreasing continuously (shown in Fig. 4). After around 10 minutes, the absorbance curves came to the third zone where the absorbance was almost the same and close to the absorbance of feed solution concentration, which indicated the adsorption amount of PNM came to the saturation.

Besides, the trend of absorbance curves of two layers PNM had a delay comparing with one layer PNM, which indicated that the second layer PNM also played a role in absorbing dyestuff.

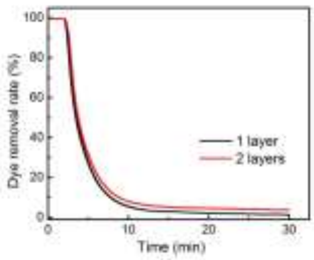
3.2 The dye removal capacity by nanofibrous membrane

In order to get the maximum dye removal capacity by PNM, the accumulated mass of dye absorbed/blocked by PNM should be in saturation state. As Figure 6 showed, the absorbance of dye solutions are almost the same with feed dye solution after 10 minutes. Therefore, the saturated value was chosen at 13 minutes. The dye removal capacity of PNM under difference feed dye solution concentrations are given in Tab. 1.





(a) (b)



(c)

Fig. 4 Dye removal rate by PNM regarding to time: (a) 0.01 g/L feed dye concentration; (b) 0.02 g/L feed dye concentration; (c) 0.03 g/L feed dye concentration

The dye removal capacity of PNM had an increase when the feed dye solution concentration increased, but the difference of dye removal capacity of PNM was very small when the feed dye solution concentrations were 0.02 and 0.03 g/L. Moreover, two layers PNMs had better dye removal capacity than one layer PNMs'. This could be due to the absorption capacity of PNM on acid dye[8].

Table 1 Dye removal values comparison while the filtration process reaches 13 minutes.

Solution concentration	Dye removal capacity (mg/g)	
g/L	1 layer	2 layers
0.01	53.9±4.28	80.5±6.23
0.02	84.9±3.65	127.9±6.74
0.03	81.7±3.35	132.4±8.96

3.3 SEM images

Some continuous films formed on the surface of the first layer PNM showed the first layer membrane adsorbed the dyestuff and meanwhile blocked larger dye particles. The coverage of the films increased as the increase of concentration of dye solution, which indicated a larger amount of dyestuff blocked by the PNM under the higher concentration acid dye solution. The second layer PNM still showed clean surfaces after filtration which indicated good effectiveness of blocking larger dyestuff particles.

4. CONCLUSIONS

Some conclusions can be drawn based on the experimental results. In the filtration process, polyamide 6 electrospun nanofibrous membrane had a very good performed on dye removal rate which can reach to 99%, but the time of effective dye removal was very short. According to the absorbance curve, the PNM had maximum dye removal rate in the first 2 minutes, and the dye removal rate of PNM reached to saturated state after 10 minutes.

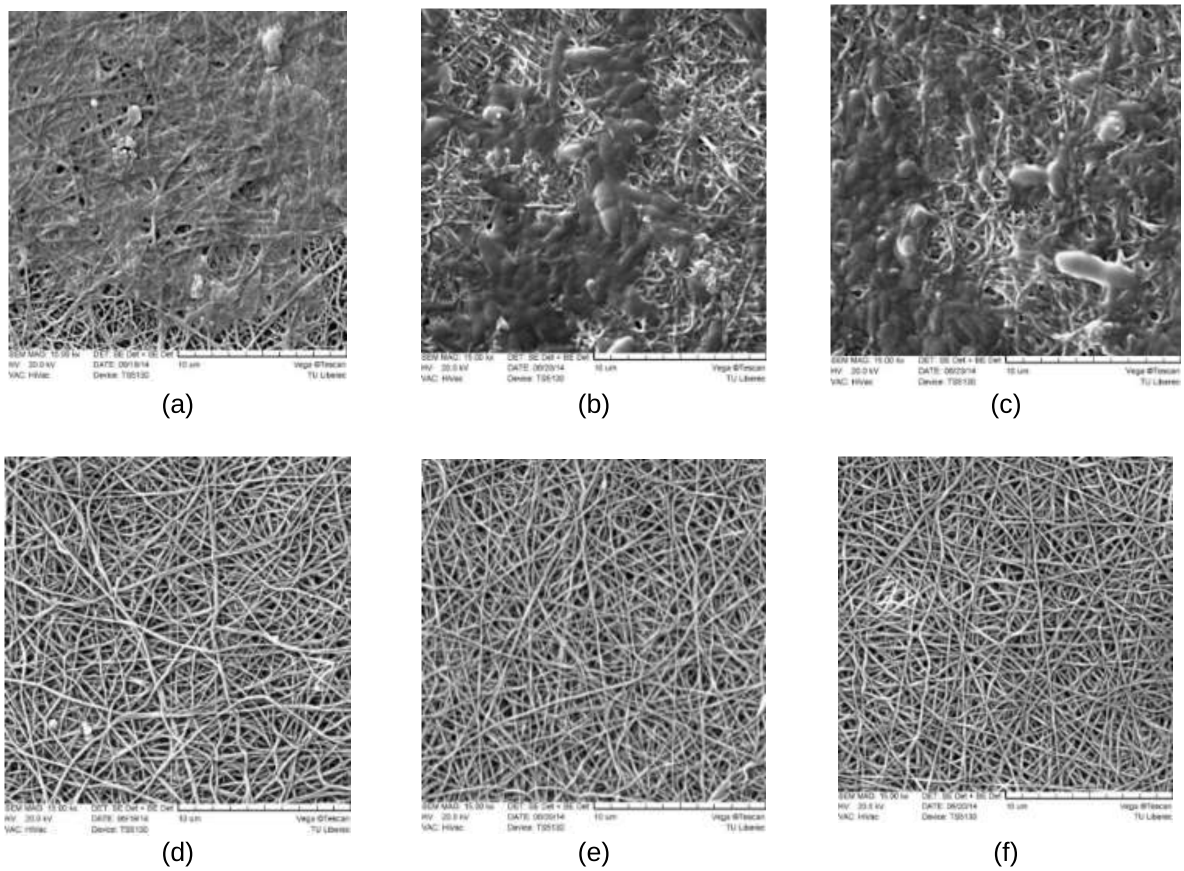


Fig. 5 SEM images of PNM after filtration: (a-c) first layer membrane after filtration with concentration of 0.01g/L, 0.02g/L, and 0.03g/L, respectively; (d-f) second layer membrane after filtration with concentration of 0.01g/L, 0.02g/L, and 0.03g/L, respectively.

The dye removal capacity of PNM increased as the increase of feed dye solution concentration, but the difference of dye removal capacity of PNM was very small when the feed dye solution concentrations were 0.02 and 0.03 g/L. Two layers PNMs had better dye removal capacity than one layer PNMs' due to the absorption property of PNM on acid dye.

REFERENCES

[1] Kabdasli, I., O. Tunay, and D. Orhon, *Wastewater control and management in a leather tanning district.* Water Science and Technology, 1999. **40**(1): p. 261-267.

[2] Ivanov, K., et al., *Possibilities of using zeolite as filler and carrier for dyestuffs in paper.* Papier, 1996. **50**(7-8): p. 456-&.

[3] Cook, S.M.F. and D.R. Linden, *Use of rhodamine WT to facilitate dilution and analysis of atrazine samples in short-term transport studies.* Journal of Environmental Quality, 1997. **26**(5): p. 1438-1440.

[4] Scarpi, C., et al., *High-performance liquid chromatography determination of direct and temporary dyes in natural hair colourings.* Journal of Chromatography A, 1998. **796**(2): p. 319-325.

[5] Slampova, A., et al., *Determination of synthetic colorants in foodstuffs.* Chemicke Listy, 2001. **95**(3): p. 163-168.

[6] Wrobel D, Boguta A, and I. RM, *Mixtures of synthetic organic dyes in a photoelectronic cell.* J Photochem Photobiol, A Chem 2001. **138**: p. 7-22.

[7] Nidal Hilal, M.K., Chris J. Wright, *Membrane Modification Technology and Applications*. 2012, Boca Raton: CRC Press Taylor & Francis Group. 259.

[8] Wang, Y., J. Wiener, and G.C. Zhu, *Langmuir Isotherm Models Applied to the Sorption of Acid Dyes from Effluent onto Polyamide Nanofibers.* Autex Research Journal, 2013. **13**(3): p. 95-98.