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Faculty of Textile Engineering

Selected Sorption Properties of Nanofibers Assembly

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SUMMARY OF THE THESIS

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Abstract

Since first synthesized and introduced in 1935, the polyamides' production quantities grow tremendously and polyamides' applications increased numerously. Polyamide 6 fibers are one of the widely used synthetic fibers in textile area due to its outstanding properties. As a sorbent to dyes, heavy metal ions, pesticides etc., the adsorption properties of polyamide 6 fibers assemblies have been studied for some extent. However, as the rapid development of nanotechnology including both electrospinning and nanoparticles technologies is changing people's life in all areas, how does nanofibers assembly behavior became an important question. A systematical study for adsorption properties of polyamide 6 nanofibers assembly will be realized in this work.

Prior to initiation of research, a detailed literature review was conducted to understand and identify their gaps to address in this work. The theories of solid-liquid sorption, thermodynamics, and photocatalysis were studied, the application of polyamide nanofibers and Titanium dioxide nanoparticles were reviewed. This comparison of dye removing methods was expected to provide insights into optimal conditions for dye removal.

In this work, nanotechnologies including electrospun nanofibers and nanoparticles were implemented for further study of adsorption properties of polyamide 6 nanofibers assembly. Dye was chosen to be a model as the sorbate for investigating the adsorption properties. Dye static and dynamic sorption properties of polyamide 6 nanofibers assembly were detected, kinetic and thermodynamic considerations were studied, and Titanium dioxide nanoparticles deposition and steam process were applied as surface modification methods for polyamide 6 nanofibers.

Static sorption and thermodynamics study revealed that Langmuir isotherm and Pseudo-second order equations fitted the sorption experimental data well, and the sorption process of acid dye on polyamide 6 nanofibers assembly was a feasibility, spontaneous, entropy-driven, and sorption. Steam treatment with temperature over 120°C encouraged the static sorption of acid dyes on polyamide 6 nanofibers assembly.

Dynamic sorption study showed that nanofibers have superior dye removal properties than conventional fibers, and hormone and dye sorption capacity of polyamide 6 nanofibers showed a positive relationship with the specific surface area.

TiO_2 nanoparticles photocatalysis self-cleaning treatment with TiO_2 nanoparticles concentration over 18 mg/m^2 and over 90 minutes under UV light could help improving the dye self-cleaning effect, and TiO_2 nanoparticles photocatalysis was proved to be one method for improving the dynamic sorption capacity of Acid Orange 7 on polyamide 6 nanofibers. Decolorization of wastewater containing soluble dyes would be one of the potential applications for this method.

Keywords: Sorption; Nanofibers; Dye; Surface modification

Summary

1 Introduction

All thermoplastic polyamides are characterized by excellent toughness and flexibility at low temperature in the absence of plasticizer, low density, high dimensional stability, ease of conventional thermoplastic processing, good chemical resistance, good environmental stress cracking resistance, good elastic recovery, and good dynamic properties [1]. Therefore, polyamides are widely used in many areas such as: technical parts, bearings, gear wheels, rollers, screws, gaskets, fittings, coverings, housings, automotive parts, houseware, sports goods, membranes, foils, packing, blow-molded parts, fibers, tanks [2].

Polyamide 6, whose main form is polymorphic monoclinic [3], is a very important engineering resin manufactured in large quantities for film, fiber and plastic applications due to its high strength, high ductility, excellent resistance to short-term heat exposure and excellent resistance to chemical solvents [4, 5]. Polyamide 6 fibers are one of the most commonly used fibers in the world, and polyamide 6 nanofibers have been widely studied as nanotechnology progressed fast nowadays.

Adsorption separation plays a significant role in the environmental pollution control and life supporting systems or planetary bases, where adsorbents may be used to process the habitat air or to recover useful substances from the local environments. A larger specific surface area of adsorbent pores provides a large adsorption capacity. The creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces.

The separation efficiency, in general, increases linearly with decreasing membrane thickness and increasing applied pressure. Thus, we can take advantage of the unique properties of electrospun membranes consisting of very-small-diameter fibers. Electrospun nonwoven nanostructure (a) has interconnected pores, (b) with pore sizes of the order of only a few times to a few ten times the fiber diameter, and (c) the pore space to material ratio is on the order of 3:1 or even higher [6].

Nanotechnology has the potential to significantly affect society. It is already used for instance by the information and communications sectors. It is also used in cosmetics and sunscreens, in textiles, in coatings, in some food and energy technologies, as well as in some medical products and medicines. Moreover, nanotechnology could also be used in reducing environmental pollution [7]. Nanotechnology is already having an impact in many spheres of chemical and materials science. It would seem that only our imagination would limit the widespread application of nanotechnology [8].

Nanostructured materials based on metal nanoparticles have been studied extensively for various applications because of their attractive physical, chemical, and catalytic properties. The nanocrystalline TiO_2 coatings that can chemically break down adsorbed organic contaminants in sunlight have received much attention due to their potential applications ranging from window glass and cement to textiles [9, 10]. Photocatalysis with TiO_2 nanoparticles has been studied for the degradation of wastewater pollutants. This process has several advantages including complete mineralization of organic pollutants like aliphatics, aromatics, polymers, dyes, surfactants, pesticides and herbicides to CO_2, water and mineral acids, no waste solids to dispose of and mild temperature and pressure conditions.

2 Purpose and the aim of the Thesis

The aim of this research is to study the adsorption properties of which dyestuff as a model onto polyamide 6 nanofibers assembly. The sorption equilibrium, the sorption kinetics, the thermodynamics, and the dynamic sorption efficiency of dyestuff and hormone onto polyamide 6 nanofibers assembly from aqueous solution will be investigated. Meanwhile, the surface modifications on nanofibers such as sterilization with steam and photocatalysis with immobilization of Titanium dioxide nanoparticles will be applied and inspected.

2.1 Evaluation on sorption properties of polyamide 6 nanofibers assembly

Sorbent performance is the critical factor in the design and operation of an adsorption system. The sorption isotherms, and kinetics equations will be applied to the experimental data, and thermodynamic parameters will be calculated. The correlation between experimental conditions such as temperature, pH, waste concentration, membrane dosage, and membrane fiber scale will be discussed.

2.2 Dynamic sorption properties study with assembled apparatus

For dynamic adsorption, the effects of structural parameters (specific surface area and pore size) on performances (efficiency, capacity, dye removal rate and life span of utilization) of nanofibers assembly will be investigated.

2.3 Surface modification of polyamide 6 nanofibers assembly

For surface modification, steam sterilization will be used as a surface etching method and the dye sorption capacity will be discussed under different steam temperatures. TiO_2 nanoparticles will be immobilized onto nanofibers assembly, the self-cleaning performance of nanofibrous membrane will be investigated under different conditions in terms of temperature, content of TiO_2 nanoparticles, time under UV, and catalyst. Dynamic sorption process with TiO_2 nanoparticles photocatalysis will be performed.

The results will be useful in their application to the design of polyamide 6 nanofibers assembly sorption systems.

3 Overview of the current state of the problem

Adsorption properties of water vapers, dyes, iodine, and lipase on conventional polyamide 6 fibers, fabrics, films, or matrix have been studied world widely [11–19]. Despite research publications and references in this field, there are still numerous open questions about the adsorption processes at the interfaces solid (fiber) / liquid (process solution), especially in nanoscale [15].

Adsorption properties of many different substances on conventional scale polyamide 6 have been studied numerously. However, systematic study of adsorption properties on polyamide 6 nanofibers assembly has rarely found. Which factors affect the adsorption properties on polyamide 6 nanofibers assembly and how do they affect has to be studied further.

Nowadays, researchers in different areas are still paying so much attention on application of nanoparticles. In wastewater cleaning area, nanoparticles have been widely studied, and the function mostly realized due to the outstanding adsorption properties and the photocatalytic properties. Photocatalytic oxidation processes have been widely considered as powerful methods to remove non–biodegradable organic pollutants in water [20]. The photocatalytic processes have the potential to mineralize the complicated organics and reduce the toxicity without the generation of sludge and by–products and TiO_2 is the most common and practical material as the environmental photocatalyst [21–23].

4 Methods used, Studied Materials

4.1 Methods

4.1.1 Batch experimental methods

Sorption experiments were carried out in batch mode. Various parameters like bath temperature, pH, solution concentration, dosage of sorbent, and fiber scale of sorbent were investigated. Sorption kinetic experiment was performed with a water bath shaker and thermodynamic parameters were calculated.

4.1.2 Dynamic sorption experimental methods

The general comparison of dynamic sorption efficiency of Hormone 17 *β*–estradiol on polyamide 6 nanofibers membranes (PNM) was conducted with vacuum sorption apparatus. The solution concentrations before and after filtration were evaluated by High Performance Liquid Chromatography. Hormone exhaustion and hormone removal capacity were calculated and compared.

The dynamic sorption of dyestuff was performed with the constant influent apparatus and on-line testing constant flow apparatus. The accumulated mass of dyestuff filtrated by PNM and the flux during the separation process were calculated. Areal density, influent concentration, and sorbent quantity were taken into consideration and compared. Morphology of samples were observed by scanning electron microscopy (SEM).

4.1.3 Surface modification methods

The steam treatment was performed in the Tuttnauer Autoclave-Steam Sterilizer with model no. 2540ML. Eight different temperatures from 100 to 135°C) were chosen for steaming experiment and 5 minutes was the chosen treating time. Batch experiment was performed to evaluate the modification effect. Fourier transform infrared spectroscopy (FTIR) was used for investigating the change in PNM's molecular chain after steam modification.

TiO_2 nanoparticles were evenly deposited onto polyamide 6 nanofibers membrane by vacuum sorption apparatus. The light source was a lamp from Bandelin Co. D–69168 Wieslich, type N–36 K which gives radiation with wavelength 254 nm and performance 4×6 W. Different TiO_2 nanoparticles concentration and various UV light treating time were applied and analyzed for the modification effect of self-cleaning.

Moreover, the dynamic sorption was performed with TiO_2 nanoparticles deposited samples and effect of the UV treating time was studied.

4.2 Assembled apparatus for dynamic sorption study

In this work, several apparatus were assembled and proposed for dynamic sorption process and study as shown in Fig. 1.

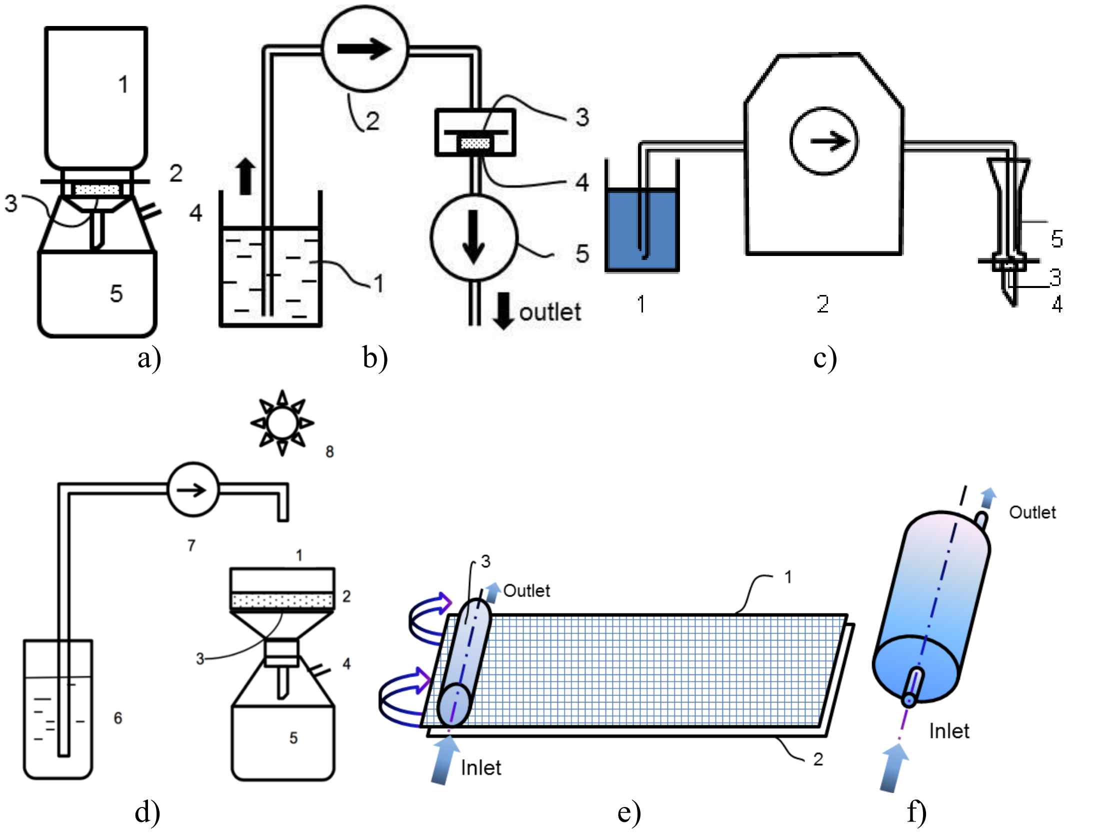


Fig. 1 a) Vacuum sorption apparatus: 1–funnel; 2–sorbent; 3–sorbent supporting unit; 4–vacuum pressure port; 5–vacuum flask.
b) Constant influent apparatus: 1–beaker with influent, 2–peristaltic pump, 3–sorbent, 4–sorbent supporting unit, 5–funnel.
c) On–line constant flow apparatus: 1–container with original solution; 2–isocratic pump; 3–sorbent; 4–sanitary in–line stainless steel holder; 5–UV–Vis variable wavelength detector.
d) Apparatus for dynamic sorption process with UV lighting: 1–funnel; 2–sorbent; 3–sorbent support unit; 4–vacuum pressure port; 5–vacuum flask; 6–container with original solution; 7–peristaltic pump; 8–UV lighting system.
e) Crossflow dynamic sorption apparatus: 1–Polypropylene web; 2–PNM1.3; 3–Glass rod.
f) Crossflow dynamic sorption unit.

4.3 Studied materials

In this study, polyamide 6 nanofibers membrane (PNM) with areal density respectively 1.3 and 2.9 g/m^2 purchased from ELMARCO s. r. o were mainly used as sorbents whose SEM images were shown in Fig. 2.

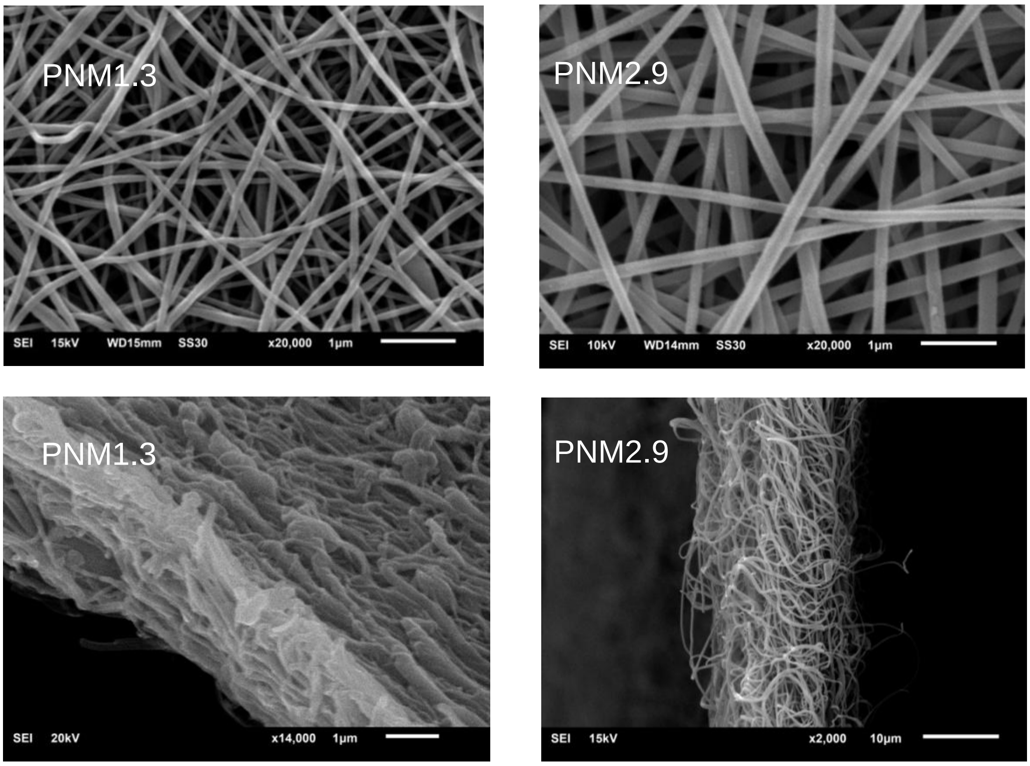


Fig. 2 Surface and cross section SEM images of polyamide 6 nanofibrous membranes (PNM) with areal density 1.3 and 2.9 g/m^2.

Electrospun polyamide 6 nanofibrous membranes with areal density of 0.5 g/m^2 purchased from ELMARCO s. r. o and spunbond nonwoven fabrics (SB) with areal density of 20–100 g/m^2 provided by Asahi KASEI fibers corporation, woven fabric from TUL, and Polyacrylonitrile (PAN) from ELMARCO s. r. o were used as sorbent for comparison.

17 *β*–estradiol with 99.7% purity purchased from SIGMA, C. I. Acid Blue 41 (AB41), C.I Acid Yellow 11 (AY11), C.I Acid Yellow 36 (AY36), C.I Acid Red 73 (AR73), and C. I. Acid Orange 7 with purity over 85% purchased from Sigma–Aldrich were used as sorbed materials. TiO_2 (P25) Anatas / Rutile 70:30, with particles diameter of 21 nm, purchased from Degussa Ltd. was used as catalyst.

5 Summary of the results achieved

5.1 Analysis of dye sorption onto polyamide 6 nanofibrous membrane

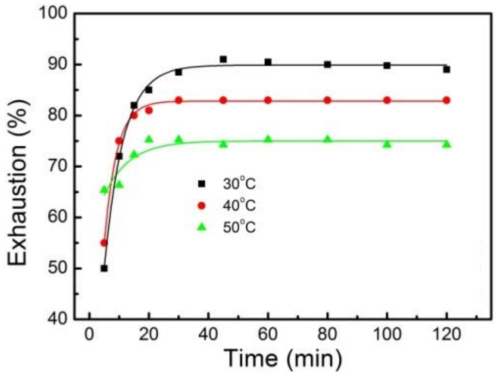


Fig. 3 Dye AB41 exhaustion under different temperatures.

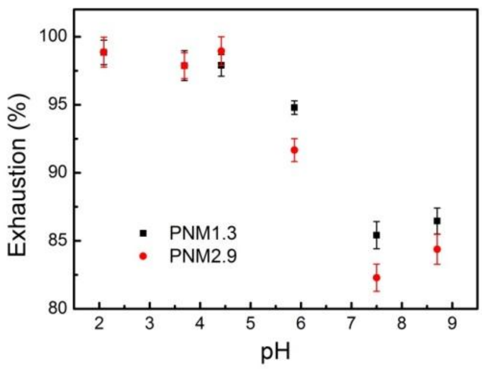


Fig. 4 The effect of initial pH on the sorption capacity of dye AB41 by PNM1.3 and PNM2.9

Fig. 3 shows the data at the beginning of experiment (5 min) indicate a rapid dye uptake before 5 minutes while the temperature was high cause 65.4% of dye has already been cleaned other than 50 and 55% under the temperature of 30 and 40^{o}C. However, the equilibrium dye removal rate shows better dye sorption of low temperature due to less desorption of dyes from the membranes. And Fig. 4 shows a better dye sorption capacity in acidic environment.

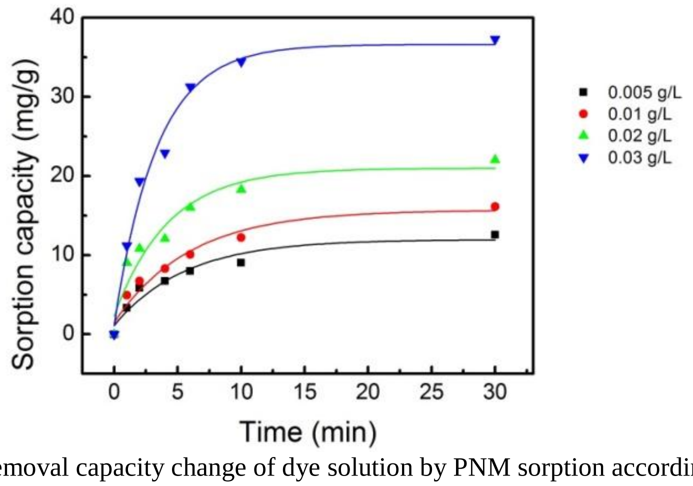


Fig. 5 Dye removal capacity change of dye solution by PNM sorption according to time.

Fig. 5 shows that the sorption of AB41 increases with an increase in time and initial concentrations. When the initial concentration increased, the mass transfer driving force became larger, hence resulting in higher AB41 sorption. Fig. 6 shows the dosage of PNM1.3 around 0.2 g/L is sufficient for dye AB41 removal and meanwhile the capacity has been used effectively. However, in order to get better sorption effect, dosage 0.4 g/L of PNM1.3 has been considered as the best dosage to continue our main experiment.

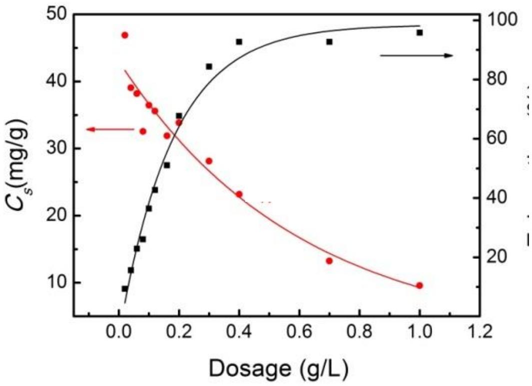


Fig. 6 Effect of dosage of PNM1.3 on sorption capacity C_S and exhaustion of AB41.

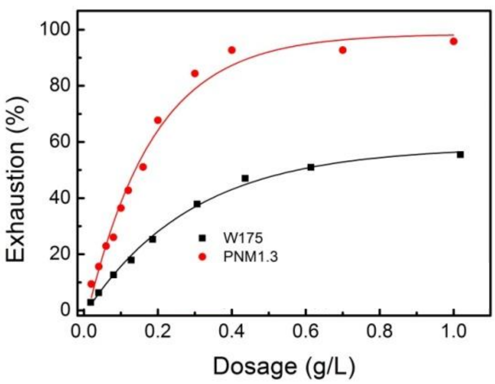


Fig. 7 Batch experimental data comparison between sorbents Woven and PNM1.3.

Fig. 7 shows exhaustion of dye solution AB41 on W175 shows the similar trend according to the change of dosage but it can reach maximum 55.5% in the range of 0.0 to 1.0 g/L.

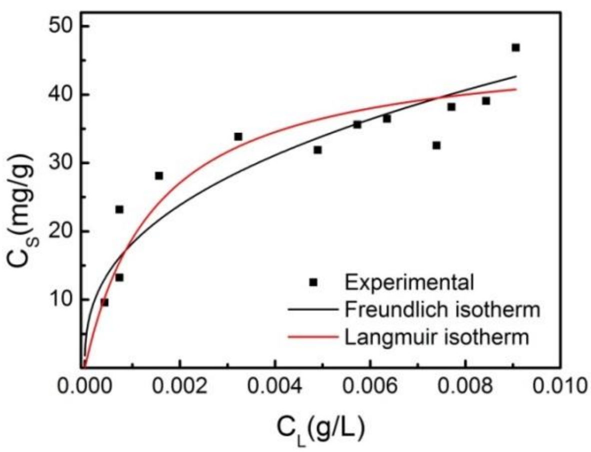


Fig. 8 Comparison among Experimental data and two isotherm models.

Fig. 8 compares the experimental data with Freundlich and Langmuir isotherms. And the coefficient of determination R^2 showed that Langmuir isotherm fitted the experimental data better.

For Kinetics parameters, the result showed in Tab. 1 below.

Table 1 Result comparison about bath temperature of linear Elovich and Pseudo-second order equation fitting.

Temp.	Elovich				Pseudo-Second Order				
ºC	R_l^2	R^2	*b* g/mg	*a* mg/(g·min)	R_l^2	R^2	q_e mmol/g	k_2 g/(mmol·min)	*h* mmol/(g·min) $\times 10^{-3}$
30	0.89	0.66	3.24	1.36	0.99	0.99	0.050	5.72	14.06
40	0.87	0.70	2.91	2.08	0.99	0.99	0.047	6.80	15.04
50	0.70	0.75	1.54	36.54	0.99	0.98	0.033	19.47	21.51

It showed with correlation coefficient R_l^2 that Pseudo-Second Order equation fitted the experimental data better in the case of acid dye removed by PNM. From constant *a* and *h* we can found that the highest temperature brought fastest sorption process.

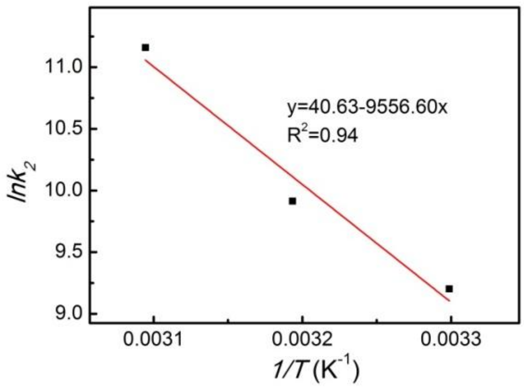


Fig. 9 Arrhenius plot for the adsorption of AB41 onto PNM1.3.

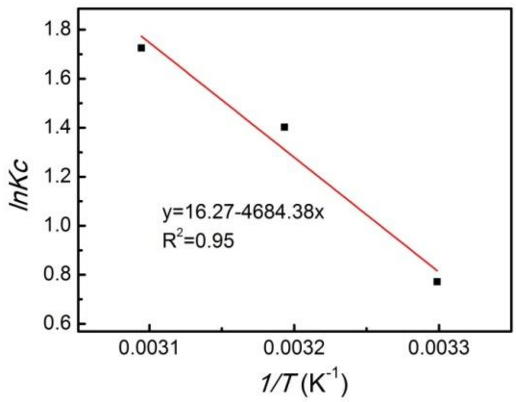


Fig. 10 Van't Hoff plots for determination of thermodynamic parameters for the adsorption of AB41 onto PNM1.3.

The values of adsorption thermodynamic parameters are listed in Tab. 2.

Table 2 Thermodynamic parameters of AB41 dye adsorption on PNM1.3.

Temperature ºC	$\triangle G°$ kJ/mol
30	-1.945
40	-3.655
50	-4.64

The Arrhenius activation energy result obtained is 79.45 kJ/mol for the adsorption of AB41 onto PNM1.3, indicating that the adsorption has a high activation energy and more orients and corresponds to a chemisorption. The negative value of the change of free energy ($\Delta G°$) confirms the feasibility of the adsorption process and also indicates spontaneous adsorption of AB41 onto PNM1.3 in the temperature range studied and the adsorption process is entropy-driven. On the other hand, the value of the standard enthalpy change ($\Delta H°$) (38.95 kJ/mol) is positive, indicating that the sorption is endothermic. The positive value of standard entropy change ($\Delta S°$) (135.26 J/mol·K) suggests the increased randomness and degree of freedom at the solid-solution interface during the adsorption of AB41 onto PNM1.3.

5.2 Analysis of dynamic sorption

The general comparison with these three groups was shown in below figure, and the large difference between nano scale fibers and conventional scale fibers can be easily observed.

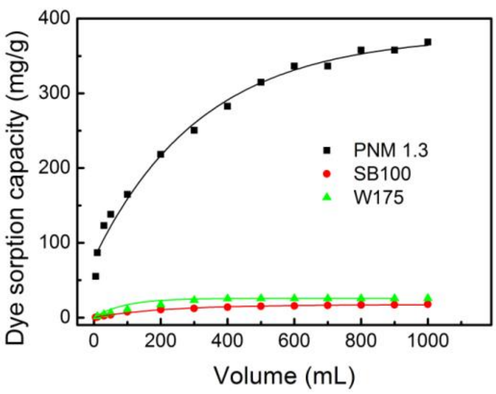
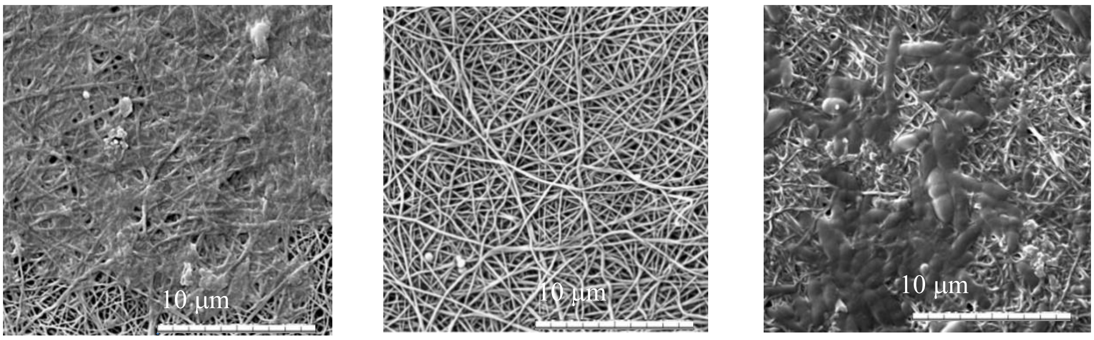


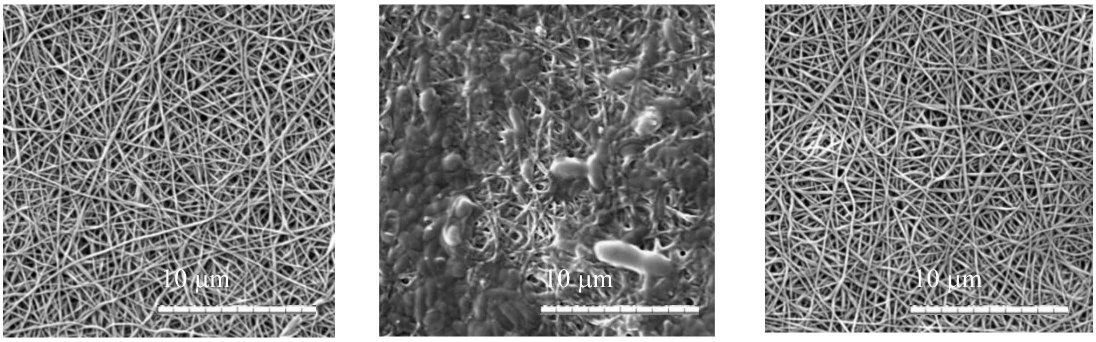
Fig. 11 Dye sorption capacity of mats with different areal densities.

Table 3 Dye removal values comparison while the dynamic sorption process reaches 13 minutes.

Solution concentration g/L	Dye removal capacity (mg/g)	
	1 layer	2 layers
0.01	53.9±4.3	80.5±6.2
0.02	84.9±3.7	127.9±6.7
0.03	81.7±3.4	132.4±9.0



a) b) c)



d) e) f)

Fig. 12 SEM images of PNM1.3 after dynamic sorption process: a, c, & e) first layer membrane after dynamic sorption process with concentration of 0.01, 0.02, and 0.03 g/L respectively; b, d, & f) second layer membrane after dynamic sorption process with concentration of 0.01, 0.02, and 0.03 g/L respectively.

The dye removal capacity of PNM1.3 had an increase when the feeding dye solution concentration increased, but the difference of dye removal capacity of PNM1.3 was very small when the feeding dye solution concentrations were 0.02 and 0.03 g/L. Moreover, two layers PNM1.3 had better dye removal capacity than one layer. This could be due to the adsorption capacity of PNM on acid dye.

5.3 Surface modification on polyamide 6 nanofibrous membrane

Fig. 13 shows the surface modification on polyamide 6 nanofibrous membrane with steam which shows an increase with steam temperature increasing. However, the control sample was tested in the same method and the dye removal capacity of it was 0.11 mmol/g, which indicated a dye removal improving only when high temperature (higher than 120 ºC) steam was applied onto PNM.

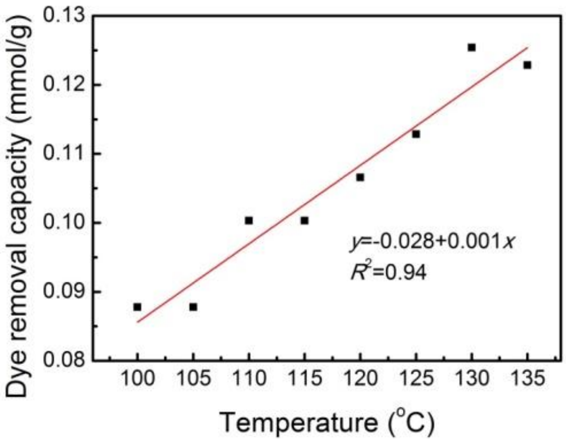
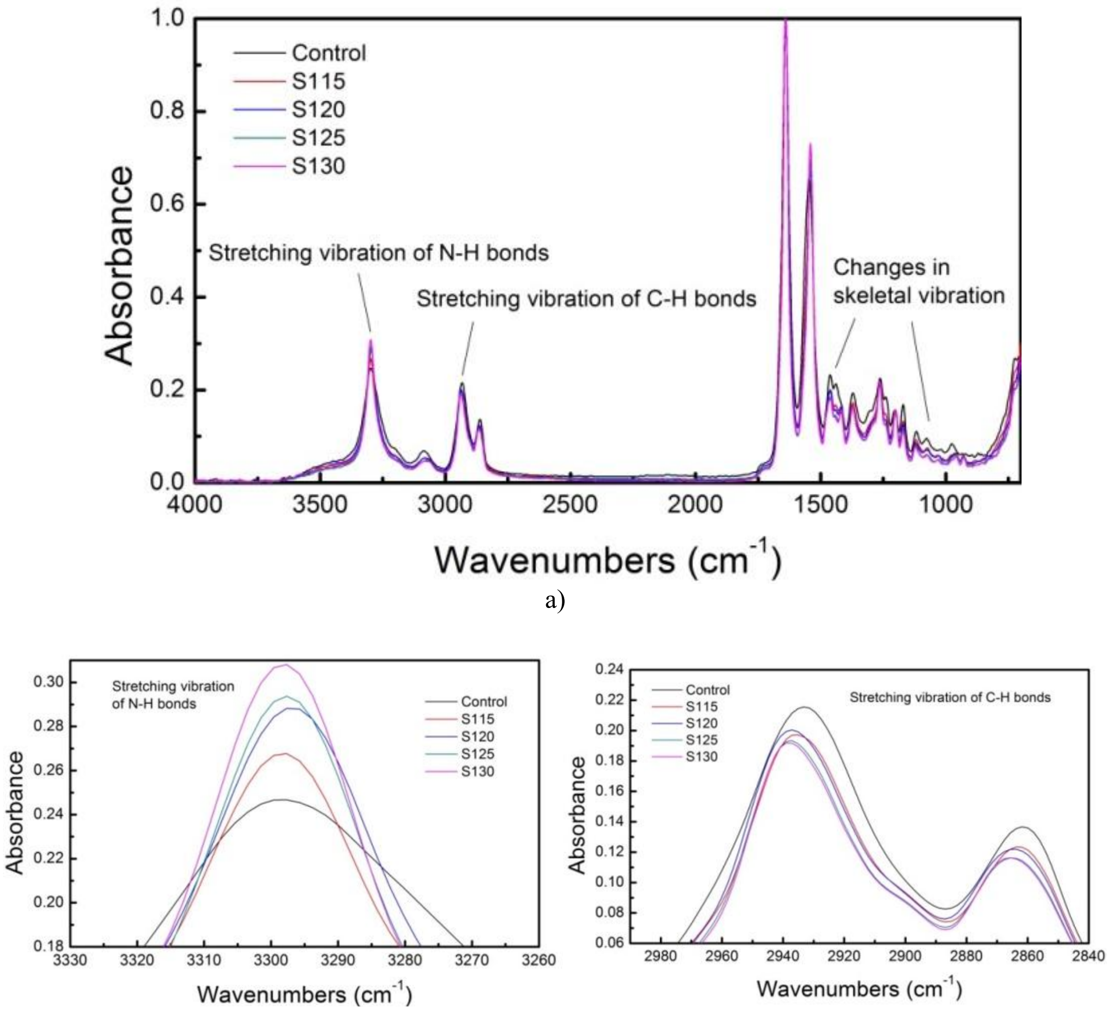


Fig. 13 Dye removal capacity changes according to steaming temperature.



a)

b)

c)

Fig. 14 FTIR spectra

The FTIR has been tested and shown in Fig. . It was shown in Fig. b) and c) that as the steam temperature increased, the absorbance peak which indicates stretching vibration of N-H bonds moved higher, and the absorbance peak which stands for stretching vibration of C-H bonds moved lower. It could mean shortening of the hydrocarbon chains with the phenomenon of increasing the intensity of stretching vibration of N-H bonds in comparison with decreasing the intensity of stretching vibration of C-H bonds. It was also found the decreasing changes in skeletal vibrations, which cannot be clearly assigned to specific bonds.

Polyamide 6 nanofibers membrane was deposited with TiO_2 nanoparticles whose SEM image is shown below:

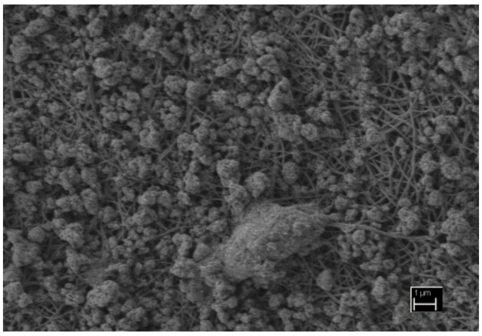
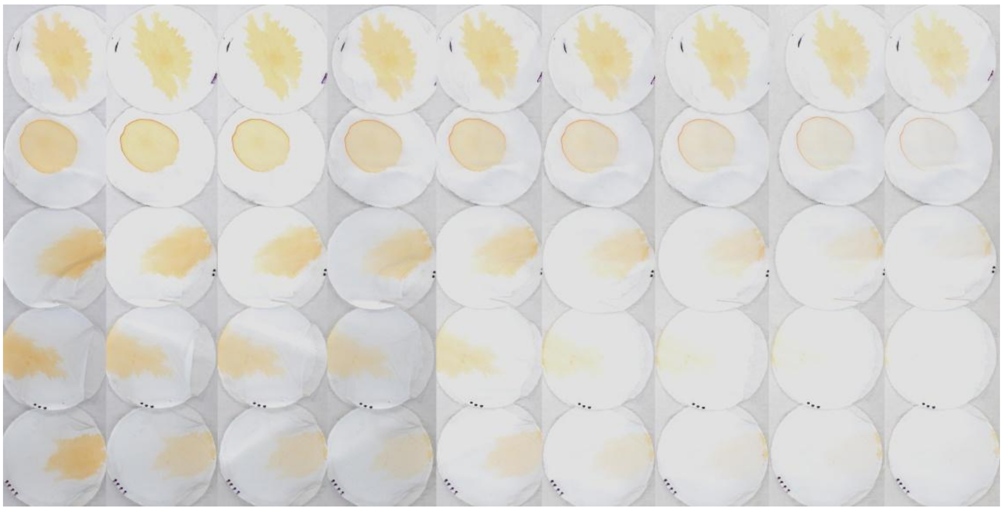


Fig. 15 Surface morphology of PNM coated by TiO_2 nanoparticles

The scanning images of samples after UV light treating are shown below:

Table 4 Scanning images of UV treated samples with different treating time-BB group.

no.	UV treating time (min)								
	0	30	60	90	120	180	240	300	400
BB1									
BB2									
BB3									
BB4									
BB5									

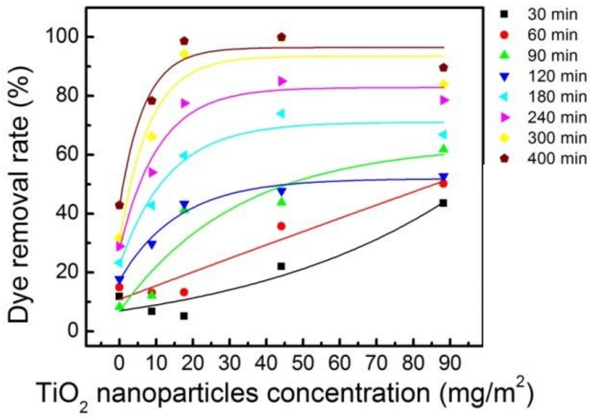


Fig. 16 Dye removal rate change according to TiO_2 nanoparticles concentration under different UV light treating time.

As shown in above figure, while long enough UV light providing (equal to or above 120 min), dye removal rate increased with the increasing of TiO_2 nanoparticles concentration. The samples with TiO_2 nanoparticles concentration above 18 mg/m^2 was obtaining similar amount of dye removal rate which means 18 mg/m^2 was a quite sufficient TiO_2 nanoparticles concentration for PNM surface self-cleaning modification by photocatalysis.

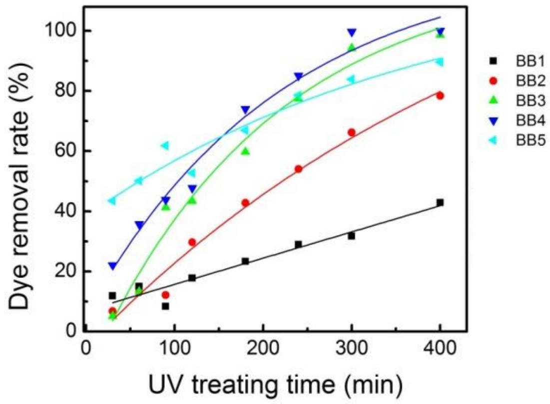
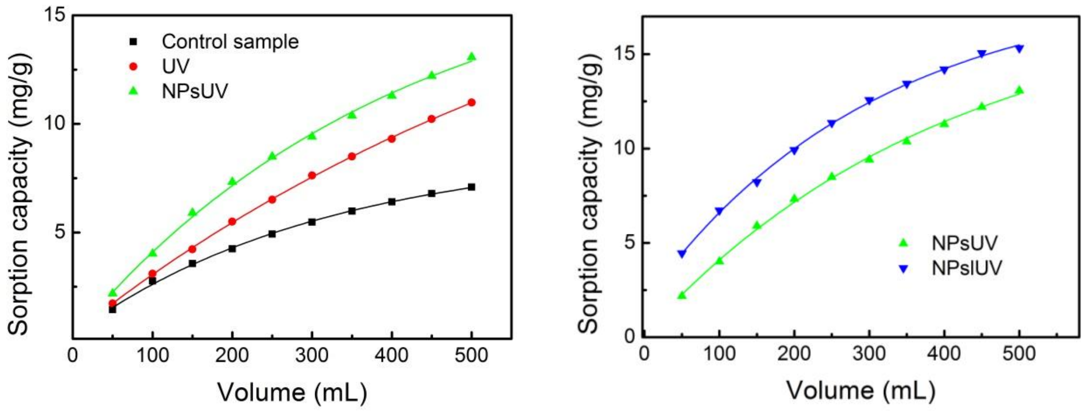


Fig. 17 Stain removal efficiency shown as dye removal rate at different point of UV light treating time.

It shows linear trend between dye removal rate and UV light treating time. In Fig. 17, As the UV light treating time prolonging, the dye removal rate increases linearly for the low TiO_2 nanoparticles concentration at around 9 mg/m^2. For higher TiO_2 nanoparticles concentrations, after 240 minutes UV light treatment, the dye removal rate can reach up to 100%, which was the maximum it can be.

The absorbance of influent and effluents after each 50 mL AO7 solution went through the dynamic sorption photocatalysis apparatus were detected. The dye removed amount, and dye sorption capacity were calculated and the results were shown in Fig. 18.



a) b)

Fig. 18 Sorption capacity comparison of different samples: a) comparison among control sample, UV, and NPsUV; b) samples with different UV treating time.

After calculation of accumulated dye removed amount, sorption capacity versus volume were plotted in Fig. 18. a) showed that after 500 mL AO7 dye solution pumped through PNM2.5, TiO_2 NPs photocatalysis improved the sorption capacity of PNM2.5 from 7.09 to 13.07 mg/g. Moreover, b) showed that comparing with the photocatalysis sample, after prolonging the UV treating time, value of dye sorption capacity reached up to 15.32 mg/g.

6 Evaluation of results and new finding

This thesis presented the sorption performance of polyamide 6 nanofibers assembly, and effect of surface modification of polyamide 6 nanofibers. The experimental results are:

1) The factors such as temperature, solution pH value, solution concentration, dosage of sorbent, and fiber scale of sorbent were studied. Result revealed that temperature and solution concentration encouraged the exhaustion of acid dye on polyamide 6 nanofibers and others have negative effect. Dye sorption was fitted better with Langmuir isotherm than Freundlich isotherm. The kinetic parameters showed the sorption rate of acid dyes a positive relationship with bath temperature, and Pseudo-Second Order equation fitted experimental data better than Elovich equation with R^2 over 0.99. Thermodynamic parameters calculation showed: the Arrhenius activation energy (E_A) was more than 40 kJ/mol which indicated a chemisorption oriented process. The negative value of the change of free energy ($\Delta G°$) confirmed a feasibility, spontaneous, and entropy-driven process in the temperature range 30–50°C. The positive value of standard enthalpy change ($\Delta H°$) and standard entropy change ($\Delta S°$) revealed an endothermic sorption process and it increased the randomness and degree of freedom.

2) Dynamic sorption process result showed that nanofibers have superior dye removal properties than conventional fibers. The hormone (17 β–Estradiol) and dye removal capacity of nanofibers increased while the diameter decreased due to the specific surface area increasing. The factors such as areal density, influent solution concentration, and fibers quantity were considered for the dye removal rate of polyamide 6 nanofibers. And it showed a positive relation with fibers mat specific surface area and quantity. Meanwhile, high feeding concentration caused much severer fouling problem.

3) The result of steam treatment showed that dye removal capacity could be improved as the temperature over 120°C. TiO_2 nanoparticles deposition and UV light treatment was tested efficiently removing the dyestuff from polyamide 6 nanofibers. TiO_2 nanoparticles concentration 18 mg/m^2 is recommended and 80% dye removal rate would be guaranteed with over 240 minutes UV light treating. TiO_2 nanoparticles photocatalysis was proved to be one method for improving the dynamic sorption capacity of Acid Orange 7 on polyamide 6 nanofibers. The initial sorption amount can be improved by prolonging the UV light treating time to some extents.

7 References

[1] Bhowmick, A.K. and H. Stephens, *Handbook of Elastomers, Second Edition*. 2000: Taylor & Francis.

[2] Martienssen, W. and H. Warlimont, *Springer Handbook of Condensed Matter and Materials Data*. 2006: Springer Berlin Heidelberg.

[3] White, J.L., *Principles of Polymer Engineering Rheology*. 1990: Wiley.

[4] Malaika, S.A., A. Golovoy, and C.A. Wilkie, *Chemistry and Technology of Polymer Additives*. 1999: Wiley.

[5] Zhang, X. and U.o.I.a. Urbana-Champaign, *Thermodynamics of Polyamide Separation Membrane in Contact with Aqueous Solutions*. 2008: University of Illinois at Urbana-Champaign.

[6] Robinson, T., et al., *Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative.* Bioresource Technology, 2001. **77**(3): p. 247-255.

[7] (SCENIHR), S.C.O.E.A.N.I.H.R. *The appropriateness of existing methodologies to assess the potential risks associated with engineered and adventitious products of nanotechnologies* 2006; Available from: http://ec.europa.eu/health/ph_risk/committees/04_scenihr/docs/scenihr_o_003b.pdf.

[8] York, C.P.S.a.t.U.o. *Nanomaterials*. 2013 18th March 2013; Available from: http://www.essentialchemicalindustry.org/materials-and-applications/nanomaterials.html.

[9] Wiener, J., S. Shahidi, and M.M. Goba, *Laser deposition of TiO2 nanoparticles on glass fabric.* Optics and Laser Technology, 2013. **45**: p. 147-153.

[10] Konstantinou, I.K. and T.A. Albanis, *Worldwide occurrence and effects of antifouling paint booster biocides in the aquatic environment: a review.* Environment International, 2004. **30**(2): p. 235-248.

[11] Wei, B., et al., *Adsorption Properties of Lac Dyes on Wool, Silk, and Nylon.* Journal of Chemistry, 2013.

[12] Rowen, J.W. and R.L. Blaine, *Sorption of Nitrogen and Water Vapor on Textile Fibers.* Industrial and Engineering Chemistry, 1947. **39**(12): p. 1659-1663.

[13] Zeng, H.Y., et al., *Lipase adsorption on woven nylon-6 membrane: Optimization, kinetic and thermodynamic analyses.* Biocatalysis and Biotransformation, 2014. **32**(3): p. 188-197.

[14] Reuvers, N.J.W., H.P. Huinink, and O.C.G. Adan, *Plasticization lags behind water migration in nylon-6: An NMR imaging and relaxation study.* Polymer, 2015. **63**: p. 127-133.

[15] Strnad, S., et al., *Surface properties of structural modified PA 6 fibers.* Macromolecular Materials and Engineering, 2002. **287**(4): p. 296-305.

[16] Strnad, S., et al., *The influence of structural properties on the dye diffusion and dyeabilty of PA 6 fibres.* Materials Research Innovations, 2003. **7**(6): p. 358-365.

[17] Avramova, N., *Effect of the structure on sorption and diffusion processes in polyamide 6, part 1: Activation energy and thermodynamic parameters of water Desorption in oriented and unoriented polyamide 6.* Journal of Applied Polymer Science, 2007. **106**(1): p. 122-129.

[18] Reuvers, N., H. Huinink, and O. Adan, *Water Plasticizes Only a Small Part of the Amorphous Phase in Nylon-6.* Macromolecular Rapid Communications, 2013. **34**(11): p. 949-953.

[19] Xia, Y.Y., et al., *Polyaniline (skin)/polyamide 6 (core) composite fiber: Preparation, characterization and application as a dye adsorbent.* Synthetic Metals, 2013. **175**: p. 163-169.

[20] Gupta, V.K., et al., *Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: A review.* Advances in Colloid and Interface Science, 2013. **193**: p. 24-34.

[21] EL-Mekkawi, D.M., et al., *Photocatalytic activity evaluation of TiO2 nanoparticles based on COD analyses for water treatment applications: a standardization attempt.* International Journal of Environmental Science and Technology, 2016. **13**(4): p. 1077-1088.

[22] Saharan, P., et al., *Ultra fast and effective treatment of dyes from water with the synergistic effect of Ni doped ZnO nanoparticles and ultrasonication.* Ultrasonics Sonochemistry, 2015. **22**: p. 317-325.

[23] Chladova, A., J. Wiener, and M. Polakova, *Testing the Photocatalytic Activity of Tio2 Nanoparticles with Potassium Permanganate Solution.* Nanocon 2011, 2011: p. 527-531.

8 List of papers published by author

Journal Publication:

[1a] Wang, Y., Wiener, J., Sorption kinetics for the removal of dyes from effluent onto polyamide 6 nanofibrous assembly, submitted.

[2a] Wang, Y., Wiener, J., Militký, J., Adsorption of Acid Blue 41 by polyamide 6 nanofibers: Isotherms, kinetics and thermodynamics studies, submitted.

[3a] Wang, Y., Wiener, J., Militký, J., Mishra, R., Zhu, G., Ozone effect on the properties of Aramid fabric, (2016) Autex Research Journal, accepted. *Impact factor: 0.460*

[4a] Wang, Y., Wiener, J., Zhu, G. Langmuir isotherm models applied to the sorption of acid dyes from effluent onto polyamide nanofibers, (2013) Autex Research Journal, 13 (3), pp. 95-98. *Impact factor: 0.460*

Conference Publication:

[5a] Wang, Y., Wiener, J. Dynamic sorption process of acid dye on nanofibers assembly with TiO_2 nanophotocatalysis, (2016) NANOCON 2016, 8th International Conference, accepted.

[6a] Wang, Y., Wiener, J. Kinetics study for the removal of acid dyes from aqueous solutions using polyamide nanofibrous membranes, (2016) Aachen-Dresden-Denkend of International Textile Conference 2016, accepted.

[7a] Wang, Y., Wiener, J., Surface modification of Polyamide 6 nanofibers with steam, (2016) Workshop Bílá voda 2016, 22-25.09.2016, Liberec, Czech Republic.

[8a] Wang, Y., Marek, J., Wiener, J., Study on the acid dye removal by polyamide 6 nanofibrous membrane, (2015) NANOCON 2015, 7th International Conference. *Thomson Reuter, Indexed in ISI Web of Knowledge.*

[9a] Wang, Y., Wiener, J., Zhu, G., Huang J. Sorption kinetics analysis of acid dye on polyamide 6 nanofibers under different pH, (2014) STRUTEX 20, 1-2, 12, 2014.

[10a] Wang, Y., Wiener, J., Zhu, G. Sorption isotherm study on two polyamide nanofibrous membranes, (2014) NANOCON 2014, 6th International Conference, pp. 405-410. *Thomson Reuter, Indexed in ISI Web of Knowledge.*

[11a] Wang, Y., Wiener, J., Stelmakh, A., Dye filtration porperties of polyamide 6 nanofibrous membrane, (2014) 16-19, 9, 2014, Rokytnice nad Jizerou, Czech Republic.

[12a] Wang, Y., Wiener, J., Zhu, G., Huang, J., Characterization of polyamide 6 membrane by BET theory, (2014) ICCE-22, 13-19, 7, 2014, Malta.

[13a] Wang, Y., Wiener, J., Zhu, G., Huang, J., Constant online apparatus to investigate filtration, (2014) Fiber Society Spring 2014 Technical Conference: Fibers for Progress.

[14a] Wang, Y., Wiener, J., Zhu, G., Sorption property of polyamide nanofibrous membrane on dyestuff for purifying wastewater, (2013) NANOCON 2013, 5th International Conference, pp. 329-333. *Thomson Reuter, Indexed in ISI Web of Knowledge.*

[15a] Wang, Y., 3D Aramid fabrics for composite reinforcement, (2013) 18-20.09.2013, Rokytnice nad Jizerou, Czech Republic.

[16a] Wang, Y., Wiener, J., Zhu, G., Huang, J., Venkataraman, M., Apparatus Assembling for Continual Filtration Study of Filter Membrane. 8th TEXSCI, 23-25.09.2013, Liberec, Czech Republic.

[17a] Wang, Y., Wiener, J., Mishra, R., Zhu, G., Venkataraman, M., Huang, J., Militký, J., Study on Ozone Treatment of Aramid Fabrics. 8th TEXSCI, 23-25.09.2013, Liberec, Czech Republic.

[18a] Wang, Y., Zhu, G., Mishra, R., Militký, J., The application of fly ash nanoparticles in composites reinforced by glass fabrics with different structures. 6th AESP, 02-06.06.2013, Wuhan, China. (*Poster Prize*)

[19a] Wang, Y., Venkataraman, M., Zhu, G., Mishra, R., Wiener, J., Militký, J., Effect of Alkali Treatment on Thermal Insulation of PET Fabric. STRUTEX, 3-4, 12. 2012. Liberec, Czech Republic, EU. ISBN: 978-80-7372-913-4. p80-81.

[20a] Wang, Y., Venkataraman, M., Mishra, R., Militký, J., Study on Impact Behavior of Textile Structures and Composites. STRUTEX, 3-4, 12. 2012. Liberec, Czech Republic, EU. ISBN: 978-80-7372-913-4. p170-171.

Book Chapter:

[21a] Mishra, R., Militky, J., Baheti, V., Huang, J., Kale, B., Venkataraman, M., Bele, V., Arumugam, V., Zhu, G., Wang, Y. The production, characterization and applications of nanoparticles in the textile industry, (2014) Textile Progress, 46 (2), pp. 133-226.

9 Curriculum Vitae

PERSONAL DATA

Name	Yan Wang (Amy)
Department:	Technical University of Liberec Faculty of Textile Engineering Department of Material Engineering
Address:	Studentska 2, 46117 Liberec, Czech Republic
Phone:	+420 774846310
E-mail:	amywang1021@hotmail.com
Date of birth	21.10.1085
Nationality	Chinese

SKILLS

- Bilingual. Demonstrated outstanding communication skills in both Chinese and English
- Demonstrated teamwork, negotiation and resolution abilities
- Recognized designing and modifying skills in textile materials
- Computer skills including MS Office and Origin
- Know well testing software like Capillary/ Cone-and-Plate Rheometer, Instron5566, SEM, and DMA
- EU driving license (group B) holder.

WORKING EXPERIENCE

Performance fibers (Kaiping) Co., Ltd– Kaiping, Guangdong, China
Technical Engineer, Jan. 2011 –Jan. 2012

- Technical support for PET fiber/tire cord/canvas production
- Customer technical service
- Developed team working skill and thinking method of facing problems

EDUCATION

Technical University of Liberec – Liberec, Czech Republic
PhD, Textile Material Engineering (Feb. 2012 till now)
Thesis: Selected Sorption Properties of Nanofibers assembly

Wuhan Textile University – Wuhan, Hubei, China
Master of Science, Textile Material and Design（Sep. 2008-Jun. 2011）
Thesis: Study on Rheology and Spinning Properties of Poly (L-lactic acid)/Polyurethanes Blends

Wuhan Textile University – Wuhan, Hubei, China
Bachelor of Science, Textile Engineering（Sep. 2004-Jun. 2008）

Thesis: Modified water vapor permeation of dry PU film with down and wood powder

PROJECTS

1. Leader of SGS project: Study on filtration and sorption properties of nanofibrous membrane. (21040) 2014
2. Leader of SGS project: Modeling the impact behavior of aramid based composite materials. (48012) 2013
3. DRDO, Development of Enhanced Thermal Insulation Material for Extreme Cold Weather Clothing. 2012
4. Research projects of Education Department of Hubei Province: A Study on the Performance and the Structure Control of Medical Porous Materials of Polyurethane and Superfine Chitosan Powder (B20091704).
5. Research projects of Wuhan Textile University: Synthesis of Biodegradable Polyurethane Based on Polyester Diol and Preparation of Medical Porous Scaffolds (093866).

HONORS AND ACTIVITIES

- Nominated for "National Outstanding Self-financed student studying abroad", 2013
- "Poster Prize" in 6th AESP conference 2013;
- Outstanding Master thesis, 2011;
- Achieved Third Scholarship Awards, 2009, 2008;
- Won First-class Prize of College Students Extra-curricular Competition on Science and Technology in Hubei province, 2007;
- Received Scholarship Awards, 2006-2007;
- Won National Scholarship, 2007;
- Excellent Young Volunteer, 2005

COMPETENCE TESTS

Mandarin Proficiency Certificate (qualified with Level 1 Grade B) – November, 2009
College English Test Band 6 for non-English majors (Scores: 425) – June, 2008

ADDITIONAL INFORMATION

I enjoy reading, singing, painting, basketball and Ping-Pong.

10 Brief description of current expertise, research and scientific activities

1) Sorption principles and its applications;

2) Application of nanofibers and nanoparticles;

3) Surface modification of conventional and nano materials;

4) Mechanical properties of Aramid fibers and assembly;

11 Record of the state doctoral exam

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ZÁPIS O VYKONÁNÍ STÁTNÍ DOKTORSKÉ ZKOUŠKY (SDZ)

Jméno a příjmení doktorandky: **Yan Wang**

Datum narození: **21. 10. 1985**

Doktorský studijní program: **Textilní inženýrství**

Studijní obor: **Textile Technics and Material Engineering**

Termín konání SDZ: **15. 4. 2015**

prospěla ~~**neprospěla**~~

Komise pro SDZ:

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Předseda:	prof. Ing. Jiří Militký, CSc.	[signature]
Místopředseda:	prof. Ing. Jaroslav Šesták, DrSc., dr.h.c.	[signature]
Členové:	doc. RNDr. Jiří Vaníček, CSc.	[signature]
	doc. Mgr. Irena Lovětinská-Šlamborová, Ph.D.	[signature]
	Ing. Blanka Tomková, Ph.D.	Tomková

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12 Recommendation of the supervisor

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OPINION OF THE DISSERTATION SUPERVISOR

THESIS TITLE: Selected Sorption Properties of Nanofibers Assembly

AUTHOR: Yan Wang, M. Eng.

I am writing this letter to recommend Ms. Yan Wang for her final defence. Ms. Yan Wang has been studying and working with me for more than 4 years. She is optimistic, intelligent, outstanding in communication, team work and research.

She specializes in sorption properties of nanofibers assembly, has completed all of the courses, and state exam successfully, as first author published 2 papers in journals with impact factor (another 2 papers under review), 14 papers in international conferences (2 more papers accepted), and 1 chapters in books. Besides, she is active in promoting international cooperation among universities.

The main specific goal of PhD candidate was to study the adsorption properties of polyamide 6 nanofibers assembly.

In this thesis, the factors such as temperature, solution pH value, solution concentration, dosage of sorbent, and fiber scale of sorbent were studied. Dye sorption was fitted with isotherms and kinetic models. Thermodynamic parameters calculation confirmed a feasibility, spontaneous, and entropy-driven process in the temperature range 30-50°C. The positive value of standard enthalpy change and standard entropy change revealed an endothermic sorption process and it increased the randomness and degree of freedom. Dynamic sorption process result showed that nanofibers have superior dye removal properties than conventional fibers. The factors such as areal density, influent solution concentration, and fibers quantity were considered for the dye removal rate of polyamide 6 nanofibers. And it showed a positive relation with fibers mat specific surface area and quantity. The result of steam treatment showed that dye removal capacity could be improved as the temperature over 120°C. And TiO_2 nanoparticles photocatalysis was proved to be one method for improving the dynamic sorption capacity of acid dye on polyamide 6 nanofibers.

I strongly recommend her for the final defence since she has fulfilled all the requirements and excellent work she has done.

4.10.2016

prof. Ing. Jakub Wiener, Ph.D.
Supervisor

13 Opponent's reviews

Review

of dissertation thesis
"Selected Sorption Properties of Nanofibers Assembly"
by
Yan Wang, M. Eng.

The thesis consists of 119 pages including literature references and lists of symbols, figures and tables. It is structured into 5 chapters.

Chapter 1 (Introduction) gives a brief background on Polyamide 6 fibers. The most important part of the chapter is the formulation and description of the aim of the work, where the reasons for this study are explained. In this section, I would appreciate a little more structured description of main goals of the thesis.

Chapter 2 (Literature Review) is focused on all important aspects necessary to understand material properties of Polyamide 6, adsorption mechanisms and their models, and nanotechnology/nanomaterials related to the research activities of the author (electrospinning, nanoparticles, surface modifications).
Significant portion of the text is dedicated to photocatalytic properties of TiO_2 particles bonded on the nanofiber surface, as an introduction to corresponding research activities of the author described in following chapters. This topic exceeds the (probably) original scope of the thesis, as these processes are only weakly related to adsorption. However, the application field (removing non-desired substances from fluids) is relevant to the title of the thesis.
The chapter is written with adequate care, and it gives sufficient introductory information above the current state of the research field where the thesis indents to contribute.

Chapter 3 (Materials and Methods) is dedicated to the choice and description of both commercial and self-built equipment used in the experimental part of the work, which is the core of the thesis. In this effort, the author is very systematic, descriptions are given in sufficient details. Also, the materials used for the sorption studies are characterized properly. In the chapter, some experimental results are also given, e.g. BET values measured on nanofiber membranes. As these experiments do not deal directly with the sorption study itself, presentation of the results in this part of the thesis is appropriate.

Chapter 4 (Results and Discussion) presents experimental results structured into three parts: (1) dye sorption onto Polyamide 6 nanofiber membrane, (2) dynamic sorption, and (3) surface modifications of the membranes. Nanophotocatalysis has been studied as a self-cleaning mechanism tor the membranes. Again, I have to note that this part of the work is not 100% compatible with the main topic of the thesis (sorption properties); however, its outputs are interesting and relevant to the aim of the study (removal of dye, hormones, etc. from fluids). I value author's effort to correlate experimental data with the theoretical models (Freundlich isotherm – p. 66, Langmuir isotherm – p. 67). Correlation coefficients obtained from the analysis (0.81 and 0.85, respectively) are sufficiently high to prove that the models are good enough for qualitative understanding of the sorption processes at nanofiber membranes.
Author's approach to the experiments is systematic. The results are presented clearly, with appropriate comments. The methods and equipment author used are appropriate. Graphs and tables are easy to understand and follow.

In Chapter 5, author clearly summarizes and generalizes the extensive results discussed in details in previous chapter. The conclusions are formulated logically. The results are qualitatively summarized, which corresponds to mostly empirical character of the work. I would appreciate in this part some vision from the author towards practical industrial applicability of the results. Also, I miss some recommendations for continuation of the research in the field.

Concluding notes and recommendations:

1. Author collected extensive and very useful amount of systematic experimental data related to the sorption processes on PA6 nanofiber membranes.
2. Graphical appearance and language of the work is very good.
3. The study is of mostly experimental character. However, author has shown good understanding of the effects observed and fitted obtained data with known theoretical models.
4. Can author comment/explain, why Langmuir isotherm fits better than Freundlich?
5. The BET values obtained for the 2 nanofiber PA6 membranes indicate, that the surface area of the samples corresponds very well to geometrical surface of the fibers (square of fiber diameter ratio is approx. 2.7, BET ratio is approx. 2.6, according to Table 3-1 on page 44). Is there any indication that some "fine" surface structure of the fibers (e.g. "nano-roughness") influences sorption mechanisms of the membrane? How important is BET value for eventual prediction of sorption kinetics and capacity of the material?
6. Author has published 4 journal papers, 16 publications at well attended international conferences, and one book chapter. I consider his publication activities so far to be sufficient prove of his independent scientific ability.
7. The importance of the work for the nanofiber industry is high, as it helps to understand added value of nanofiber materials in many practical applications. The thesis solved just a part of what the industry would need; however, this is a good start and inspiration for eventual continuation of the research in this direction.

I recommend the thesis for the defense
by the Committee for Doctoral Dissertations
of the Faculty of Textile Engineering of the Technical University of Liberec.

Liberec, December 16, 2016

doc. Ing. Stanislav Petrík, CSc.

Opponent's review

This opponent's review was elaborated based on Ing. Jana Drašarová, PhD. (dean of Faculty of Textile, Technical University in Liberec) assignment for review Ph.D. dissertation thesis (ref. no. TUL-16/4814/041920, dated 10. 11. 2016) of **Yan Wang, M.Eng.** entitled **"Selected Sorption Properties of Nanofibers Assembly"**. Tutor of the PhD. student was Prof. Ing. Jakub Wiener, Ph.D.

Theses presented has a technological impact for dyes recovery from the solutions and waste waters.

Polyamide fibers have found a broad application in textile industry due to their properties, such as high mechanical strength, flexibility, abrasion resistance, excellent dyeability, and easy material maintenance. As a sorption material for waste water treatment a polyamide 6 with nanofibrous membrane (PNM) with the ability of removal of bacteria, dye adsorption and hormone removal from the solutions. This capability was improved by the surface treatment of PMN by means of UV light irradiation and water steam, by means of the deposition of TiO_2 nanoparticles. Material characterization as the adsorption substrate was studied by means of adsorption isotherm determination BET (pore size and specific surface area determination), Freundlich and Langmuir isotherms determination for a given pair of adsorption material and adsorbing substrate. Furthermore, there were applied methods of FTIR and UV VIS for characterization of dyes and DSC for the characterization of the physico-chemical properties of the materials under study. Microscopic picture of the PNM was obtained by means of scanning electron microscopy, SEM. Adsorption capacity of the tested materials was performed at various temperatures, pH and dyes concentration on apparatuses constructed at constant flow rate, dynamic sorption process with UV light etc. The chosen methods fully characterize adsorption profile of the tested material PNM for given application.

Major results of the thesis are focused on utilization of PNM as a sorption material. The best for describing the adsorption process, according to the applicant's judgement seems to be the Langmuir adsorption isotherm, characterizing mainly the monomolecular adsorption. According to the thermodynamic calculations the studied adsorption process is entropy driven spontaneous process in the temperature range of 30 to 50°C, where the concentration and temperature increase consumption of the acidic dye. For different adsorbates studied this effect was negative. Surface treatment of the material further more increases its sorption capacity. For the calculation of the adsorption formal kinetics, the Elovich formula and the pseudo second order kinetics approach were applied. By the latter method and application of the least square calculation there was selected the better fitting model of the given type adsorbent-adsorbate. From the formal point of view, results of the theses and the thesis itself are well written, results are presented in the form of tables and graphs. Thesis represent typical material science oriented study focused on polymeric fibers characterization for textile industry.

Thesis are written in English language in the form of the monograph. Thesis total references cited was 142. There were cited fundamental research articles as well as the latest publications. However the format of the reference list is not fulfilling requirements of the citation standard CSN ISO 690.

Results of the thesis of the applicant Wang were published in 2 scientific papers in impacted journals and two more papers are under evaluation and submitted to the journals. She was attending several scientific conferences at home as well as abroad. she is the coauthor of one contribution in the book entitled "The production, Characterization and Applications of Nanoparticles in Textile Industry" published in 2014.

Questions to be answered during thesis defense:

1) Quantify the reproducibility of your sorption experiments.
2) Verify the results by means of statistical ANOVA analysis.
3) Did you performed desorption experiments as well?

Based on the latter mentioned facts and by the course of law (Higher Education Law No. 111/1998. Sb.) §47 I recommend to accept the PhD. dissertation thesis of Yan Wang, M.Eng. for defense.

In Zlín, December 2, 2016

Doc. Mgr. Barbora Lapčíková, Ph.D.

Associated professor for materials science and engineering
Tomas Bata University in Zlín