Engineering and Applied Science Research July – September 2020;47(3):222-231 Research Article

Engineering and Applied Science Research
https://www.tci-thaijo.org/index.php/easr/index
Published by the Faculty of Engineering, Khon Kaen University, Thailand

Functionalized nonwoven Nylon fabrics for cadmium ion exchange applications

Wichuda Chanprapanon and Nithinart Chitpong*

Department of Textile Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi,
Pathumthani 12110, Thailand

Received 1 November 2019
Revised 5 January 2020
Accepted 14 January 2020

Abstract

Water pollution is a big issue of our world. This research aims to study the possibility of using carboxylate functionalized synthetic nonwoven fabrics for removing heavy metals from contaminated water. Poly(acrylic acid) (PAA) and poly(itaconic acid) (PIA) were grafted from the surfaces of individual Nylon 6,6 fibers of nonwoven fabrics by radiation induced-polymerization with Gamma-rays under various conditions. FTIR spectra show evidence of the carboxylate groups of PAA and PIA after polymer grafting. A comparison of fiber sizes and surface morphology of nonwoven Nylon fabrics before and after PAA and PIA grafting was examined using optical microscopy (OM) and scanning electron microscopy (SEM). The shrinkage, curl and non-uniformity of fibers observed by OM and SEM after polymer grafting might cause the changes in the water permeabilities of the modified Nylon fabrics. After hydrolyzation of modified Nylon fabrics with sodium hydroxide, static cadmium (Cd^{2+}) ion exchange capacities were measured for all fabric samples. The Langmuir model was used to calculate parameters, including maximum static Cd^{2+} ion exchange capacities and the association coefficients to explain behaviors of unmodified and modified nonwoven Nylon fabrics. Using unmodified and PAA- and PIA- modified Nylon fabrics as ion-exchange membranes, these membranes provide higher water flowability than conventional membranes. Furthermore, the static Cd^{2+} ion exchange capacities of these ion-exchange membranes are comparable to commercial ion-exchange materials. It was also found that duration time of radiation inducing and heating steps along with various types of polymer grafting affected the ion exchange capacities and membrane performance.

Keywords: Nonwoven, Functionalization, Heavy metals, Ion-exchange, Radiation

1. Introduction

Nowadays, polymers such as plastics, rubbers, adhesives, fibers and coatings have useful applications in daily life due to their various properties. Depending on purpose of a product, numerous synthetic and natural materials are available. Both synthetic and natural polymers are created via polymerization of hydrocarbon molecules or monomers [1-2]. Various types of polymers are suitable for given applications. For example, water bottles generally are made from polyethylene terephthalate (PET). Pipes typically are manufactured from polyvinyl alcohol (PVC). Polyesters are the main polymeric materials for synthetic textiles products. However, for specific industrial applications, such as membranes for removing heavy metal ions from industrial wastewaters, functionalization of polymers for property improvement has been rapidly developed using various new technologies. Copolymers can be synthesized to add functional groups or improve the properties of polymers. Conceptually, copolymers can be a single long chain of two types of monomers such as alternating, random, block copolymers. Conversely, they may consist of a backbone of a single monomers with branches of other types of monomers. This is called a “graft copolymer” [1]. Currently, there are three methods of producing graft copolymers, grafting from, grafting onto and grafting through. The “grafting from’’ method is practical since there are a broad range of monomers and polymers can be applied under various conditions, while other methods have various advantages and disadvantages [1]. Wang et al. [3] used a “grafting from” method with atom transfer radical polymerization (ATRP) to modify cellulose membrane surfaces using poly(glycidyl methacrylate) (PGMA) for antibody purification. Similarly, Chenette and Husson [4] also used this method to graft glycopolymers for targeted lectin binding. However, the “grafting onto” method was alternatively selected to graft polyacid polymers onto surfaces of regenerated cellulose nanofibers instead of the “grafting from” method. This was due to the slower kinetics of the ATRP method [2, 5].

Radical graft polymerizations were mostly used for synthesizing graft copolymers. However, ionic graft polymerizations are also possible. Various techniques have been used to graft copolymers onto the surfaces of polymer materials to initiate polymerization involving radicals. These methods include thermal decomposition, redox initiation,

---

*Corresponding author. Tel.: +6681 720 7075
Email address: nithinart_c@rmutt.ac.th
doi: 10.14456/easr.2020.25

living radical polymerization and ionizing radiation [1]. Living radical polymerizations of the ATRP technique have been a common way to graft polymers. It has excellent control of the lengths of the grafting chains. Alternatively, irradiation of a mixture of polymers and monomers to ionizing radiation, such as ultraviolet radiation [6-7], Gamma radiation [8-9], plasma [10], and electron beam [11], can produce polymer radicals using various types of monomers. According to multiple literature reports, the ATRP method can be used to graft several monomers onto polymeric material surfaces [3-4, 12-13]. However, it was found that using itaconic acid as a monomer showed slow kinetics with polymerization times longer than 6 h (up to 60 h) [12]. With this limitation, using irradiation technique with high energy rays to produce radicals for "grafting from" polymerization is a good approach for the current research.

Cadmium is a highly toxic heavy metal that causes Itai-Itai disease [14]. Even though cadmium is rarely found in the environment, its level can be increased through the discharge of industrial wastes of factories involved in metal finishing and coating, as well as manufacture of nickel-cadmium batteries [14]. Therefore, the removal of cadmium from wastewater is of great environmental concern.

Materials with functional groups have been prepared for a variety of technical applications such as ion-exchange for water purification. A wide range of functional groups, such as hydroxyl, carboxyl, sulfonyl, thiol, amino, and amide groups, are useful in binding heavy metal ions including lead, copper, nickel, iron, zinc, and cadmium [15-17]. It was reported that carboxyl functional groups have been successfully used in sequestering heavy metal ions including those of cadmium and nickel [2]. Functionalization of the surfaces of polymeric materials, including poly(acrylic acid) and poly(itaconic acid) has been used for removing cadmium, nickel, copper and lead ions with low power requirements [2, 18-21]. Chitpong and Husson [2] reported that poly(acrylic acid) and poly(itaconic acid) functionalized regenerated cellulose nanofiber membranes were useful for removal of cadmium and nickel ions using a "grafting to" method for functionalization. It was also reported that ceric ions were an initiator to grafting poly(acrylic acid) onto cellulose surfaces for absorbing lead, copper and cadmium ions [18, 21]. Carboxyl groups of oxolane-2,5-dione modified cellulose material were successfully used to capture cadmium and lead ions in wastewater [19]. Moreover, it was shown that chitosan with modification by poly(itaconic acid) cross-linking with glutaraldehyde and epichlorohydrin by ammmonium persulfate-initiated graft copolymerization was a potential absorbent material for removing cadmium and lead ions from wastewater [20]. Consequently, PAA and PIA were selected as the "grafting from" strategy using an irradiation technique in this research work.

Various ion exchange materials including resins and membranes have been used to capture heavy metals from wastewaters. Membrane technology is an alternative process used in this research to avoid high pressure drops during ion exchange resin processes [22-23]. Moreover, a further advantage of membrane processes is that membrane sheets can be customized to different sizes and used with a variety commercial ultrafiltration methods [22]. Synthetic nonwoven fabrics with a high porosity such as polyethylene (PE), polypropylene (PP) and Nylon are available in the market. Therefore, in this research, Nylon 6, 6 nonwoven fabrics were exploited for their potential as ion exchange membranes.

The main objective of this research is to develop Nylon 6, 6 nonwoven fabrics for capturing heavy metals from wastewater using an ion exchange membrane. Poly(acrylic acid) and poly(itaconic acid) were grafted onto a Nylon substrate using Gamma irradiation in a "grafting from" method at different irradiation levels and heating times to study the main impact factors for developing ion exchange capacity. The success of graft polymerization was confirmed by surface chemistry evaluation using attenuated total reflectance Fourier-transform infrared spectroscopy. Characteristics of ion exchange membrane materials, including physical properties such as tensile strength, surface morphology and fiber diameters were investigated using tensile testing, optical microscopy and scanning electron microscopy. Finally, membrane performance, including water permeability and static Cd-ion exchange capacity are discussed and compared to other ion-exchange materials.

2. Materials and methods

2.1 Materials

The chemicals and solvents used in the current study include acrylic acid with an inhibitor (AA, 99%), cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\bullet}4H_2O$), ethanol (EtOH, reagent grade), itaconic acid (IA, $\geq$99%), and sodium hyrodoxide (NaOH). They were purchased from Sigma-Aldrich (St. Louis, MO, USA). Silica gel (SiO_2) was purchased from EMD Millipore Corporation (Billerica, MA, USA). Nylon 6,6 nonwoven fabrics were obtained from the Department of Textile Engineering at Rajamangala University of Technology Thanyaburi, Thailand.

2.2 Functionalization

2.2.1 Preparation of monomer solution

Nylon 6,6 nonwoven fabric was cut into 10 cm × 20 cm pieces and six samples were placed into 100 mL glass bottles. AA was passed through SiO_2 to remove the inhibitor and 9.5 mL of this solution was put into each of three samples of nonwoven Nylon. IA powder (5 g) was added to other three nonwoven fabric samples. EtOH (70 mL) was added to all six samples to dissolve the monomers. The entire preparation was done under an inert atmosphere (nitrogen gas) inside a glove box.

2.2.2 Polymer grafting method

All samples were placed inside a Gamma Cell 220 (Nordion, Canada) with a velocity of 0.89 Gy/s and heated in a water bath at 60 °C to 70 °C for various duration times as shown in Table 1. Afterward, all samples were rinsed twice in deionized water to remove residual monomers and then dried in an oven at 70 °C for 2 h before characterization and performance testing. Figure 1 displays the basic concept of PAA and PIA functionalization of Nylon fabrics for capturing positive ions or heavy metal ions.

2.3 Characterizations

2.3.1 Surface chemistry

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) analysis was conducted using a Perkin Elmer Frontier model (Waltham, MA, USA) with Omnic software. All measurements used 16 scans and a 4 cm resolution after scanning the background. The spectra were obtained with an ATR and manual baseline corrections.

Table 1 Radiation induced polymerization conditions

Sample	Monomer in EtOH	% by wt	Gamma-rad. (time, h)	Heating (time, h)
NPAA_1_1	AA	10	1	1
NPIA_1_1	IA	5	1	1
NPAA_1_5	AA	10	1	5
NPIA_1_5	IA	5	1	5
NPAA_5_1	AA	10	5	1
NPIA_5_1	IA	5	5	1

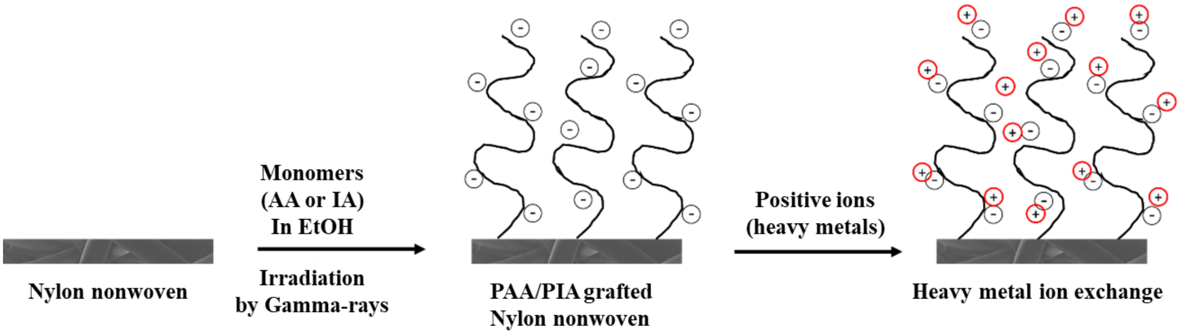

Figure 1 Basic concept for PAA and PIA modified nonwoven Nylon fabrics for heavy metal removal

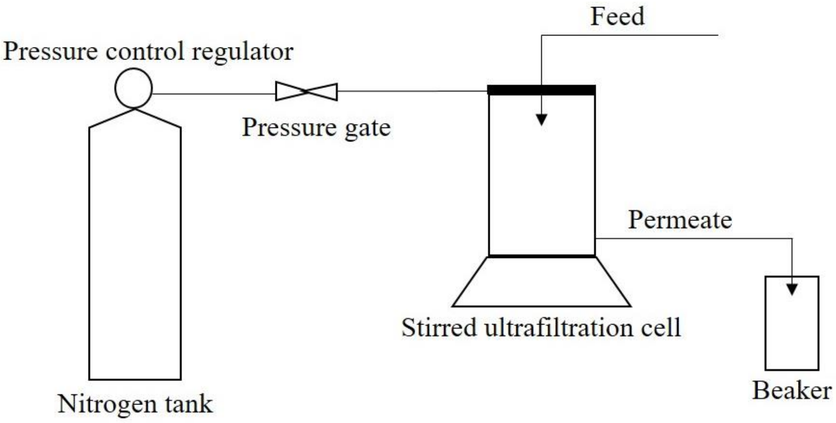

Figure 2 Permeability measurement apparatus

2.3.2 Fiber diameter and surface morphology

The average size and surface morphology of fibers were examined using optical microscopy (OM model: CX41RF, Olympus, Waltham, MA, USA) and scanning electron microscopy (SEM model: JSM-5410LV, JEOL, Peabody, MA). OM was used to check the quality of nonwoven Nylon fabrics before and after polymer grafting at 10× magnification. Axio Vision LE digital image processing software was used to manually measure fiber diameter in the obtained OM images. Before SEM analysis, carbon tape was used to fasten PAA and PIA - grafted nonwoven Nylon samples (~0.5 cm^2) to aluminum stubs. SEM images were captured at a voltage of 15.0 kV, current of 2 mA, and at magnifications of 500× and 2000×. Average fiber diameters and the quality of fiber surfaces were determined from SEM images.

2.3.3 Physical properties

Tensile strengths of Nylon 6,6 nonwoven samples before and after PAA and PIA modification were measured using a tensile tester (Instron Tensile Tester Model 5560, Norwood, MA, USA) following the procedures outlined in ASTM D 3822 01 with a 10 kN load cell employing a gage length of 25±2 mm and a crosshead speed of 50 mm/min. At least 10 nonwoven samples were cut to rectangular shapes (1 cm × 6 cm) before testing.

2.4 Performance tests

2.4.1 Permeability studies

A schematic of the permeability measurement apparatus is shown at Figure 2. Each cut nonwoven sample (60 mm width) was placed into a 200 mL ultrafiltration dead-end cell (Amicon Model 8200, EMD Millipore, Billerica, MA). DI water was introduced into the cell under nitrogen. The permeability measurements were made at three constant pressures (34.47, 48.26, and 68.95 kPa). All actual pressures were measured and recorded from a pressure gauge. After applying the gas to the cell, permeate was collected in a beaker. The calculated flux and permeability were determined using recorded permeate mass and filtration time. At each pressure, three measurements were made in the order of increasing pressure and reported as average values.

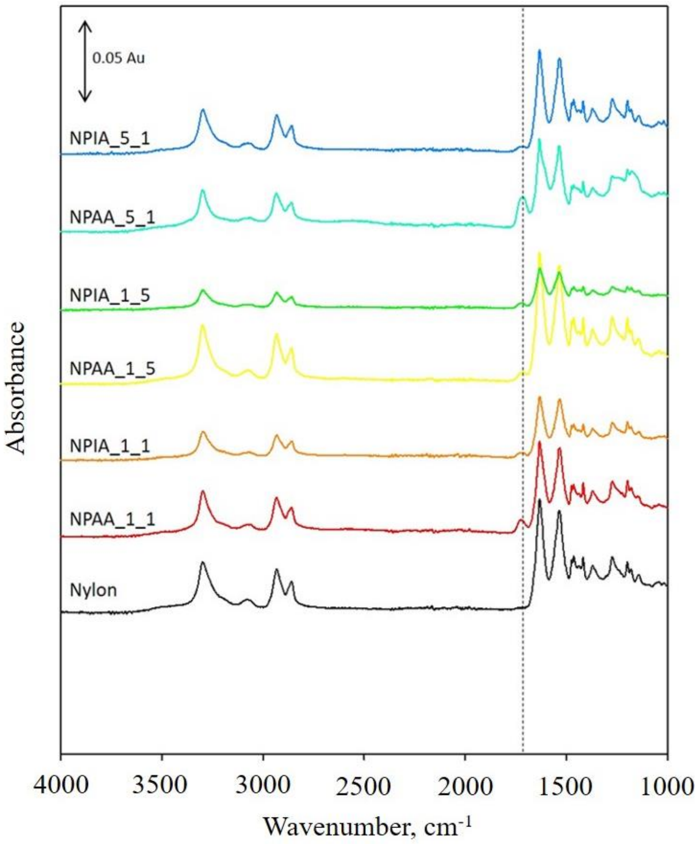

Figure 3 ATR-FTIR spectra of nonwoven Nylon, PAA and PIA modified nonwoven Nylon at various irradiation and heating times

2.4.2 Cadmium static ion exchange capacity

The preparation of a cadmium solution at 1000 mg/L in DI water was made using $Cd(NO_3)_2 \cdot 4H_2O$ as a solute. The 1000 mg/L cadmium solution was diluted to concentrations ranging from 10 mg/L to 100 mg/L. A sodium hydroxide solution (0.01 M) was prepared to neutralize PAA and PIA-functionalized nonwoven samples for 1 h before cutting them into small pieces. The weight of each sample was measured before and after exposure to 3 mL of prepared cadmium for at least 24 h to reach equilibrium [5]. The actual concentrations of cadmium solutions before and after the ion exchange process were measured using inductively coupled plasma optical emission spectroscopy or ICP-OES (Perkin Elmer, 2000DV model, Waltham, MA, USA). Standard solutions were used to create a linear calibration curve before experiments examining ion exchange. A standard deviation of reported cadmium static ion exchange capacity values was calculated using two modified fabric samples.

3. Results and discussion

3.1 Characterizations

3.1.1 ATR-FTIR

Nylon 6,6 nonwoven fabrics were grafted using two types of polymers (PAA and PIA). The functional group characterizations on the surfaces of nonwoven Nylon samples before and after modification with polymers were evaluated using ATR-FTIR. According to Figure 3, all samples exhibited absorbance due to N-H stretching at ~3315 cm^{-1}, C=O stretching of –CONH- at ~1645 cm^{-1} and absorbance by C-N stretching and CO-N-H bending at ~1555 cm^{-1}, as reported for Nylon fabrics in the literature [24]. Absorbance for C=O stretching of COOH of PAA and PIA after functionalization obviously appeared at 1740 cm^{-1} as reported in the literature for PAA- and PIA-functionalized membranes, but was not observed from fabrics before grafting polymers [2]. This evidence shows the success of surface modification for both polymers by Gamma radiation induced polymerization with various conditions as shown in Table 1.

3.1.2 OM images

Figure 4 provides representative OM images of Nylon fibers before and after PAA and PIA modifications. Nylon fibers before modification are uniform and straight, while individual fibers after PAA and PIA modification for all samples are shrunken, curl and non-uniform. The shrinkage and curl possibly occurred due H-bonding between polymers themselves, arising from O-H bonds between polymers and Nylon fabrics N-H bonds, as previously reported [25]. Additionally, the average Nylon fiber diameters slightly increased from less than 20 µm to 20–40 µm after grafting polymers, as seen in Table 2. It was shown in the literature that the thin film polymer coatings on fiber surfaces were found after polymer grafting [5]. However, from the OM images in Figure 4, it is still unclear that the sizes of fibers increased due to fiber shrinkage or polymer films on their surfaces. The distributions of fiber diameters of Nylon samples after polymers modification clearly increased, especially for NPAA_1_5 and NPAA_5_1 samples.

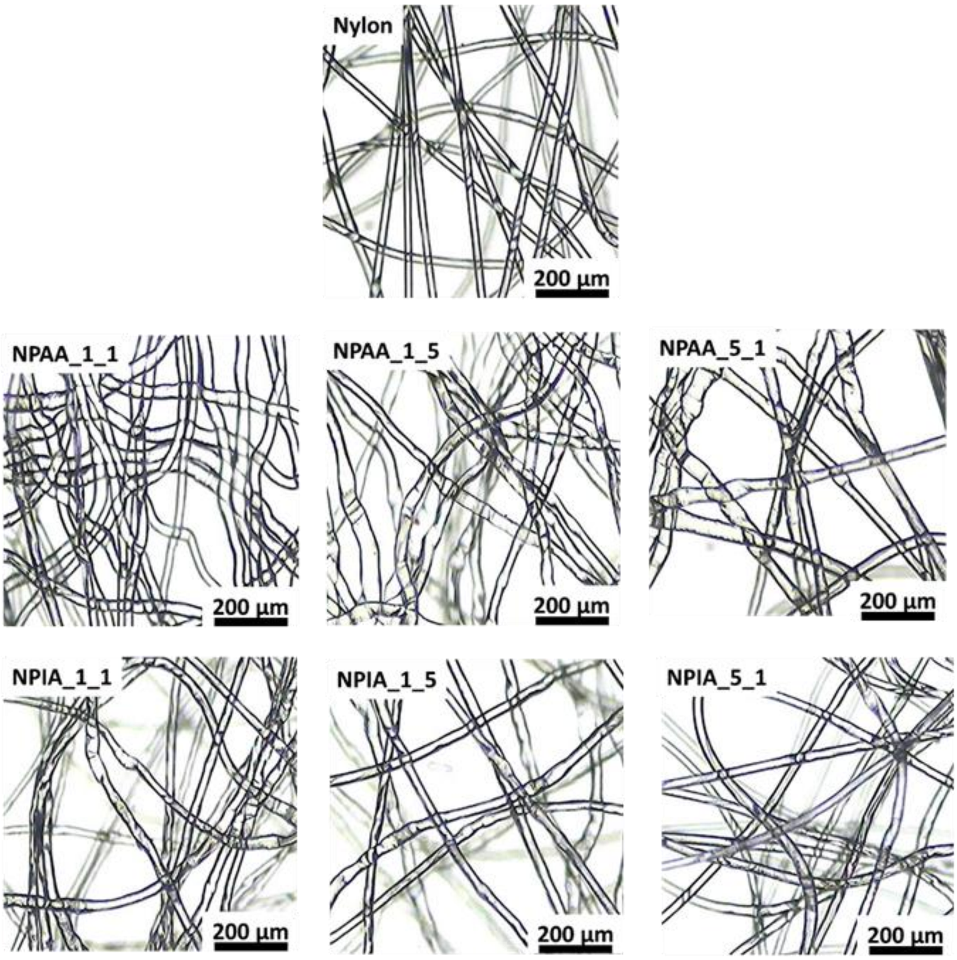

Figure 4 OM images of nonwoven Nylon, PAA and PIA modified nonwoven Nylon at various irradiation and heating times

Table 2 Average fiber diameter

Sample	Diameter (μm)
Nylon	19.74 ± 2.87
NPAA_1_1	30.00 ± 5.59
NPIA_1_1	25.71 ± 3.56
NPAA_1_5	30.67 ± 6.69
NPIA_1_5	26.97 ± 5.67
NPAA_5_1	32.78 ± 8.34
NPIA_5_1	24.36 ± 3.94

samples, as shown in Figure 5. This was mainly due to the non-uniformity of fibers.

3.1.3 SEM images

Since optical microscopy might not be able to check the polymer coatings on the fiber surfaces, SEM was performed at high-resolution to show images of the surface morphology of fiber samples. In Figure 6, smooth surfaces are seen in Figure 6A for unmodified nylon sample, while curl and non-uniformity of fibers after polymer grafting were also observed as reported by OM. Moreover, there are polymer agglomerates on fiber surfaces that might be resulted by polymer grafting. Small agglomerates are seen in NPAA_1_1 and NPIA_1_1 samples. NPAA_5_1 samples displayed larger sized agglomerates, possibly caused by higher Gamma radiation dosage, resulting in more polymer grafting. Barsbay and Güven reported that polymer grafting possibly produces the gelation of PAA [9]. Similarly, polymer films of PAA and PIA were coated on regenerated cellulose nanofiber surfaces after grafting [2].

3.1.4 Tensile strength

The strength of fabrics is important in direct-flow membrane processes. Tensile strengths and extension at breakage values of Nylon 6,6 nonwoven samples before and after PAA and PIA modification were measured. From Figure 7, the average maximum loads of Nylon samples slightly increased after polymer grafting under some conditions, especially for NPAA_5_1 and NPIA_5_1 samples, while their average extension at breakage decreased insignificantly. The increased strengths were possibly caused by shrinkage of fibers and polymer agglomerates on fiber surfaces after polymer grafting. This is supported by OM and SEM images.

3.2 Performance tests

3.2.1 Permeability

The water flux and permeabilities of unmodified, PAA, and PIA modified Nylon fabrics were compared to study membrane performance properties. Pressures, filtrate mass, fabric areas and filtration times were measured to determine

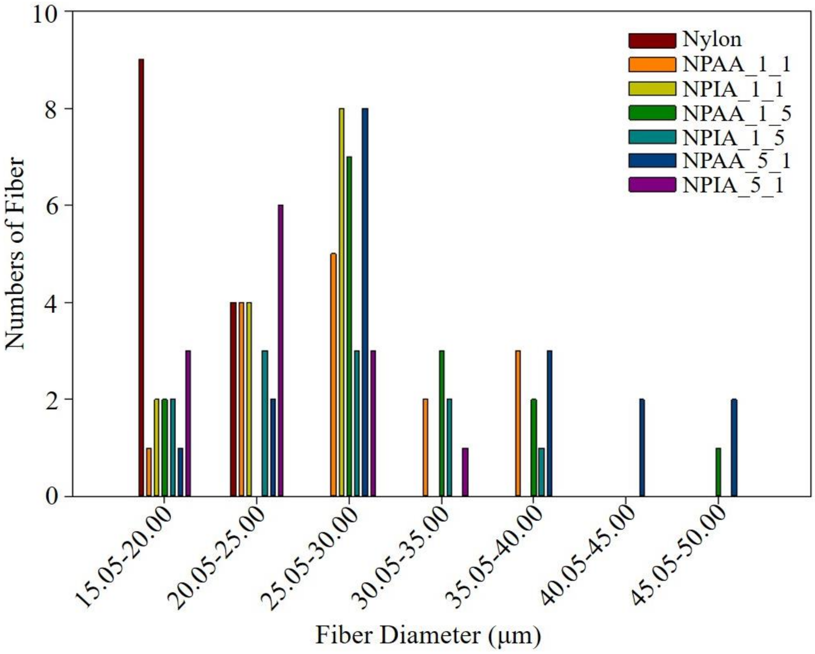

Figure 5 Fiber diameter distribution of nonwoven Nylon, PAA and PIA modified nonwoven Nylon at various irradiation and heating times

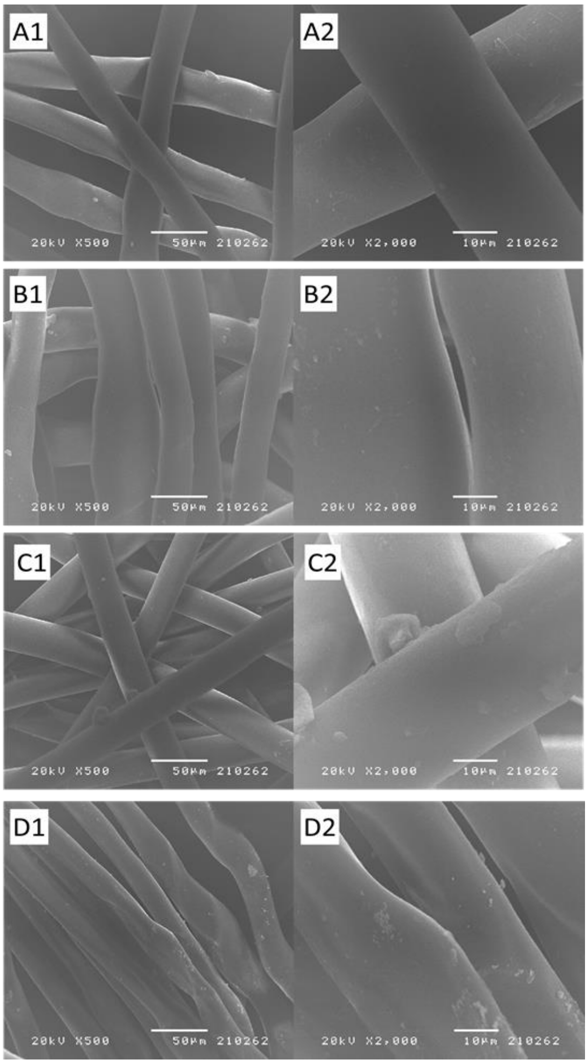

Figure 6 SEM images of Nylon (A), NPAA_1_1 (B), NPAA_5_1 (C), and NPIA_1_1 (D)

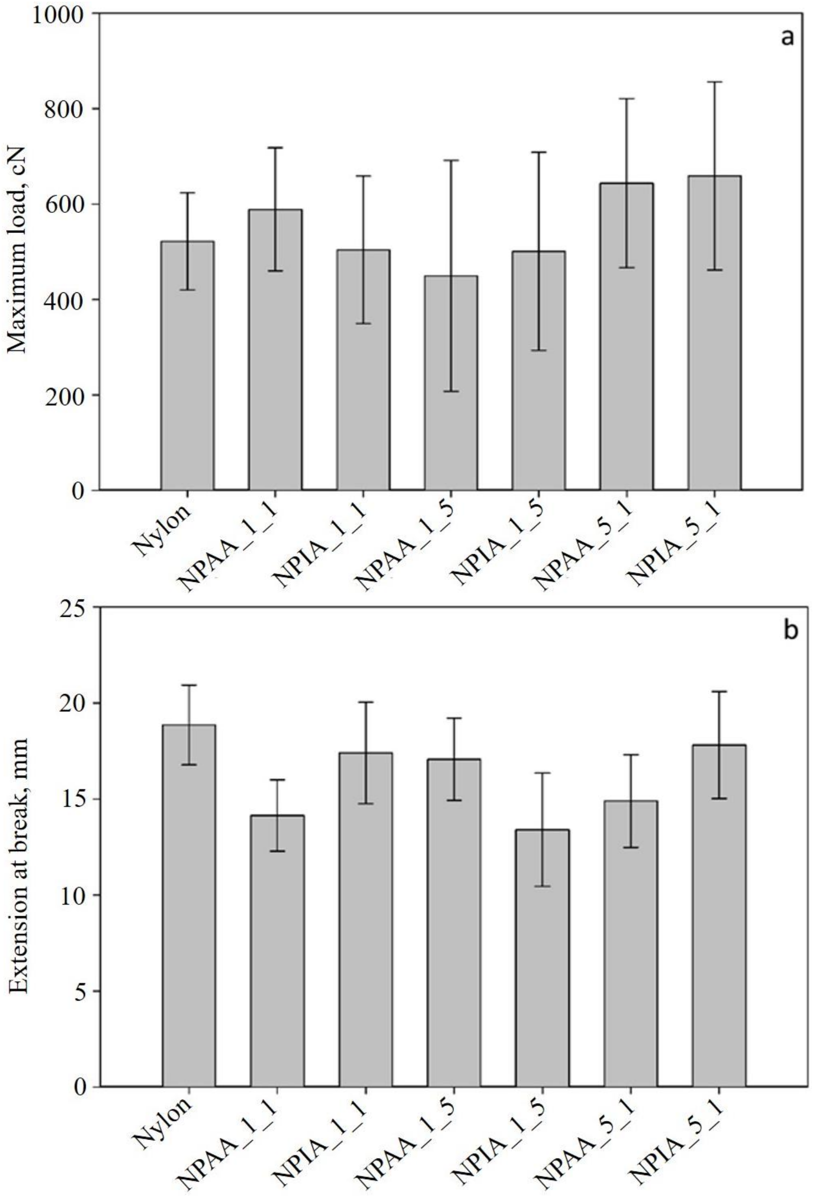

Figure 7 Tensile test of nonwoven Nylon, PAA and PIA modified nonwoven Nylon at various irradiation and heating times, (a) maximum load and (b) extension at breakage

the water permeability following Eq. 1. Figure 8 demonstrates that there are no significant changes in permeability values after modification. Insignificant changes in permeability possibly occurred due to the impact of non-uniform shrinkage of fibers and polymer agglomeration on fiber surfaces after polymer grafting. Obtaining high permeability is an important factor indicating good performance of membrane materials. However, it was shown that the permeability values of all modified Nylon fabric samples decreased with increasing applied pressure. This phenomenon was also reported in the literature. The permeability values of regenerated cellulose nanofiber membranes decreased at higher applied pressures because of material compaction [3]. Despite the decreases due to compaction, the permeabilities of the modified Nylon fabrics remain much higher than commercial membrane used in processes such as reverse osmosis and nanofiltration. (e.g., polyamide RO membranes, Model: UB70, Toray) 2.8 L/m^2/h/bar and polyamide NF membrane (Model: SB90, Trisep, 5.8 L/m^2/h/bar [5]).

$$Permeability = \frac{\text{Water permeate (L)}}{\text{area } (m^2) \times \text{pressure(bar)} \times \text{time(h)}} \tag{1}$$

3.2.2 Cadmium static ion exchange capacity

Ion exchange capacity is an important property that impacts membrane performance. The isotherms of cadmium static ion exchange properties were constructed by measuring equilibrium ion exchange capacities at various initial concentrations (10-100 mg/L) at room temperature. It was shown through application of the Langmuir model that all ion exchange sites are identical since only one type of functional group (both PAA and PIA) was grafted onto the fabric surfaces. A further assumption that monolayer adsorption occurred during ion exchange. The resulting data were fitted to the Langmuir isotherm model. The association coefficients for Cd^{2+} (K_{Cd}) and maximum ion exchange

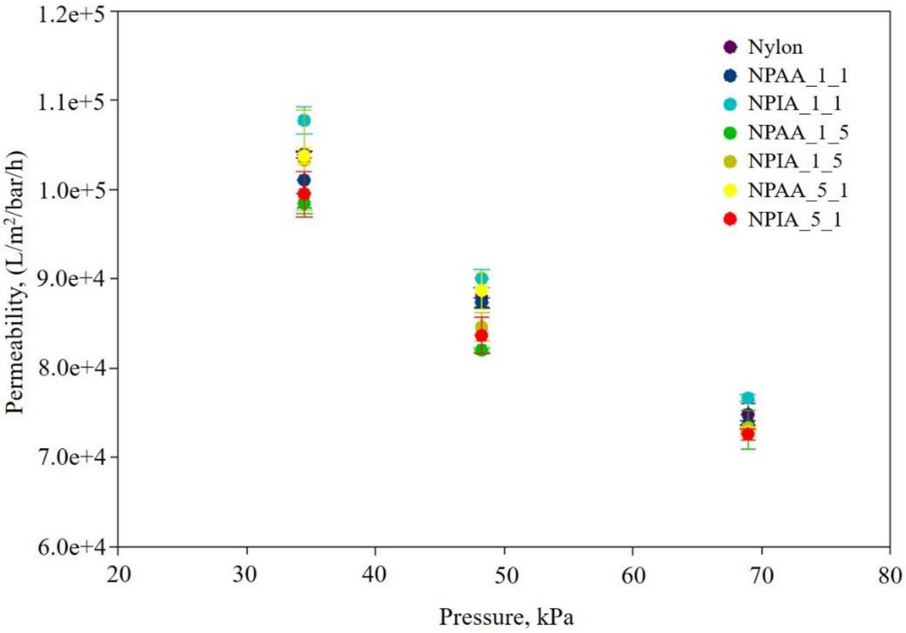

Figure 8 Permeability measurement of nonwoven Nylon, PAA and PIA modified nonwoven Nylon at various irradiation and heating times and three different pressures (34.47, 48.26 and 68.95 kPa)

Table 3 Langmuir parameters of nonwoven Nylon, PAA and PIA modified nonwoven Nylon at various irradiation and heating times

Sample	**Maximum Cd^{2+} ion exchange capacity (mg/g)**	**Association coefficient for Cd^{2+}, K (mL/mg)**	**R-square**
Nylon	19.0	9.9×10^{-1}	0.9064
NPAA_1_1	82.3	4.8×10^{-1}	0.9745
NPIA_1_1	28.1	4.6×10^{-1}	0.7291
NPAA_1_5	23.6	6.6×10^{-1}	0.2697
NPIA_1_5	77.72	5.4×10^{-1}	0.9292
NPAA_5_1	423.8	3.7×10^{-2}	0.5815
NPIA_5_1	25.0	N/A	0.0152

capacities for Cd^{2+} (Q_{max}, Cd) are evaluated from obtained isotherms following Eq. 2 [5, 26-27].

$$\frac{Q_{Cd}}{Q_{max,Cd}} = \sum \frac{K_{Cd}C_{e,Cd}}{1+K_jC_{e,j}} \tag{2}$$

where Q_{Cd} is the equilibrium uptake of Cd per unit mass of membrane, C_e is equilibrium concentration of ion j in solution, and K_{Cd} is the association constant of ion j [5]. The calculated Langmuir parameters are summarized in Table 3. However, according to R-square values in Table 3, it was found that several samples did not fit the Langmuir model with R-square values lower than 0.9. Table 3 and Figure 9 show that the maximum ion exchange capacity of PAA and PIA functionalized nonwoven Nylon fabrics significantly increased, especially for NPAA_1_1, NPIA_1_5, and NPAA_5_1. For PAA modification, the increase of ion exchange capacity might have been affected by the duration of Gamma irradiation producing longer polymer chains with more carboxyl functional groups. Alternatively, excessive heating time might have caused lower capacity values. The results show the opposite trend for PIA modification, where longer heating times led to higher maximum capacity, but not for longer irradiation times. Oddly, the NPAA_5_1 sample provides extremely high ion exchange capacity and its isotherm did not fit the Langmuir model well. Therefore, higher initial cadmium concentrations may be required in further work to obtain more information to develop better isotherms. However, the maximum capacity and association coefficient of the NPIA_5_1 sample did not fit the Langmuir model as evidenced by its extremely low R-square value.

PAA and PIA exhibit different numbers of repeating functional groups per unit. They are monocarboxylate and bicarboxylate repeating units, respectively. Therefore, the initial concentration of IA monomer used was twice the initial concentration of the AA monomer during the grafting step to produce similar carboxylate functional group numbers in monomer solutions for all grafted samples. Consequently, Cd-ion binding occurring with similar numbers of carboxylate functional groups, but with different interaction structures of monocarboxylates and bicarboxylates can be compared. However, the maximum Cd binding capacity of PIA-modified Nylon was lower than for the PAA-modified Nylon, which contradicts literature stating that bicarboxylate functional groups show higher Cd binding capacity due to higher complex stability than monocarboxylate groups [2]. The lower capacity for PIA modification might have been caused by the slower polymerization kinetics of IA, as previously discussed [12].

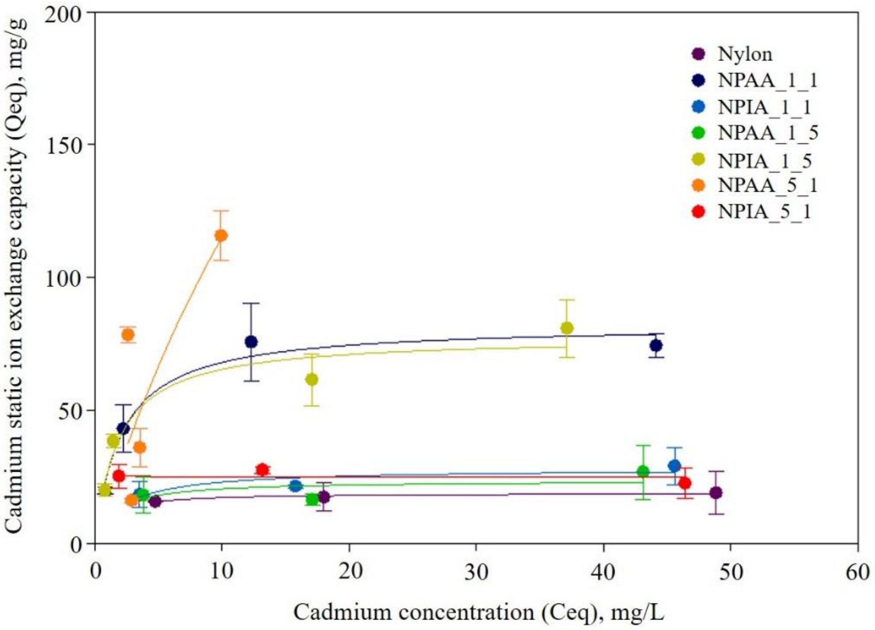

Figure 9 Ion exchange isotherms of nonwoven Nylon, PAA and PIA modified nonwoven Nylon at various irradiation and heating times

Table 4 Summary of ion exchange data for Cd on ion-exchange materials

Ion exchange materials	Maximum Cd^{2+} ion exchange capacity (mg/g)	Reference
Poly(acrylic acid) functionalized cellulose nanofiber	10 – 162.5	[5]
Poly(itaconic acid) functionalized cellulose nanofiber	222	[2]
Poly(acrylic acid) functionalized cellulose material	20.21	[18]
Oxolane-2,5-dione functionalized cellulose material	14.61-66.32	[19]
Poly(itaconic acid) cross-linking with glutaraldehyde or epichlorohydrin modified chitosan powders	331-405	[20]
Poly(acrylic acid) functionalized cellulose material	11.53	[21]
Duolite CT-73 ion exchange resin	105.7	[28]
Amberlite 200 ion exchange resin	224.8	[28]
Cellulose/alginic acid IEX membrane	44.4	[29]
Activated carbon (Sigma C-3104)	1.5	[30]
Poly(acrylic acid) functionalized nonwoven Nylon	23.6-423.8	This research
Poly(itaconic acid) functionalized nonwoven Nylon	25.0-77.72	This research

Permeability results in the range of 70,000 to 100,000 L/m^2/h/bar and maximum ion exchange capacities, possibly up to 420 mg/g of Nylon fabric with PAA and PIA functionalization, were compared to other ion exchange materials. The results are shown in Table 4. PAA and PIA functionalized cellulose or chitosan materials in previous studies gave maximum Cd-ion exchange capacities in the range of 11.53 to 405 mg/g [2, 5, 18-21]. It was reported that ion exchange resins provide maximum Cd capacity for Duolite CT-73 at 105.7 mg/g and Amberlite 200 at 224.8 mg/g [28]. For an ion-exchange membrane, a cellulose/alginic acid IEX membrane yields a maximum Cd capacity of 44.4 mg/g and a permeability of 8.0 L/m^2/h/bar [29]. Even activated carbon (Sigma C-3104) gives a much lower maximum Cd capacity of 1.5 mg/g [30]. Therefore, these functionalized membranes show very high membrane performance in terms of permeability and capacity.

4. Conclusions

A preparation of cation-exchange membranes by polymer grafting onto nonwoven Nylon fabrics and an evaluation of trace cadmium ion removal from water were studied in this research. Irradiation induced polymerization using Gamma-rays was used to graft polymers with carboxyl functional groups. PAA and PIA functionalized nonwoven Nylon fabrics show higher static cadmium ion exchange capacities than unmodified Nylon fabrics. They are competitive with commercially available ion-exchange materials. Using the functionalized nonwoven Nylon fabrics in membrane applications, the permeabilities of all samples were found much higher than commercial membrane processes such as reverse osmosis and nanofiltration. Although RO and NF systems show higher capacity to remove ions, more selective interaction between carboxylate functional group and cadmium ions was obtained from these ion exchange membranes. Polymer types and grafting conditions produced polymers with longer chains resulting higher ion exchange capacities. To improve membrane performance, polymer types are not limited to only PAA and PIA and polymer grafting conditions can be adjusted. Additionally, dynamic binding capacity evaluation should be further studied for these new membrane materials.

5. Acknowledgements

This work was supported by a RMUTT research foundation scholarship in 2018 (Grant Number: NRF04076103), Rajamangala University of Technology Thanyaburi, Thailand. We thank the Office of Atoms for Peace (OAP) for providing access to and assistance with their Gamma cell. We appreciate help from the Department of Materials and Metallurgical Engineering, Rajamangala University of Technology Thanyaburi, Thailand for providing access to and assistance with ATR-FTIR. We thank the Department of Chemical Engineering, Chulalongkorn University, Thailand for providing access to and assistance with ICP-OES.

6. References

[1] Odian G. Principles of polymerization. New Jersey: John Wiley & Sons; 2004.

[2] Chitpong N, Husson SM. High-capacity, nanofiber-based ion-exchange membranes for the selective recovery of heavy metals from impaired waters. Separ Purif Tech. 2017;179:94-103.

[3] Wang J, Sproul RT, Anderson LS, Husson SM. Development of multimodal membrane adsorbers for antibody purification using atom transfer radical polymerization. Polymer. 2014;55(6):1404-11.

[4] Chenette HC, Husson SM. Membrane adsorbers comprising grafted glycopolymers for targeted lectin binding. J Appl Polymer Sci. 2015;132(21):1-7.

[5] Chitpong N, Husson SM. Polyacid functionalized cellulose nanofiber membranes for removal of heavy metals from impaired waters. J Membr Sci. 2017;523:418-29.

[6] Bhattacharya S, Inamdar M. Polyacrylic acid grafting onto isotactic polypropylene fiber: methods, characterization, and properties. J Appl Polymer Sci. 2007;103(2):1152-65.

[7] Zheng Y, Liu H, Gurgel PV, Carbonell RG. Polypropylene nonwoven fabrics with conformal grafting of poly (glycidyl methacrylate) for bioseparations. J Membr Sci. 2010;364(1-2):362-71.

[8] Shim JK, Na HS, Lee YM, Huh H, Nho YC. Surface modification of polypropylene membranes by γ-ray induced graft copolymerization and their solute permeation characteristics. J Membr Sci. 2001;190(2):215-26.

[9] Barsbay M, Güven O. RAFT mediated grafting of poly (acrylic acid)(PAA) from polyethylene/polypropylene (PE/PP) nonwoven fabric via preirradiation. Polymer. 2013;54(18):4838-48.

[10] Kováčik D, Zahoranová A, Černák M, Mazúr M. Surface modification of polypropylene non-woven fabrics by atmospheric-pressure plasma activation followed by acrylic acid grafting. Plasma Chem Plasma Process. 2005;25(4):427-37.

[11] Abdel-Hamid H. Effect of electron beam irradiation on polypropylene films—dielectric and FT-IR studies. Solid State Electron. 2005;49(7):1163-7.

[12] Sankhe AY, Husson SM, Kilbey SM. Effect of catalyst deactivation on polymerization of electrolytes by surface-confined atom transfer radical polymerization in aqueous solutions. Macromolecules. 2006;39(4): 1376-83.

[13] Vural S, Seckin T. Brush-type surface modification of kapton with a new approach. Adv Polymer Tech. 2018;37(6):1703-11.

[14] World Health Organization. Exposure to cadmium: a major public health concern. Preventing Disease through Healthy Environments. Geneva: WHO; 2010.

[15] Arthur DE, Jonathan A, Ameh PO, Anya C. A review on the assessment of polymeric materials used as corrosion inhibitor of metals and alloys. Int J Ind Chem. 2013;4:1-9.

[16] Ma H, Burger C, Hsiao BS, Chu B. Ultra-fine cellulose nanofibers: new nano-scale materials for water purification. J Mater Chem. 2011;21(21):7507-10.

[17] He J, Chen JP. A comprehensive review on biosorption of heavy metals by algal biomass: materials, performances, chemistry, and modeling simulation tools. Bioresour Technol. 2014;160:67-78.

[18] Okieimen F, Sogbaike C, Ebhoaye J. Removal of cadmium and copper ions from aqueous solution with cellulose graft copolymers. Separ Purif Tech. 2005;44(1):85-9.

[19] Stephen M, Catherine N, Brenda M, Andrew K, Leslie P, Corrine G. Oxolane-2, 5-dione modified electrospun cellulose nanofibers for heavy metals adsorption. J Hazard Mater. 2011;192(2):922-7.

[20] Kyzas GZ, Siafaka PI, Lambropoulou DA, Lazaridis NK, Bikiaris DN. Poly (itaconic acid)-grafted chitosan adsorbents with different cross-linking for Pb (II) and Cd (II) uptake. Langmuir. 2014;30(1):120-31.

[21] Güçlü G, Gürdağ G, Özgümüş S. Competitive removal of heavy metal ions by cellulose graft copolymers. J Appl Polymer Sci. 2003;90(8):2034-9.

[22] Chitpong N, Husson S. Nanofiber ion-exchange membranes for the rapid uptake and recovery of heavy metals from water. Membranes. 2016;6(4):1-16.

[23] Ramakrishna S, Ma Z, Matsuura T. Polymer membranes in biotechnology: preparation, functionalization and application. London: Imperial College Press; 2011.

[24] Du Y, George S. Molecular layer deposition of nylon 66 films examined using in situ FTIR spectroscopy. J Phys Chem C. 2007;111(24):8509-17.

[25] Wang L, Fu Y, Wang Z, Fan Y, Zhang X. Investigation into an alternating multilayer film of poly (4-vinylpyridine) and poly (acrylic acid) based on hydrogen bonding. Langmuir. 1999;15(4):1360-3.

[26] Limousin G, Gaudet JP, Charlet L, Szenknect S, Barthes V, Krimissa M. Sorption isotherms: a review on physical bases, modeling and measurement. Appl Geochem. 2007;22(2):249-75.

[27] Tofighy MA, Mohammadi T. Adsorption of divalent heavy metal ions from water using carbon nanotube sheets. J Hazard Mater. 2011;185(1):140-7.

[28] Kumar U. Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: a review. Sci Res Essays. 2006;1(2):033-7.

[29] Zhang L, Zhou J, Zhou D, Tang Y. Adsorption of cadmium and strontium on cellulose/alginic acid ion-exchange membrane. J Membr Sci. 1999;162 (1-2):103-9.

[30] Üçer A, Uyanik A, Aygün Ş. Adsorption of Cu (II), Cd (II), Zn (II), Mn (II) and Fe (III) ions by tannic acid immobilised activated carbon. Separ Purif Tech. 2006;47(3):113-8.