



Fabrication of Acrylic Modified Surface of Polyamide 6/CaO Electrosynthesized Nanofibrous Membrane for Effective Dye Removal

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POLYAMIDE 6 nanofibrous membrane of low molecular weight were obtained with various concentration between 25 and 45% (wt/v) by electrospinning of the polymer solution. Polyamide 6 nanofibers containing calcium oxide nanoparticles (PA6/CaO) were successfully obtained with various CaO concentration (0.2-1.0 % wt/wt). The structure of the electrospun nanofiber was studied with the aid of scanning electron microscopy that indicated that smooth and continuous electrospun nanofibers were obtained at optimum conditions with nanofibrous diameter about 60-70 nm and CaO nanoparticles were distributed through the nanofibers with a slightly increase in the nanofibrous diameter. The surfaces of the obtained PA6 and PA6/CaO nanofibers were modified by grafting polymerization with methacrylic acid MAA. The grafting polymerization was investigated through SEM and ATR-FTIR. The grafting polymerization was investigated also by examination of the sorption capacity of the produced modified PA6-g-MAA and PA6/CaO-g-MAA nanofibrous membranes in removal of basic dye by studying removal of Basic Red BR18 dyestuff. The data showed that the percentage of dye removal using polyamide6 / CaO nanofibrous membrane grafted with MAA is more than that of grafted pure polyamide 6 nanofibrous membrane. The optimum conditions for removal of BR18 dye was observed at pH 10 under 60 °C.

Keywords: Electrospinning, Polyamide 6, Nanofibrous membrane, Basic dye removal.

Introduction

Electrospun membranes have been prepared from a broad range of materials and they have various applications in various fields as biomedical and environmental [1]. Membranes from nanofibrous materials can act as an extracellular matrix with special characterized advantages as they have multiporous structure with a high surface area to volume ratio [2]. Electrospinning has attracted a great attention because it provides a simple and vital method for nanofibers formation from a variety of polymers or polymers loaded with non-spinnable materials, producing a wide variety of functional membranes [3, 4]. An electrospinning setup composed of a high voltage DC (or AC) supply (in the range of 10–50kV), a spinneret with a metallic needle and a collector [5]. Nanofibers have high surface area, high porosity, a strong penetrability and interaction with other compounds that make sorption method

more preferable and more suitable for the dye removal in water treatment and the high porosity results in smaller driving forces to facilitate pushing the water through the membrane which make the process less required energy and offer a high permeability to water filtration [6,7]. Polyamide 6 is an engineering resin, consists of amide groups separated by methylene sequences, can make very good fibers with good mechanical, thermal and chemical properties through electrospinning [8]. The surface of polyamide 6 can be modified by grafting with various vinyl monomers as acrylate, acrylic and methacrylic acid (MAA) to allow the introduction of active functional groups onto a hydrophobic polymer backbone to have a better affinity with water [9-14]. In addition, nanosized inorganic and organic materials can be embedded through the electrospinning of polymer solution or matrix, similarly, nanometal oxides, can be incorporated as an additive to polymer matrix and used for multifunctional textile applications such

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as flammability, UV protection, and antibacterial activities [15-18].

Dyes are considered a troublesome problem in water pollution because of their huge usage in many industries as textile, leather, paper, plastics, rubber, cosmetics, pharmaceutical and food industries, besides their adverse ecological and human health effects [19, 20]. Among these dyes are the bright colored cationic dyes, examples of them, methylene blue(MB), Basic Red (BR18),.. etc. Basic Red BR18 is bright red dye soluble in water but it is a corrosive and irritant material. Its chemical structure is shown in Figure (1). Its chemical formula and IUPAC name as $C_{19}H_{25}ClN_5O_2^+$ and 2-[4-[(2-chloro-4-nitrophenyl) diazenyl]-N-ethylanilino]ethyl-trimethylazanium, respectively.

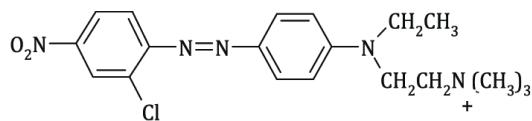


Fig.1. Chemical structure of Basic Red BR18 dye

Numerous techniques have been used to remove dyes from aqueous solutions, like precipitation, ion exchange, solvent extraction, adsorption and membrane filtration [21-23].

The aim of this work is to prepare nanofibrous membrane of PA6 and PA6/CaO with several PA6 concentrations and modify the surface of the produced nanofibrous membranes by grafting polymerization with methacrylic acid MAA. The grafting polymerization was confirmed by testing the sorption capacity of the produced surface grafted PA6-gMAA and PA6/CaO-g-MAA nanofibrous membranes for the removal of Basic Red BR 18 dyestuff from water solution.

Experimental

Materials

Polyamide 6 with low molecular weight was purchased from Sigma-Aldrich, Germany and Methacrylic acid (MAA) was from Across , USA. Calcium oxide CaO nanoparticle was gift from ITCF-Denkenorf- Stuttgart, German. Potassium persulfate PPS was from Modern Lab of purity > 98%. Formic acid (85%) was supplied from ADWIC, El-Nasr pharmaceutical chemicals co., Egypt. Basic dyestuff, namely, Basic Red BR18 was supplied by Bayer AG (Leverkusen, Germany).

Preparation of Polymer PA6 solution

Polyamide 6 was dissolved in formic acid (85%) with various concentration (25, 30, 35, 40 and 45% w/v) by magnetic stirring at ambient temperature for few hours. The viscosity of the polymeric solutions was measured by Brookfield Viscometer (Model DV-III Ultra, UK) at ambient temperature prior electrospinning. The polymeric solution was put in the stainless steel container connected with a temperature controller. Measurements of viscosity were done using S21 spindle at 50 RPM under uniform temperature.

Preparation of PA6/CaO nanocomposite:

Certain amounts of calcium oxide CaO nanoparticle (0.2, 0.4 and 1%) were weight and suspended in the polyamide 6 solution with concentration as 35% by the aid of sonicator water bath for 60-90 min for complete suspension (Ultrasonic Cleaner, Model UD 50 SH-2LQ, China) with ultrasonic power 50W and power supply: 220 VAC, 50 Hz.

Electrospinning

The electrospinning experiments were performed at room temperature. The polymer solution was injected into a 1-mL syringe fitted with a metallic needle (20 G). A piece of aluminum foil was used as a collector at a distance of 10 cm from the needle tip. A high voltage power supply was adjusted using a Glassman High Voltage Series (voltage range 0-20 kV) to charge the spinning PA6 solutions by connecting the emitting electrode of positive polarity to the nozzle (the needle) and the grounding electrode to the collective screen. The polymer jets generated from the needle by high voltage flew to the collector and formed the nanofiber mesh. Finally, the electrospun samples were dried overnight at 40°C. The voltage Syringe Pump Series 100 regulated the flow rate of the solution at 0.2 ml/h. Electrospinning was done at ambient temperature and at a relative humidity (RH) of $40 \pm 2\%$ [7]. The morphologies of the obtained dried nanofibrous membrane were checked via Scanning Electronic Microscope (SEM).

Grafting polymerization procedure

1g in weight of PA6 and PA6/CaO electrospun nanofibrous were independently placed in a stoppered glass vessel containing 50-mL distilled water, PPS as initiator (4 mmol/l) and traces from ammonium ferrous sulfate, then the vessel was vigorously shaken for 10 min with thermostatic shaker water bath (HWT-10C with temperature range up to 100 °C and speed up 200 rpm, China).

0.2 mol of methacrylic acid MAA monomer was added to the mixture. Then the temperature was adjusted to 60°C and the graft polymerization was held under shaking for the desired time (2h). After that, the modified electrospun fiber was separated and washed with distilled water to remove the homopolymer and the unreacted materials [24]. The obtained grafted copolymer PA6-g-MAA and PA6/CaO-g-MAA nanofibrous membrane were then dried at 40°C for 12h and weighed to determine the grafting percentage according to Eqn(1).

$$\text{Grafting percentage(GP)} = \frac{(A-B)}{B} \times 100$$

where A and B are the weights of the electrospun nanofibrous membrane after and before grafting respectively [24].

The dried grafted electrospun fiber was characterized by Scanning Electronic Microscope (SEM) and Attenuated Total Reflectance-FTIR (ATR-FTIR).

Scanning Electronic Microscope (SEM)

The morphologies of the dried electrospun nanofibers samples before and after grafting were checked via scanning electronic microscope SEM (a QUANTA FEG250 model- Japan). By fixing a small piece of the fiber on a small copper plate and taking a light gold layer for 1 min on the surface of the fiber. The images were taken at HV as 20.00KV with various magnifications and an appropriate one was chosen. The diameter of the obtained nanofiber were measured.

Fourier Transform Infrared ATR-FTIR Spectroscopy

The graft copolymers PA6-g-MAA and PA6/CaO-g-MAA after washing and drying was further characterized by FTIR (VERTEX 70 Optics Layout, BURKER, German) via

Attenuated Total Reflectance technique ATR. Where, an ATR is a sampling technique used in conjunction with infrared spectroscopy which enables samples to be examined directly in the solid or liquid state without further preparation and operates by measuring the changes that occur in an internally reflected IR beam when the beam comes into contact with the surface of the sample [25].

Removal of basic dye from water solution by sorption-filtration process:

The PA6 and PA6/CaO electrospun nanofibrous membrane was used as a sorbent during sorption nanofiltration. The sorption – filtration process (Figure 2) was performed under vacuum pressure created by suction pump where the vacuum flask was used to collect the filtered sample. Pieces with diameter of 2cm were used for the experiments. Aqueous solution of the basic dye with concentration 0.5gm /L. The sorption capacity of the MAA grafted nanofibrous membrane was determined through measuring the dye concentration in the unfiltered and filtrate solution using the UV-Vis spectrophotometer. The dye concentrations in the supernatant were determined by measuring the absorbance at maximum wavelength (λ_{\max}) of BR18 dye (489 nm) on a Shimadzu ultraviolet-visible spectrophotometer with double beam using a standard calibration curve experimentally obtained with aqueous solution of dye [26].

The dye removal % was determined by the following equation Eq.(2):

$$\text{Dye Removal \%} = \frac{C_o - C_e}{C_o} \times 100$$

Where: C_o is the initial dye concentration, C_e is the final dye concentration

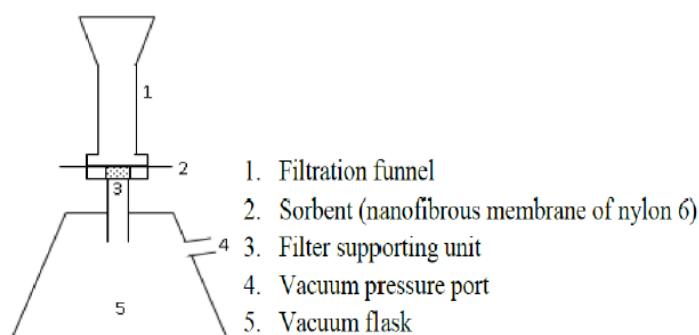


Fig. 2. Filtration unit used in dye removal by sorption process.

Results and Discussion

Electrospinning of PA6 with different polymer concentration

The effect of PA6 concentration on the resulting electrospun fibers was studied. Where, solutions of PA6 dissolved in formic acid 85% v/v were prepared with various concentrations, ranging from 25, 30, 35, 40 and 45% w/v. The viscosity values of PA6 solutions were measured as a function of concentration. It was found that the viscosity values increase with increasing PA6 concentration. Specifically, the viscosity increased from 767 cp at PA6 conc. 25% w/v to 2845 cp at 45% w/v. Table (1) represents the relationship between the PA6 concentration in formic acid by weight percentage (from 25 to 45 wt %) and the solution viscosities in centipoises and the viscosities of polyamide 6 exponentially increased with the concentration.

It was noted that the solution viscosity rapidly increased from 25 wt % PA6 as a result of onset of the chain entanglement [21, 27].

PA6 solution was injected into a 1-mL syringe with a metallic needle. The high voltage source was connected between the needle and the flow rate was adjusted to 0.2ml/h. As a result, a drop of the polymer solution from the spinneret will be electrified forming a Taylor cone that can overcome the surface tension by increasing the electric force and undergo a continuous elongation to form the electrospun fibers on the collector [8]. At higher concentrations and higher viscosities, the chain entanglements increased and hence the viscoelastic force increased to become sufficient to prevent the break-up of the charged jet into small droplets and to allow the further elongate the charged jet during its travelling to the collector, resulting in ultimately thinned down the charged jet diameter [8, 28].

Electrospinning of PA6 solution of concentration below 25 wt% provided a sum of smooth fibers and minute, discrete droplets that were observed at many parts. At slightly higher concentration 25% to 30% (with viscosity 767 to 1005 cp) only a sum of smooth and beaded fibers was formed and with increasing the concentration (or viscosity) the number of beads was noted to decrease along the fibers but braked and uncontinuous nanofibers were obtained. However, at increased concentration of the solution at 35% w/v (with viscosity as 1313 cp), all beads disappeared and only smooth ultrafine fibers were left on the collector. Hence, uniform and continuous nanofibers were formed at concentrations between 35 % to 40%, as shown in Figure 3(b,c). At higher concentrations the chain entanglements and the viscoelastic force were excessively increased to become sufficient to prevent the breakup of the charged jet into small droplets, and become too viscous to electrospinning. But PA6 solution of concentration of 45% produced few fibers with diameter of about 400 nm. Attempts were made to measure the average diameter values of the PA6 electrospun nanofibers with various concentration from SEM images. It was found that the average diameter of the electrospun nanofibers increased slightly from 52 ± 7 nm to 56 ± 9 nm with PA6 conc. 30% and 35%, respectively. But the average diameter of nanofiber suddenly increased to 141 ± 20 nm with PA6 40% and greatly increased to 400 ± 80 nm with PA6 45%. Therefore, the properties of the produced electrospun PA6 nanofibers are greatly influenced by the conc. of the polymer solution and appropriate chain entanglements were necessary to provide continuous fibers by electrospinning, so, the concentration of PA6 as 35 wt % was chosen to produce nonwoven PA6 nanofibrous membrane with nanoscale diameters [8, 19, 29-31].

TABLE 1.The viscosity values for polyamide 6 solution in formic acid (85%) with various concentration .

PA6 %	25%	30%	35%	40%	45%
Viscosity cp	767	1005	1313	1830	2845

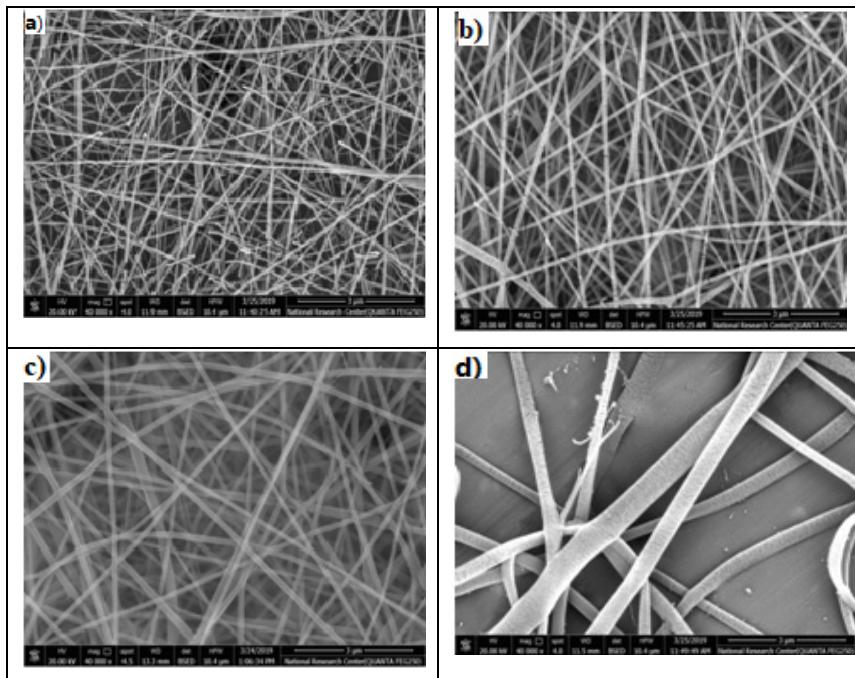


Fig3. SEM images of electrospun PA6 nanofibrous with Mag. 40,000 and 20,00 KV at concentrations of a) 30, b) 35, c) 40 and d) 45% w/v.

Electrospinning of PA6 / CaO

PA 6 solution with concentration of 35% was prepared by dissolving in 85% v/v formic acid. Then, CaO was suspended in PA6 solution with various concentration as 0.2, 0.4, 0.6 and 1% (wt/wt) using sonicator water bath for 60-90 min for complete suspension. The solution samples were undergone the electrospinning for 2 min to obtain an appropriate film for SEM for morphological studies of the nanofibrous membrane. The obtained PA6/CaO electrospun fibers were collected on aluminum foil and characterized by SEM-Edax analysis.

Figure 4 illustrates SEM micrograph of PA6/CaO electrospun nanofibers and it was noted that the existence of CaO with PA6 improved the resulting nanofibers properties, where, the SEM images showed uniformly smooth and continuous nanofibers. When the average values of the PA6/CaO electrospun nanofibers were measured and compared with that of 35%PA6 electrospun nanofibers, it was found that the diameter increased from 56 ± 9 nm to approximately $9020 \pm$ nm in case of PA6/CaO with 0.2%CaO nanofibers [32]. However, there was no a significant difference detected in the diameter of the nanofiber with exceeding CaO

percentage to 1% in the nanofibers. Where, the obtained PA6/CaO with 1%CaO electrospun fiberous was with diameter range between 81 to 113nm which confirm the successful preparation of PA6 in presence of CaO nanoparticle. But formation of a few agglomeration of CaO was noted in case of 1%CaO, so, no further excess of CaO was permitted. The incorporation of 1% CaO nanoparticles in the 35% PA6 electrospun nanofibrous membrane was confirmed also by Edax analysis on a selected region [33].

Grafting of Methacrylic acid (MAA) onto the PA6 and PA6/CaO electrospun nanofibrous membrane

1 ml of the prepared solution of 35% PA6 and PA6/CaO with 1%CaO were undergone the electrospinning to obtain an appropriate film of the electrospun nanofibrous membrane. It was well known that the polyamide 6 has high affinity to acid dyes [26]. So, the main target of grafting the polyamide 6 with methacrylic acid MAA is to introduce carboxylic functional groups on the surface of the produced electrospun fibers to accept it the affinity to basic dyes too. The mechanism of the graft copolymerization of PA6 with methacrylic acid was shown in Scheme-1 [34].

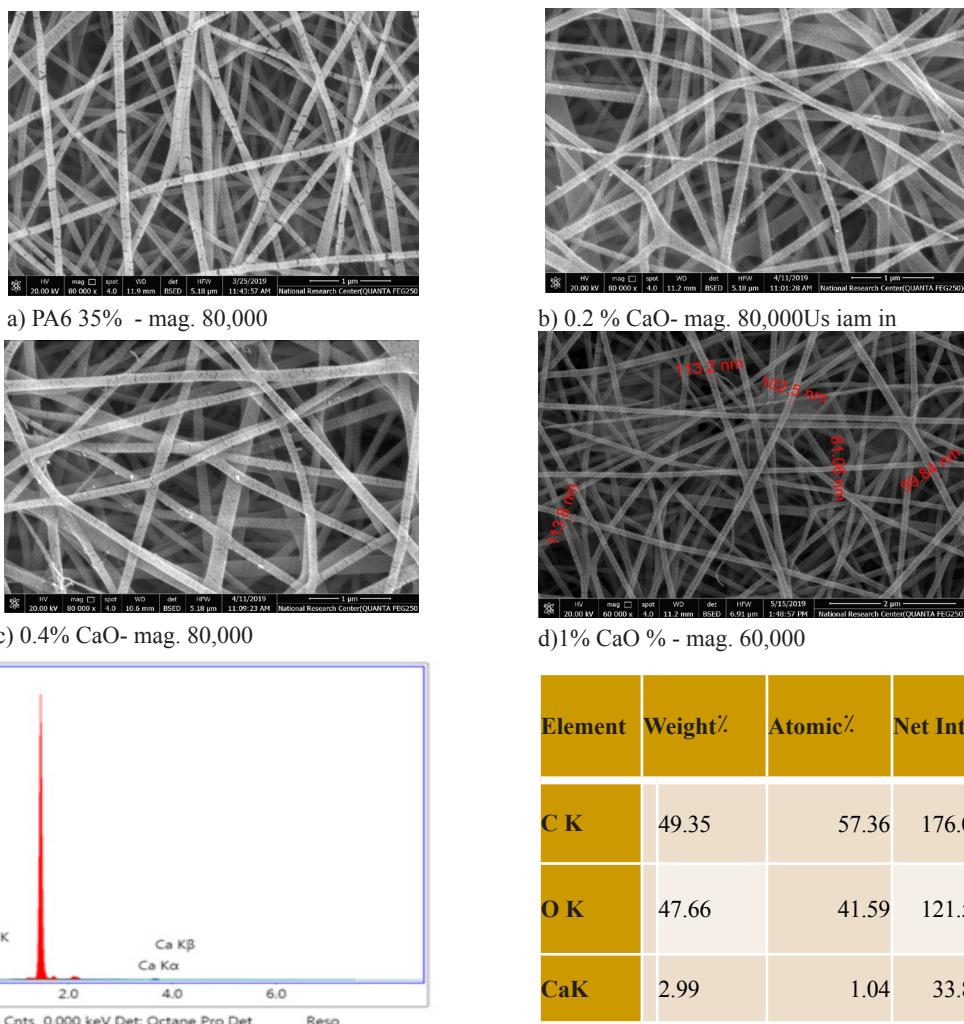
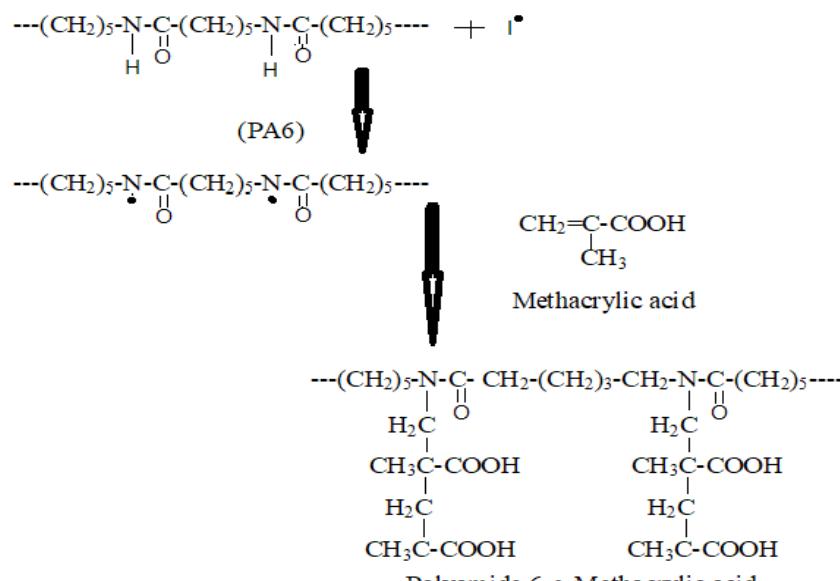


Fig.4. Scanning electron micrographs of electrospun PA-6 nanofiber of 35% w/v (a) and with CaO of conc. As 0.2% (b) 0.4% (c) and 1% (d) and its edax result.(20,00KV).



Scheme 1. Grafting of copolymerization of PA6 with methacrylic acid MAA.

Grafting of MAA onto the electrospun nanofibrous membrane was achieved using potassium persulphate (PPS) as initiator for 2hr at 60 °C. The obtained grafted nanofibrous was washed with distilled water to extract any further homopolymer or unreacted agent then dried for 12hr at 40 °C. The grafted nanofibrous membrane samples were weighed to determine the grafting percentage according to Eqn(1).

$$\text{Grafting percentage(GP)} = \frac{(A-B)}{B} \times 100$$

where A and B are the weights of the electrospun fiber after grafting and the electrospun fiber before grafting respectively [24]. It was detected that the grafting percentage in the case of PA6 and PA6/CaO were 27% and 43%, respectively. So, the existence of 1% CaO with PA6 nanofibrous raised the grafting percentage.

The produced surface modified PA6 and PA6/CaO electrospun nanofibrous membrane were investigated by SEM and ATR-FTIR analysis .

Scanning Electron Microscope (SEM)

Figure 5 represents the micrographs of PA6 electrospun nanofibrous membrane and

its MAA grafted surface as well as PA6/CaO electrospun nanofibrous membrane and its MAA grafted surface. From the figure, it is clear that, the unmodified nanofibers were completely separated from each other, however, in the MAA grafted surface modified sample, a rough and irregular surface of modified PA6 nanofibrous membrane was observed. Furthermore, the SEM images clarifies that the modification process did not distort the fibrous structure of PA6 nanofiber and formation of the fiber network between PA6 and polyMAA during the graft polymerization process, indicating that a successful attachment of MAA onto PA6 nanofibers is obtained. It is also observed that, the grafting of PA6 nanofibers with MAA led to enlargement of its diameter, as well as the formation of heterogeneous plateau [35].

From the figure also, it is clear that, the presence of CaO nanoparticles play an important role in the enhancement of fibrous membrane where a full fibrous membrane was obtained in case of PA6/CaO electrospun fiber after modification by MAA via grafting polymerization process [36].

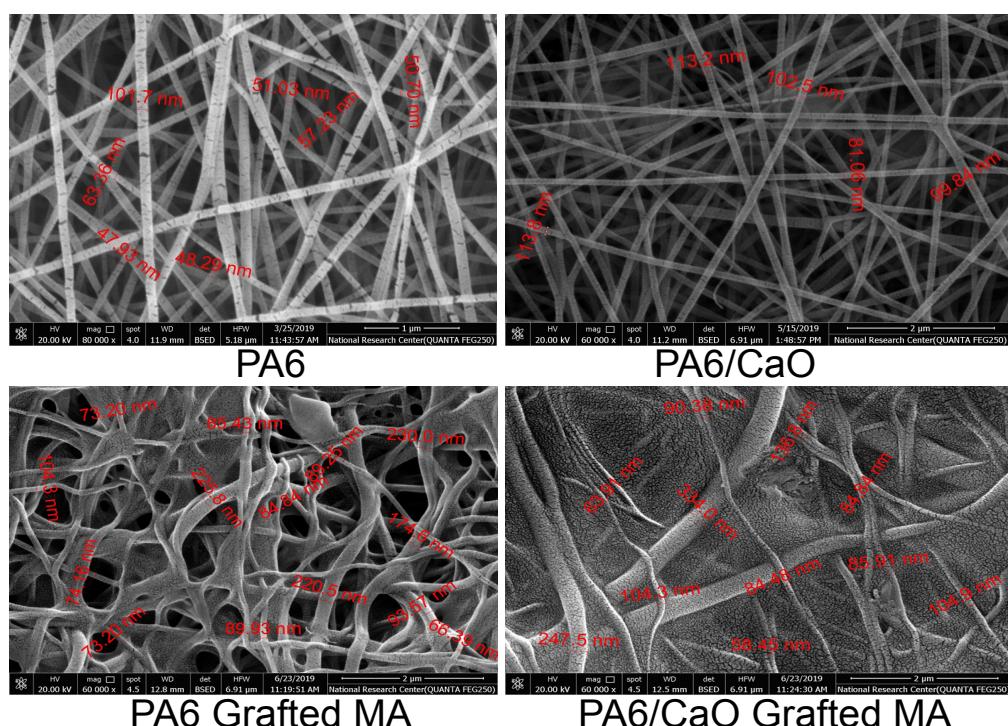


Fig.5. SEM micrographs for the prepared unmodified and MAA grafted modified electrospun fibers.

ATR-FTIR Spectroscopy

Grafting of PA6 and PA6/CaO nanofibrous membrane with methacrylic acid were validated by ATR-FTIR spectroscopy for PA6, PA6-g-MAA, PA6/CaO and PA6/CaO-g-MAA nanofibers. Figure 6 shown IR spectrum and it is observed the appearance of peak at 1164 cm^{-1} that may refer to the formation of new amide groups. Also, it is observed an additional stronger absorption band at 1727 cm^{-1} that corresponds to the characteristic carbonyl group in methacrylic acid and C-O stretching of acid. The previous peaks were absent from the FT-IR spectrum of pure PA6 or PA6/CaO before grafting that confirms that the grafted of methacrylic acid monomer PA6 or PA6/CaO effectively [34]. In addition, the hydroxyl group of MAA and sum of absorption of the carboxylic and alcoholic O-H stretching bands appeared in the range region of $2660\text{--}3500\text{ cm}^{-1}$ [37].

Removal of BR18 dyestuff from water solution

The sorption capacity of the prepared MAA surface modified PA6 and PA6/CaO electrospun nanofibrous membranes were examined used in the removal of basic red BR18 dyestuff from aqueous solution via sorption-filtration process under different temperatures and pH values.

Effect of pH value

The PH value of the dye solution is a vital parameter for sorption process of the dye and its influence has been examined by studying the removal of BR18 basic dye from aqueous solution with different pH values in the range of pH 8:12 at temperature 30°C Where the concentration

of the dye was determined in the filtrate via the UV-Vis spectrophotometer by measuring the dye absorbance at maximum wavelength (λ_{\max}) of BR18 dye (489 nm) using a standard calibration curve experimentally obtained with aqueous solution of dye and the resulted data were illustrated in Figure 7. From the figure it is clear that the dye removal reached its maximum value at pH 10 and then entered the fixed area which confirm the successful removal of basic dye after grafting of MAA polymer onto the polyamide nanofibrous membrane. Also, it is clear that, the presence of CaO nanoparticle has an important rule in the enhancement of BR18 basic dye removal using the PA6 nanofibrous membrane [38, 39].

Effect of temperature

Effect of temperature on the sorption process of the basic BR18 dye has been studied by measuring the removal of dye % from aqueous of dye with PH 8 under different temperatures in the range of $40\text{--}70^\circ\text{C}$. The concentration of the dye was determined in the unfiltered and filtrate solution. The resulting data were illustrated in Figure 8 and show that the BR18 dye removal increased by increasing the temperature and reached its maximum under temperature 60°C by using grafted PA6-g-MAA or PA6/CaO-g-MAA nanofibrous membrane.

From the figure also, it is clear that, the presence of CaO nanoparticle resulted in enhancement of the dye removal percentage in all studied temperature [38, 39].

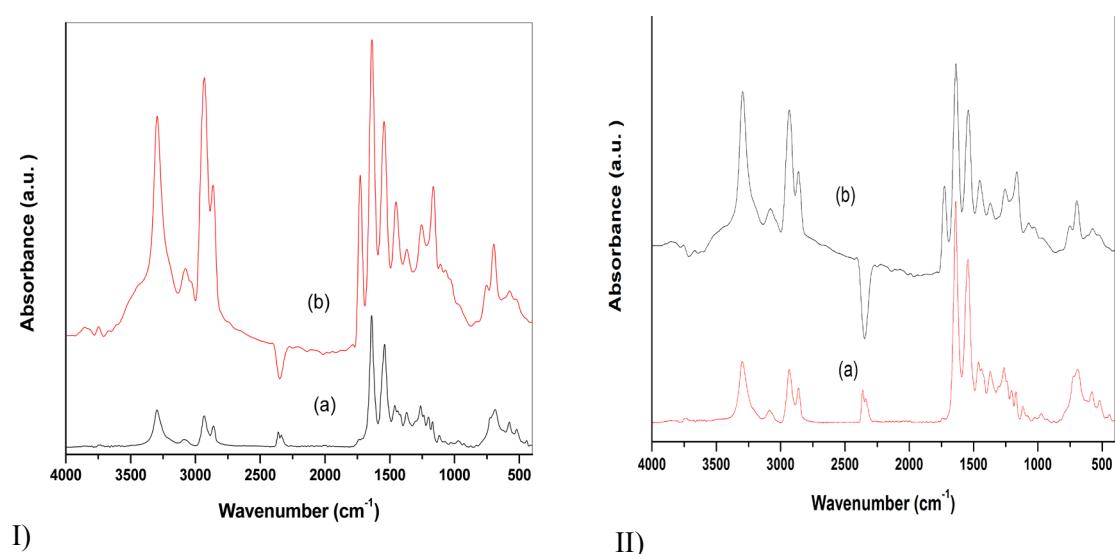


Fig.6. ATR-FTIR spectra of the polyamide nanofiber, (I) PA6 (a) Pa6-g-MAA(b) and (II) PA6/CaO (a) PA6/CaO-g-MAA (b).

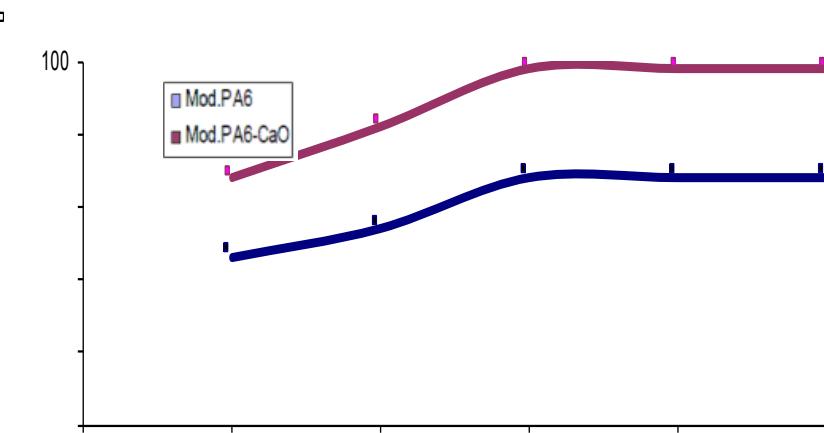


Fig.7. Effect of pH value on removal % of BR18 basic dye.

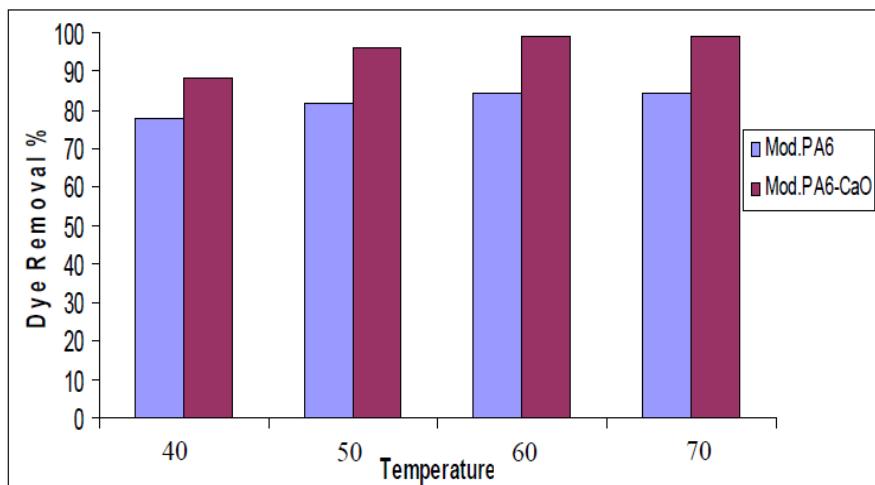


Fig. 8. Effect of temperature on removal % of BR18 basic dye.

Conclusion

PA 6 and PA 6/CaO electrospun nanofibrous membranes were successfully prepared with various concentrations of PA6 between 25 and 45% (wt/v) and various CaO concentration (0.2-1.0 % wt/wt) by electrospinning of polymer solution. The SEM images investigated the structure and the average diameters of the produced electrospun nanofibers to be largely affect by concentration of the polymer solution. And CaO resulted in production of smooth and continuous nanofibers and caused in slightly increase in the nanofiber diameters. The prepared PA6 and PA6/CaO electrospun membranes surfaces were modified by grafting polymerization with methacrylic acid. The produced modified nanofibrous membranes of

PA 6 and PA 6/CaO were used in sorption of basic red BR 18 dye from water solution via sorption-filtration process under different temperatures and pH values and the results showed that the optimum condition for dye removal was pH 10 under temperature of 60°C.

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**تصنيع غشاء ليفي نانوى مغزول كهربيا من البولي أميد ٦ أكسيد الكالسيوم معدل السطح بالأكريليك لإزالة الصبغة بفعالية
مطلوب أسماء المؤلفين وعناوينهم بالعربي**

لقد تم الحصول على أغشية من البولي أميد ٦ الليفي النانوى له وزن جزيئى منخفض بتركيزات مختلفة تتراوح بين ٢٠ و ٤٥٪ بواسطة الغزل الكهربى لمحلول البوليمير. كذلك تم الحصول بنجاح على البولي أميد ٦ الليفي النانوى الذى يحتوى على الجزيئات الدقيقة من أكسيد الكالسيوم بنسبة تصل إلى ١٪ تركيز أكسيد الكالسيوم. تمت دراسة تركيب الألياف المغزولة كهربيا بمساعدة الميكروسكوب الإلكترونى الماسح التى أشارت إلى أن الألياف المغزولة كهربيا فى الظروف المثالية عبارة عن خطوط مستقيمة لها قطر تقريريا ٧٠-٦٠ نانوميترا و أشارت كذلك إلى التوزيع الجيد لجزيئات أكسيد الكالسيوم محققتا بالحجم النانوى للقطر الليفى .

و كذلك تم تعديل سطح الألياف التى تم الحصول عليها عن طريق بلمرة التعليم لحمض الميثاكريليك و تم استخدام الأغشية الليفية النانوية الناتجة فى إزالة الصبغة القاعدى BR18

أوضحت النتائج أن نسبة الصبغة التى تم إزالتها باستخدام أغشية ألياف البولي أميد ٦ أكسيد الكالسيوم تفوق التى تم إزالتها باستخدام أغشية البولي أميد ٦ النقى. وكانت الظروف المثالية لإزالة الصبغة عند رقم هيدروجيني pH 10 تحت درجة حرارة 60 °C مستخدما لأكسيد الكالسيوم ١٪ .