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Removal of hexavalent chromium using polyacrylonitrile/titanium dioxide nanofiber membrane

Şerife Parlayıcı[a], Adem Yar[b], Ahmet Avcı[b], Erol Pehlivan[a,*]

[a]*Department of Chemical Engineering, Selcuk University, Campus, Konya 42079, Turkey, email: serife842@hotmail.com (Ş. Parlayıcı), Tel. +90 332 2232127; Fax: +90 332 2410635; email: erolpehlivan@gmail.com (E. Pehlivan)*
[b]*Department of Mechanical Engineering, Selcuk University, Campus, Konya 42079, Turkey, email: admyr42@gmail.com (A. Yar), aavci@selcuk.edu.tr (A. Avcı)*

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ABSTRACT

Polyacrylonitrile/titanium dioxide nanofiber (PAN/T-nF) membrane was prepared with TiO_2 nanoparticles which dispersed into polyacrylonitrile (PAN) matrix with ultrasonic probe in ultrasonic bath. The amount of TiO_2 loaded in the membrane was 1 and 3 wt% to explore the activity of membranes in the adsorption process. PAN/T-nF membrane was prepared by electrospinning technique. The potential of the prepared PAN/T-nF membrane was investigated for the removal of Cr(VI) from aqueous solutions. The adsorption equilibrium was investigated in the batch process. The adsorption process displayed pH dependence and the maximum Cr(VI) adsorption took place at pH 2. The equilibrium was attained at a contact time of 180 min and Langmuir adsorption model was suitable for the adsorption isotherms. Maximum adsorption capacities 245.3 and 280.4 mg Cr(VI)/g were calculated for 1 and 3% PAN/T-nF membrane, respectively. The adsorption of Cr(VI) on PAN/T-nF was related to the mechanism of surface complexation, coordination, and electrostatic attraction. This new fabrication method for PAN/T-nF membranes showed an excellent thermal stability that can persist up to 400°C and has a big capacity for Cr(VI) ion.

Keywords: Mixed matrix membrane; Electrospinning; Hexavalent chromium; Equilibrium

1. Introduction

In membrane technology, engineered nano materials (ENMs) have opened a great scope for research and development. These can be synthesized by constituting two or more compounds with unique properties and applied for various environmental applications. Today, ENMs deal with scale between 1 and 100 nm having physical and chemical properties that differ significantly from the particles of larger dimension [1].

PAN/T-nF membrane is a promising material for the adsorption of Cr(VI) because of its high stability, good efficiency, and better usability. Membranes with a good thermal and mechanical stability and good solvent resistance are important for industrial applications. For the development of inorganic and polymeric membranes, PAN/T-nF membrane is suitable for the separation of metal ions from wastewater [2]. The fillers such as TiO_2 improve the mechanical stability and resistance against compaction. PAN micro- and

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*Corresponding author.

ultrafiltration membranes are widely used for water treatment and recycling of industrial wastewater especially in the pulp and paper industry [3].

In recent years, special attention has been given to chromium due to its high toxicity [4]. The presence of high amounts of chromium in effluents produces a harmful effect on the human health and the environment [5]. Heavy metal ions, such as arsenic, mercury, lead, and chromium, are generally non-biodegradable, highly toxic, and carcinogenic. Among them, arsenic and chromium ions are the most dangerous toxic metals. Chromium is often present in the wastewater drain of many industries such as steel manufacturing, electroplating, leather tanning, mining industry, pesticide application in wood industry, textile manufacturing, and photography [6]. Generally, chromium occurs in the environment in two valence states: trivalent Cr (III) chromium and hexavalent chromium Cr(VI). Cr (III) is not so much toxic as Cr(VI). Many efforts have been carried out for the removal of Cr(VI) from industrially polluted wastewater such as solvent extraction, filtration [7–9], ion exchange, membrane process, precipitation, and adsorption [10].

Recently, nanoparticles have been incorporated into nanofibers using various methods and studied for the removal of toxic metal, and membrane separation is one of the preferable methods as compared to others. After mixing the nanoparticles, such as titanium and aluminum with polymer solutions followed by electrospinning, the obtained nanocomposite membranes can be tested for the chromium separation. Development of new membranes with high removal capacity and good stability in different media is highly desired for environmental applications [10]. Membranes are promising separation candidates due to the advantages of high stability, efficiency, low energy need, and easy operation in many industrial applications [2]. Polymers are the most widely used membrane materials, but their thermal stability and solvent resistance are important for the applications. Hence, more attentions are being drawn to the new types of thermal and solvent stable membranes in the last few decades. Inorganic nanoparticles such as TiO_2 as fillers were introduced into the polymer membrane matrix to reduce the swelling of the membrane in solvents [11]. PAN is an important polymer for manufacturing high-performance carbon fibers. PAN/T-nF membranes can be prepared by electrospinning method and have unique properties such as high specific surface area and high porosity with fine pores. Electrospinning is a process capable of producing ultrafine fibers, with diameters in nano- to micrometer range, from the materials of diverse origins, including polymers. Therefore, the electrospun nanofiber membranes have been successfully used for the removal of heavy metal ions [12–14].

In the present research, PAN/T-nF membrane was obtained by the electrospinning method and its application for the removal of Cr(VI) ion from aqueous solution was investigated. The effects of contact time, pH, and initial Cr(VI) ion concentration were optimized for the maximum adsorption capacity. The nature of the adsorption process in a batch system with respect to equilibrium parameters was evaluated.

2. Experimental

2.1. Materials

All the chemicals applied in the experiments were of analytical grade and double-distilled water was used to prepare the required solutions. A stock solution of Cr(VI) ions with a concentration of 1×10^{-3} M was prepared by dissolving $K_2Cr_2O_7$ salt (Merck) in double-distilled water. NaOH and HCl solutions were purchased from Merck. A series of calibration standards were prepared by dilution of the Cr(VI) stock solution for each experiment. PAN (MW:150,000) was obtained from Sigma-Aldrich and dimethylformamide (DMF) was obtained from Merck. TiO_2 nanoparticles were synthesized by arc-discharge method in Nanomaterial science laboratory.

2.2. Electrospinning of PAN/T-nF membrane

0.01–0.03 g TiO_2 nanoparticles were dispersed in 10 ml DMF using a probe and then immersed in an ultrasonic bath for 30 min and then 1 g of PAN was added to this solution. The solution was stirred at 80°C for 12 h to obtain a homogeneous and viscous solution and it was cooled to room temperature before electrospinning. In the electrospinning technique, high voltage is applied between the nozzle and the collector. An electrically charged jet of polymer and a composite solution is obtained during the electrospinning process. The solvent was evaporated before reaching the collector and the fibers with nanosized diameters were collected on the collector.

The prepared solution was transferred to a 10-ml syringe with 19-gage needle tip. The distance was 15 cm between the needle tip and the grounded collector. The syringe with polymer solution was placed into syringe pump and adjusted to a feed rate of 0.35 ml/h. The applied voltage supply was adjusted to 20 kV and the steel webs [mesh (Ø = 4 cm) diameter] were cleaned with ethanol and acetone solution before electrospinning process. The webs were stacked onto the square collector which is wrapped onto the aluminum foil. Electrospinning process was performed in the petri glass cabin and optimum parameters were applied then the nanofibers were continuously produced (Fig. 1). The nanofibers were coated absolutely to the steel mesh onto the grounded collector. Then, this PAN/T-nF membrane was stored for further use in the removal of Cr(VI).

3. Results and discussions

3.1. Characterization of PAN/T-nF electrospun webs

The most important property of an adsorbent is the surface area and structure. Furthermore, the chemical nature and the polarity of the adsorbent surface can influence the attractive forces between the adsorbent and adsorbate. The chemical structure of the prepared PAN/T-nF was characterized by Fourier transform infrared spectroscopy (FT-IR). After PAN/T-nF synthesis, the outer surface and cross-section of the membrane were observed by scanning electron microscope (SEM), and the crystal structure was identified by X-ray diffraction (XRD).

Fig. 2 indicates SEM images of pure PAN electrospun nanofiber (a), PAN nanofiber with TiO_2 nanoparticle (c), and after the adsorption of pure PAN and PAN nanofiber with TiO_2 (b and d). Fig. 2(a) shows that PAN nanofibers have smooth and bead-free structure and the average diameter of PAN nanofibers is between 40 and 400 nm. It can be seen from Fig. 1(c) that incorporation of TiO_2 nanoparticle into PAN polymer changes the surface morphology of electrospun nanofiber, resulting in a bead-like and non-uniform structure with the diameter of fibers ranging from 30 to 100 nm. This morphology is due to the agglomeration tendency of TiO_2 nanoparticle or inhomogeneous distributions of TiO_2 nanoparticle in the PAN polymer matrix. Fig. 2(b) demonstrates that the surface of PAN nanofibers becomes rougher after the adsorption activity is applied. The fiber diameter of Cr(VI)-loaded PAN/T-nF in Fig. 2(d) is wider than that of PAN/T-nF Fig. 2(c) and in this way, the beads disappeared and became enlarged due to the adsorption of Cr(VI). Thus, the PAN/T-nF gains a larger effective surface area. It was observed that as soon as PAN/T-nF deposited on the collecting steel frame, they quickly combined to form mat fibers.

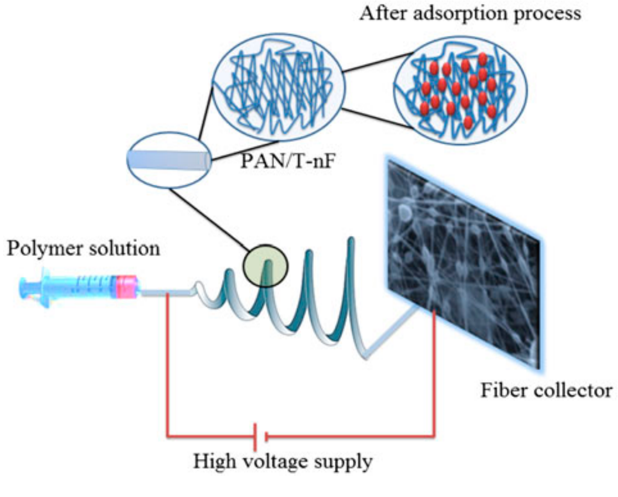

Fig. 1. Schematic illustration of PAN/T-nF fabrication.

Fig. 3(a) shows the XRD peak of pristine PAN nanofiber and PAN/T-nF. The XRD pattern of PAN nanofiber displays an amorphous structure and the peaks are between 15° and 20°, 20° and 30°. PAN/T-nF patterns express the crystal structure of tetragonal rutile TiO_2 which are correspondent with standard peak (JCPDS No. 88-1175) and confirm embedding of TiO_2 nanoparticle within PAN polymer matrix. It is significant to notice that the deposited material consists of titanium and after washing, remarkable amount of titania is still present on the PAN surface. This means that TiO_2 particles are tightly fixed to the surface of PAN fibers.

The FT-IR spectra of PAN and PAN/T-nF are given in Fig. 3(b). The spectrum of PAN and PAN/T-nF displayed characteristic peaks of nitrile (2,250 cm^{-1}), carbonyl (1,640 cm^{-1}), and C–H stretching (2,970 cm^{-1}). Usually, the carbonyl peak is observed at 1,700 cm^{-1}. But, when PAN was dissolved in DMF, the carboxyl transmission band is shifted towards a lower wavenumber. Ti–O bands cannot be seen and this peak could be less than a wavenumber of 800 cm^{-1} [15].

3.2. Effect of contact time and pH

Hydrolysis, pH of the solution, redox reactions in the solution phase, and the coordination as well as the ionic state of the functional groups on the surface of the membrane can effect the Cr(VI) removal. The pH of the aqueous solution is one parameter that plays an important role in the chromium adsorption process. Usually, at below pH 2.0, partial chromium ions in the solution exist as trivalent state, while above pH 3.0, chemical reduction of Cr(VI) to Cr(III) occurs to a lesser extent and anionic chromium species, such as $HCrO_4^-$ and $Cr_2O_7^{2-}$ are the major species [16].

The effect of solution pH on the adsorption of Cr (VI) onto PAN/T-nF membrane was displayed in Fig. 4(a). As seen from the figure, the adsorption capacity of membrane was highly dependent on the pH with maximum adsorption took place at pH 2. After increasing pH ($pH > 3$), the amount of Cr(VI)

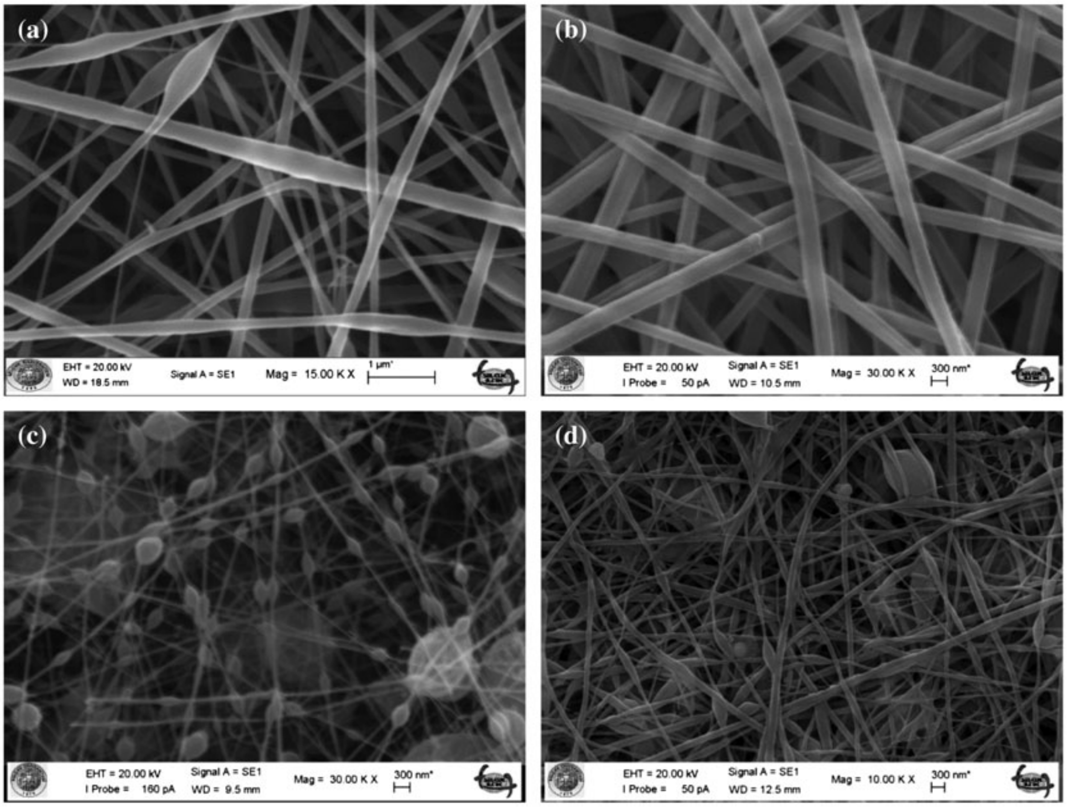

Fig. 2. SEM images of (a) PAN nanofibers, (b) PAN-Cr(VI), (c) PAN/T-nF, and (d) PAN/T-nF-Cr(VI).

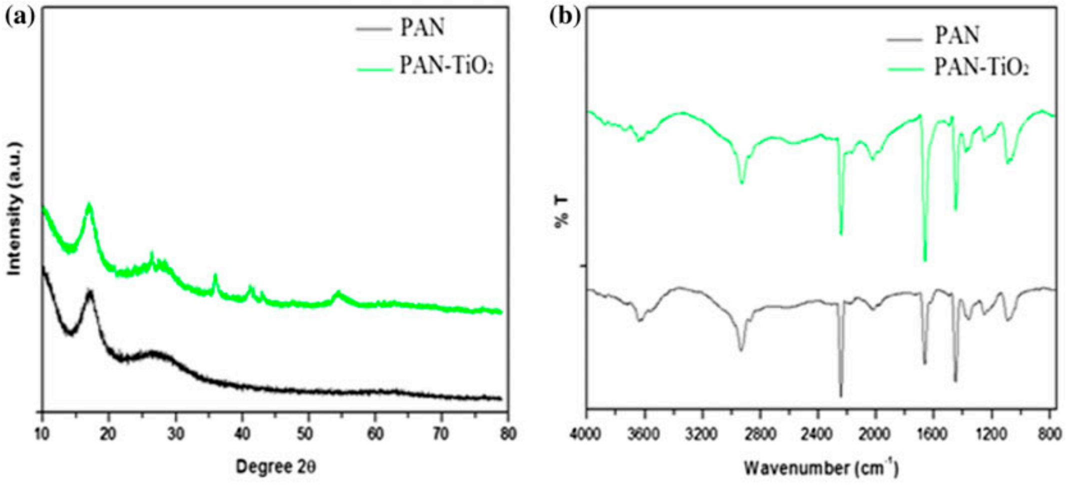

Fig. 3. (a) XRD pattern of PAN/T-nF membrane and (b) FT-IR spectra of PAN and PAN/T-nF membrane.

adsorbed from the solution decreased. The variation in the removal of Cr(VI) at different pH values may be related to the affinities of PAN/T-nF membrane for the different species of Cr(VI) existing at an acidic pH values, namely H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$. It is apparent that negatively charged $HCrO_4^-$ and $Cr_2O_7^{2-}$ can be adsorbed in a high probability to the positively charged PAN/T-nF membrane at low pH values due to the electrostatic attraction.

The experimental results suggested some information about the mechanism of Cr(VI) removal. Many ideas related to the Cr(VI)-binding mechanisms through membranes have been suggested in the membrane application processes, such as: ion exchange, complexation, electrostatic interaction, chemisorption, and coordination. At lower pH values, such as 2, the membrane surface was positively charged and it attracts the negatively charged Cr(VI), favoring adsorption. At higher pH values, the opposite phenomenon occurs on the surface of the membrane. Similarly, the membrane surface is negatively charged and repels the Cr(VI).

The contact time was in the range of 30 min to 24 h for the removal of Cr(VI) ion using the PAN/T-nF membrane. The equilibrium between solution and membrane was reached after 180 min as seen in Fig. 4(b).

3.3. Effect of initial Cr(VI) ion concentration

The effect of initial Cr(VI) concentration on the adsorption of PAN/T-nF nanofibers was studied in order to determine the maximum loading capacity and Fig. 4(c) shows smooth curves which indicate the setting up monolayer of Cr(VI) on the surface of PAN/T-nF membrane. The obtained experimental results were fitted using Langmuir [17–19].

Freundlich and Langmuir isotherm models (Eqs. (1)–(4)) are preferred as the Cr(VI) amount which is adsorbed on the PAN/T-nF membrane surface.

Freundlich equation:

$$q = K_F C_e^n \tag{1}$$

where n is the Freundlich constant, K_F is the adsorption coefficient, q is the weight adsorbed Cr(VI) per unit weight of adsorbent, and C_e is the equilibrium Cr (VI) concentration in bulk phase. Eq. (1) can be rearranged as following:

$$\log q = \log K_F + n \log C_e \tag{2}$$

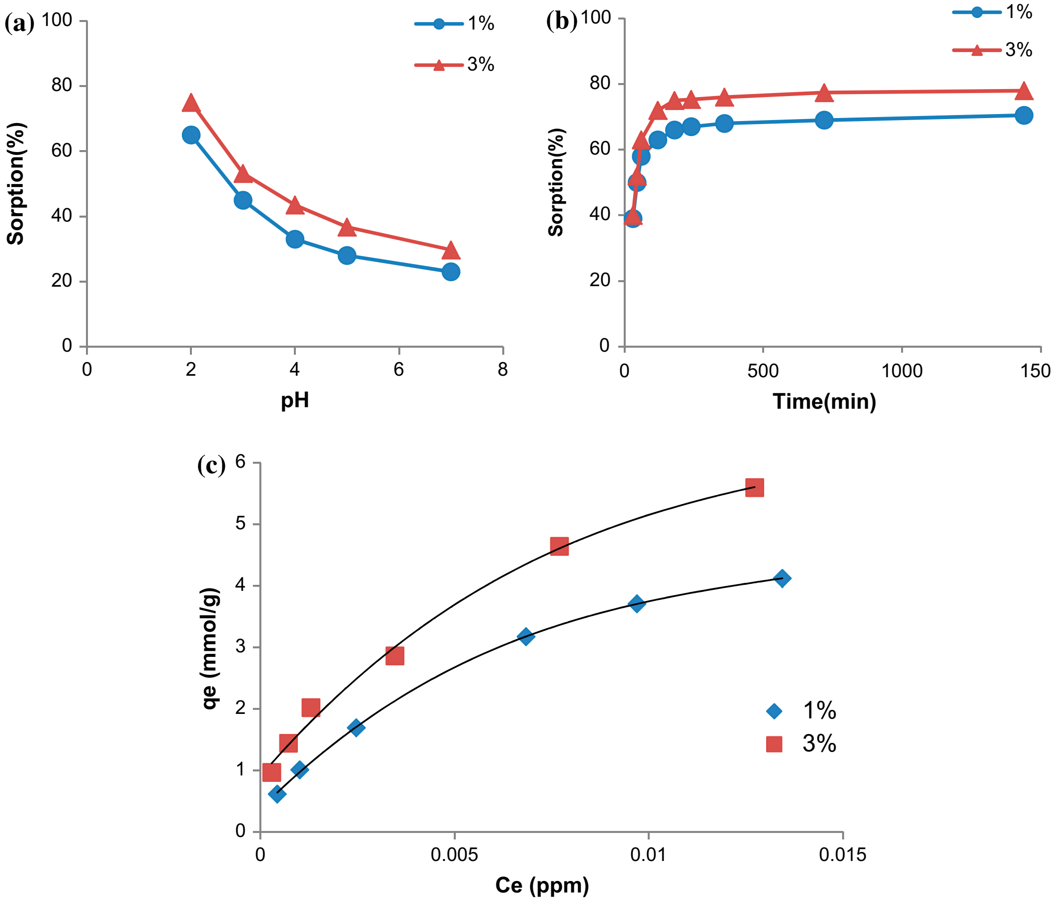

Fig. 4. Effect of (a) pH, (b) contact time, and (c) initial concentration on the adsorption of Cr(VI) for 1 and 3% PAN/T-nF membrane.

Table 1
Freundlich and Langmuir adsorption isotherm parameters

	Freundlich isotherm method			Langmuir isotherm method		
Adsorbent	K_F (mg/g)	n	R^2	A_s (mg/g)	K_b (L/mg)	R^2
1% PAN/T-nF	0.17	0.56	0.93	245.3	0.19	0.98
3% PAN/T-nF	2.92	0.29	0.92	280.4	0.22	0.99

The Langmuir model assumes the adsorption of Cr (VI) occurs as a monolayer on a homogeneous surface and is expressed by the following equation,

Langmuir equation:

$$q_e = \frac{A_s K_b C_e}{1 + K_b C_e} \tag{3}$$

where q_e is the equilibrium loading capacity (mg/g), C_e is the equilibrium Cr(VI) concentration in the aqueous phase (mg/L), A_s (mg/g) and K_b (L/mg) are the coefficients. By rearranging Eq. (3), Eq. (4) was obtained.

$$\frac{C_e}{q_e} = \frac{C_e}{A_s} + \frac{1}{A_s K_b} \tag{4}$$

It can be seen that Cr(VI) adsorption rate was fast in the initial stage, and gradually reached a plateau toward equilibrium with maximum adsorption of 245.3 and 280.4 mg Cr(VI)/g 1 and 3% PAN/T-nF membrane, respectively (Table 1). The percent Cr(VI) ion adsorption on PAN/T-nF membrane was high and when Cr(VI) ion concentration increased, more Cr (VI) ions passed into the solution-phase because of the saturation of binding sites of PAN/T-nF membrane. Moreover, the Langmuir isotherm can be represented in terms of a separation factor, R_L, a dimensionless constant term defined by [20]:

$$R_L = 1/(1 + K_b C_o) \tag{5}$$

where C_o is defined as the initial concentration (mg/L), K_b is the Langmuir isotherm constant (L/mg), and R_L is the dimensionless Langmuir separation factor. R_L values between 0 and 1 indicate that the isotherm can be applicable for the equilibrium. Based on the obtained experimental data, the R_L was determined to be 0.7, at initial Cr(VI) concentrations of 100 mg/L. The reusability of PAN/T-nF membrane was determined after five adsorption–desorption cycles and no deformation occurred in the structure of the membrane.

4. Conclusions

PAN/T-nF membrane was prepared by the electrospinning technique. PAN with a higher percentage of TiO_2 resulted in the higher percentage of Cr(VI) removal. PAN prepared with TiO_2 exhibited an impressively high efficiency for the removal of Cr(VI) from aqueous solution. Higher efficiency of Cr(VI) adsorption is displayed at a lower pH value of 2.0. The highest adsorption capacity was found as 245.3 and 280.4 mg Cr(VI)/g for 1 and 3% PAN/T-nF membrane respectively. Langmuir adsorption equation fits into the equilibrium data.

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