

Preparation and Adsorption Behavior of Novel Sandwiched Composite Electro-Spun Aminated Membrane for Hexavalent Chromium Removal

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Abstract—Novel sandwiched composite electro-spun membranes (SCEM) were fabricated by sandwiching the chitosan incorporated polyvinyl butyral (PVB) nanofiber mat between two layers of polyacrylonitrile (PAN) electro-spun mats. In order to generate inner layer of membrane, PVB-Ch nanofiber mat was collected onto the prepared PAN mat by electro-spinning. After reaching desired thickness of PVB-Ch nanofibers, top layer of membrane consisting of PAN nanofiber was composed by electro-spinning procedure under the same circumstances. After fabrication stages, SCEM was examined in respect to chromium removal from aqueous solutions. However, it can be reported that no removal was achieved even under different conditions. Therefore, surface of fabricated sandwiched composite was aminated and coated with chitosan to develop an affinity membrane for removal of hexavalent chromium. Adsorption of hexavalent chromium (Cr^{6+}) ions were carried out in a batch arrangement. Experiments were performed as a function of contact time, solution pH, and initial Cr^{6+} ion concentration. The maximum adsorption capacity of 16.64 mg of Cr^{6+} /g for A-SCEM was obtained at $\text{pH}=2$ according to the Langmuir adsorption isotherm. This work demonstrated that the novel electrospun membrane has potential for membrane applications in wastewater treatment systems.

Index Terms—Chitosan, electro-spinning, hexavalent chromium, membrane, nanofiber.

I. INTRODUCTION

Pollution of water sources due to the contamination of heavy metals is a serious environmental problem. Metals such as lead, copper, silver and chromium can cause to many problems for both environment and living organisms. Chromium is the most common heavy metal as a groundwater contaminant and it occurs in two oxidation states; Cr^{6+} such as chromate and bichromate (CrO_4^{2-} , HCrO_4^-) and trivalent chromium (Cr^{3+}). Cr^{6+} is more carcinogenic and toxic to humans than Cr^{3+} [1]. There needs to remove these toxic metals from water by using proper water treatment techniques. Among adopted treatment techniques, adsorption process is one of the methods, which is gaining more attention because of its easy operations, the simplicity of design and versatility [2]. Many types of adsorbent such as activated carbon, oxide minerals, polymer

materials, resins, and biosorbents have been used for efficient adsorbent. The adsorption efficiency of these adsorbents depends on the functional groups on the surface of adsorbent [3]. Particularly, amino, carboxyl and thiol groups on the adsorbents have been reported to be effective in the removal of hexavalent chromium from water sources [4].

With the advances in science it is possible to fabricate new materials at nanoscale level. Nanofibers are the member of this type of novel materials. In recent years, non-woven fibrous products have been used as an adsorbent with interesting characteristics such as fine diameters (ranging from submicron to several nanometers), large surface area, high porosity, high gas permeability, and small interfibrous pore size in order to remove heavy metal and other toxic contents [5]. Electrostatic interaction, surface complexation or ion exchange mechanisms are responsible for adsorption of metal ions onto these kind of adsorbents. The usage of nanofibers for adsorption method have recently been increased. Nanofibers have been produced by an electro-spinning technique which provides the capacity to lace together types of nanofillers, nanoparticles or other additives to be incorporated into an electrospun nanofiber matrix. This application method allows to create new nanofiber composites having various properties to be used in different fields.

In this research area, PAN polymer has been widely used to fabricate nanofibers due to its excellent characteristics and its non-toxic nature. However nanofibers should be modified with amine or amidoxime groups to create functional groups onto their surfaces to remove various metal ions. Furthermore, important way to increase the mechanical properties of nanofibers is to combine with other nanofibers forming a composite as commercial membranes. For this purpose, PAN has been chosen to constitute top and bottom layer for PVB mat due to its mechanical stability.

In this respect, the main aim of this study is to generate a novel sandwiched composite electro-spun membrane (SCEM) in order to remove Cr^{6+} ions from waste water. This process was carried out by sandwiching the chitosan incorporated polyvinyl butyral (PVB) nanofiber mat between two layers of polyacrylonitrile (PAN) electro-spun mats. After fabrication of membranes, amination treatment was performed in order to obtain an affinity between membranes and Cr^{6+} ions. Because, this process allows achieving a high amine loading for the removal of metal ions. One other important point, chitosan was used in PVB polymer for inner layer and in modification of outer layer of membrane surface due to the high hydrophilicity and presence of a large number of

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hydroxyl groups of glucose units and functional groups (acetamido, primary amino and/or hydroxyl groups) in its structure [6]. According to the results, the aminated sandwiched composite electro-spun membranes (A-SCEM) were then investigated as an adsorbent in a series of batch adsorption experiments to remove Cr^{6+} ions.

II. EXPERIMENTAL

A. Materials

Polyacrylonitrile (PAN, average MW 150000), polyvinyl butyral (PVB, MW 150000), chitosan (Ch, MW average = $342,500 \text{ g mol}^{-1}$), ethanol (EtOH), N,N Dimethylformamide (DMF), sodium hydroxide (NaOH), hydrochloric acid (HCl, 37%), ethylenediamine (EDA, 99%), glutaraldehyde (GA, 25%), acetic acid (AA, 99%), sodium acetate (CH_3COONa), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) were purchased from Sigma-Aldrich.

B. Fabrication of Sandwiched Composite Electro-Spun Membrane (SCEM)

In brief, before fabricating of SCEM, PAN and PVB polymers were dissolved in DMF and ethanol, respectively. Polymer solutions were mixed by magnetic stirrer in order to achieve homogeneous solutions. Firstly, PAN/DMF solution was placed in a 10-ml syringe with 19-gage needle tip and electrospun onto a aluminum foil to produce PAN nanofibers. Similarly, PVB/EtOH-Ch solution was electrospun with different parameters to determine the proper conditions.

In order to set the appropriate electrospinning conditions, various parameters such as applied voltage, volumetric flow rate of the solution, and distance between nozzle tip and collector were changed at different intervals. This preliminary study is essential to generate smooth nanofibers with desired diameters without bead formation.

After optimization of the parameters, SCEM was generated by sandwiching the chitosan incorporated polyvinyl butyral (PVB) nanofiber mat (PVB-Ch) between two layers of (PAN) electro-spun mats. This produced membrane consists of three basic layers.

C. Functionalization and Characterization of SCEM

The porous SCEM was modified by multiple steps with EDA and chitosan according to the procedure reported by Zhang *et al.* [7]. First, membranes cut in circle geometry was immersed in 15% NaOH at 50°C during 60 min to apply hydrolysis pre-treatment followed by washing with DI water. This treatment cause to turn color of membrane in yellowish. After immersion in a 1.0 M HCl solution for 120 min at room temperature, membranes turned back to white. Afterwards, membrane was kept in 100 mL 10% solution of ethylenediamine (EDA) for 60 min at room temperature. After that, membrane was transferred into 10% GA for 1 h followed by washing with DI water. Usage of GA solution was for cross linking of chitosan on the surface of membrane. Finally, membrane was immersed in chitosan solution for 24 hours at room temperature. Before performing characterization and adsorption experiments, A-SCEM were dried at room temperature for 3 days. Consequently, the rigid nanofiber networks was developed.

The morphology of PAN, PVB-Ch mats, and A-SCEM membrane were examined by scanning electron microscopy (SEM). This spectroscopic measurement of the synthesized mats and membranes were studied using a ZEISS evo LS10 electron scanning microscope.

FT-IR spectrum was recorded at range 400 to 4000 cm^{-1} at 4 cm^{-1} resolution using a Bruker Vertex FT-IR spectrometer.

D. Adsorption Procedures

Adsorption experiments in batch mode were performed by mixing 15 ml of Cr^{6+} aqueous solutions in a concentration range of 10 to 100 mg/L, at room temperature with constant amounts of membranes (70 mg) using a shaker. The pH of the solutions (pH range of 1.0 to 5.0) was controlled using 1.0 M HCl or 1.0 M NaOH standardized solutions and confirmed with pH measurements. Adsorption of Cr^{6+} ions from solutions has been systematically investigated as a function of contact time from 10 min to 180 min at room temperature. The concentrations of Cr^{6+} in the initial and final solutions were determined by UV-vis spectrophotometer (Shimadzu UV-1700).

III. RESULTS AND DISCUSSIONS

A. Characterization of SCEM

Fig. 1 showed the morphology of mats and membranes. The surface of PAN and PVB-Ch nanofibers did not present any crack, damage or degradation. They showed clearly good uniformity. Furthermore, the average diameters were 380 and 100 nm for PAN and PVB-Ch nanofibers.

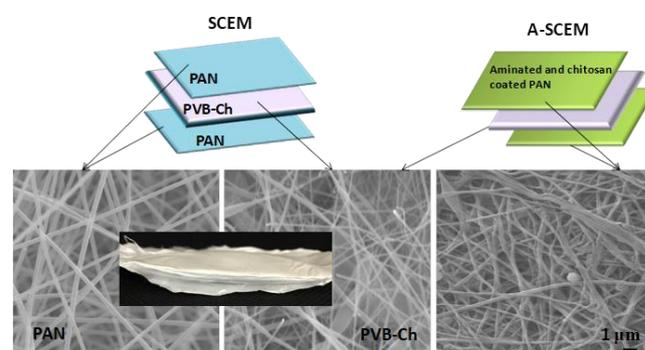


Fig. 1. SEM micrographs of electrospun PAN and PVB-Ch mats and A-SCEM membrane.

Aminated and coated with chitosan membrane top layer is shown in Fig. 1. It can be seen from the figure neighboring points and cross-points were occurred between the fibers due to chitosan coating.

Fig. 2 shows the spectrum of functionalized sandwich membrane (A-SCEM). The bands at 2933 cm^{-1} and 2860 cm^{-1} are due to the C-H stretching in the carbonic chains of PAN fiber. Peaks at 1556 and 1637 cm^{-1} corresponding to -NH bending motion combined with a -CN stretching vibration of the C(=NH)-NH- group appear. Therefore, it is suggested that the nitrile group of the PAN was hydrolyzed into an amide group.

The characteristic nitrile peaks of PAN at around $\sim 2200 \text{ cm}^{-1}$ were disappeared due to the conversion of nitrile to amidoxime. Characteristic peaks of amidoxime, from the

spectrum, can be observed at 3100–3500 cm^{-1} (broad, assigned to both N-H and O-H) [2].

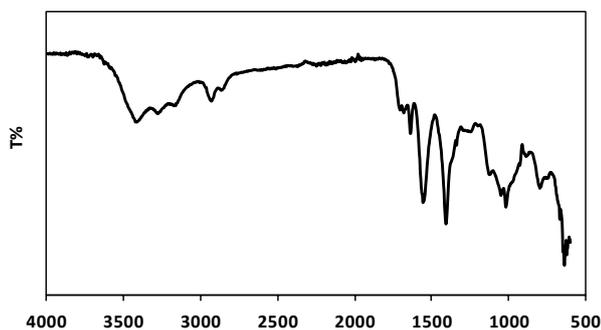


Fig. 2. FT-IR spectrum of A-SCEM membrane.

B. Effect of Contact Time and Solution pH

In order to determine the time required to reach equilibrium during Cr^{6+} adsorption for efficient and more economical water treatment processes, different contact time should be investigated. The removal of chromium onto A-SCEM is shown in Figure 3.a. as a function of shaking time from 10 min to 180 min. As seen from the profile, removal of metal ion increased with contact time until the equilibrium point. Reaching the equilibrium after 120 min, the highest percent of sorption capacity of A-SCEM was achieved, being 95%. It is clear that the increase in contact time from 10 to 60 min accompanied an increase in the percentage of sorption of Cr^{6+} ions.

On the other hand, the adsorption of Cr^{6+} onto SCEM membrane (non-aminated) was examined under the same circumstances as a function of pH and contact time; however there was no removal of chromium ion (the amount of adsorbed chromium onto SCEM was zero); therefore, as mentioned before, the adsorption of Cr^{6+} was mainly related to the presence of NH_2 functional groups.

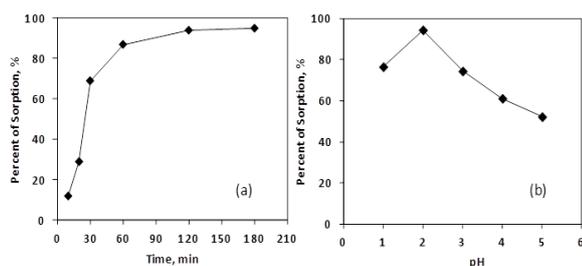


Fig. 3. Effect of (a) contact time, and (b) pH on the adsorption of Cr^{6+} on A-SCEM membrane.

Generally, it is well-known that pH has significant effect on the adsorption process. In this study, the effect of pH on the adsorption of 52 mg/L solutions of Cr^{6+} at pH range 1.0-5.0 after 120 min of contact time with A-SCEM is shown in Fig. 3.b. In the case of pH value is higher than 6.0, metal ions tend to precipitate. For this reason, in order to examine the effect of pH of Cr^{6+} solution on adsorption capacity by A-SCEM, experiments were performed at a pH range of 1-5. The amount of Cr^{6+} removed from aqueous solution decreased with increasing pH ($\text{pH} > 2$). The difference in percent of sorption of Cr^{6+} at different pH values may be attributed to the affinities of A-SCEM for various species of

Cr^{6+} existing at acidic pH values designated HCrO_4^0 , HCrO_4^- , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$. NH_2 groups on the A-SCEM may be protonated to create NH_3 at low pH values or be deprotonated to occur $\text{NH}_2\cdots\text{OH}$ at high pH [2].

Cr^{6+} suggesting that the amine and oxime group of amidoxime are involved in the binding of chromium during Cr^{6+} uptake.

It can be reported that negatively charged HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ are easily to be adsorbed to the positively charged A-SCEM nanofibers at low pH values due to the electronic attraction. At $\text{pH}=1$ the binding sites of A-SCEM are protonated which will bind to the negatively charged species [2].

C. Effect of Initial Cr^{6+} Ion Concentration

For large-scale applications of adsorption, examining the equilibrium data has great importance due to providing an information for comparison with different adsorbents. Because, interpretation and modelling of the data to proper isotherm models lead to optimize and design the operating conditions very well. The effect of initial concentration of chromium ions on the adsorption process was evaluated at its optimum pH ($\text{pH}:2$) with a contact time of 120 min by varying the initial concentration ranging from 10 to 100 mg/L.

As seen from the Figure 4, it can be reported that Cr^{6+} adsorption by A-SCEM was 92%. Upon increasing the concentrations, more Cr^{6+} ions cannot adsorb to the membrane surface and stay in the medium due to the saturation of binding groups of A-SCEM. Freundlich and Langmuir isotherm models were used to identify the equilibrium data of adsorption of Cr^{6+} on A-SCEM. Used isotherms explain Cr^{6+} adsorption per unit weight of adsorbent, q_e , and the equilibrium Cr^{6+} amount in the solution phase, C_e . Langmuir isotherm model supposes monolayer coverage of adsorbate over a homogenous adsorbent surface [8]. In the following equation, K_b (L mol^{-1}) and A_s (mol g^{-1}) are the Langmuir isotherm constants;

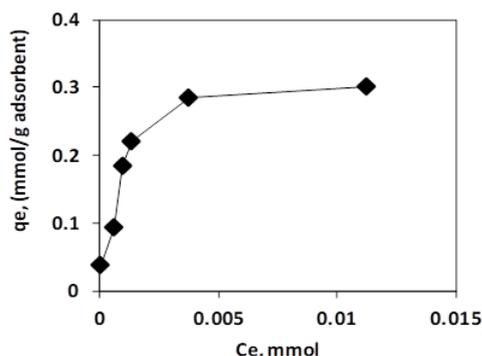
$$\frac{C_e}{q_e} = \frac{C_e}{A_s} + \frac{1}{A_s K_b} \quad (1)$$

q_e is the weight adsorbed per unit weight of adsorbent and C_e is the concentration of metal in equilibrium. Hence by plotting, C_e/q_e against C_e it is possible to gain the value of K_b from the intercept, which is $(1/K_b)$, and the value of A_s from the slope, which is (A_s/K_b) . Freundlich equation assumes that as the adsorbate concentration increases so too does the concentration of adsorbate on the adsorbent surface:

$$q_e = K_f C_e^{1/n}$$

In this equation, K_f and a are the Freundlich constants and q_e is the mass of Cr^{6+} per unit weight of adsorbent and C_e is Cr^{6+} concentration in liquid phase.

Langmuir model was able to describe the adsorption isotherm results of the A-SCEM nanofiber membrane for chromium ions better than the Freundlich model. Based on these models, important parameters were calculated, as shown in Table I.

Fig. 4. Sorption isotherm of Cr⁶⁺ on A-SCEM.

As seen from the Table I, the experimental data obtained were correlated very well to the Langmuir model based on R² values indicating homogeneous distribution of adsorptive sites and monolayer adsorption [6]. The maximum adsorption capacity of 16.64 mg of Cr⁶⁺/g for A-SCEM was obtained according to the Langmuir adsorption isotherm. As a result, it can be claimed that this generated novel membrane could be considered to be a very effective and promising adsorbent for further waste water treatments.

TABLE I: ADSORPTION CAPACITIES AND CORRELATION COEFFICIENTS FOR CR⁶⁺ SORPTION ON A-SCEM.

Adsorbent	Freundlich Isotherm			Langmuir Isotherm		
	K _f ^a	n	R ²	K _b	A _s ^a	R ²
A-SCEM	2.08	2.64	0.92	1420.45	0.32	0.99

^a mmol/g dry adsorbent.

IV. CONCLUSIONS

In this study, we have demonstrated that a concept to fabricate a membrane involving the use of electro-spun nanofibers and aminating the top layer of membrane followed by coating with chitosan. This generated sandwiched membrane had a good adsorption performance for hexavalent chromium removal and had a mechanical stability in aqueous medium due to the using PAN which is more stable polymer. As a result, this novel adsorbent material is a promising candidate for wastewater treatments.

REFERENCES

- [1] D. H. Moon, M. Wazne, A. Koutsospyros, C. Christodoulatos, H. Gevgilili, M. Malik, and D. M. Kalyon, "Evaluation of the treatment of chromite ore processing residue by ferrous sulfate and asphalt," *Journal of Hazardous Materials*, vol. 166, no. 1, pp. 27-32, July 2009.
- [2] M. Avila, T. Burks, F. Akhtar, M. G  helid, P. C. Lans   ker, M. S. Toprak, M. Muhammed, and A. Uheida, "Surface functionalized nanofibers for the removal of chromium (VI) from aqueous solutions," *Chemical Engineering Journal*, vol. 245, pp. 201-209, June 2014.
- [3] R. Coskun, C. Soykan, and M. Sacak, "Adsorption of copper (II), nickel (II) and cobalt (II) ions from aqueous solution by methacrylic acid/acrylamide monomer mixture grafted poly (ethylene terephthalate) fiber," *Separation and Purification Technology*, vol. 49, pp. 107-114, April 2006.
- [4] S. Deng and R. Bai, "Removal of trivalent and hexavalent chromium with aminated polyacrylonitrile fibers: Performance and mechanisms," *Water Research*, vol. 38, no. 9, pp. 2424-2432, February 2004.
- [5] P. K. Neghlani, M. Rafizadeh, and F. A. Taromi, "Preparation of aminated-polyacrylonitrile nanofiber membranes for the adsorption of metal ions: comparison with microfibers," *Journal of Hazardous Materials*, vol. 186, no. 1, pp. 182-189, February 2011.

- [6] H. T. Kahraman, "Development of an adsorbent via chitosan nano-organoclay assembly to remove hexavalent chromium from wastewater," *International Journal of Biological Macromolecules*, vol. 94, pp. 202-209, January 2017.
- [7] H. Zhang, H. Nie, D. Yu, C. Wu, Y. Zhang, C. J. B. White, and L. Zhu, "Surface modification of electrospun polyacrylonitrile nanofiber towards developing an affinity membrane for bromelain adsorption," *Desalination*, vol. 256, no. 1-3, pp. 141-147, June 2010.
- [8] J. Tao, J. Xiong, C. Jiao, D. Zhang, H. Lin, and Y. Chen, "Cellulose/polymer/silica composite cotton fiber based on a hyperbranch-mesostructure system as versatile adsorbent for water treatment," *Carbohydrate Polymer*, vol. 166, pp. 271-280, June 2017.



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