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Evaluation of heavy metals removal by cross-linked (polyvinyl alcohol/chitosan/magnetic) nano fibrous membrane prepared by electro spinning technique

Katayoon Kalantari[a,b,*], Amalina M. Afiffi[a,b,*], Ariesman Salleh[a], Edzrol Niza Mohamad[a], Zahra Izadiyan[c]

[a]*Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia, email: katayoon@um.edu.my (K. Kalantari), Amalina@um.edu.my (A.M. Afiffi), ariesman@um.edu.my (A. Salleh), edzrol@um.edu.my (E.N. Mohamad)*
[b]*Centre of Advanced Materials (CAM), Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia*
[c]*Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, Kuala Lumpur, Malaysia, email: zahra.i6539@yahoo.com (Z. Izadiyan)*

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ABSTRACT

In this study, chitosan/polyvinyl alcohol (PVA)/magnetic nano fibrous membrane was fabricated via electro spinning. First, magnetic nano particles with average size of 7.98 nm, were fabricated using co-precipitation method. Then, chitosan solution was blended with aqueous PVA solution in different weight ratios. The electro spun fibers were kept in a glass desiccator saturated with (50% aqueous solution) of glutaraldehyde vapor for 24 h. Morphological analysis of chitosan/PVA electro spun nano fibrous showed a defect-free nano fiber material with 50:50 weight ratio of chitosan/PVA. Subsequently, 1 wt.% of magnetic nano particles was added to 50:50 chitosan/PVA solution and then, fine bead free nano fibrous electro spun was fabricated. The resulting nano fiber was characterized with field emission scanning electron microscopy, energy dispersive X-ray spectroscopy, X-Ray diffraction, Fourier transform infrared spectroscopy, swelling test, and adsorption test. The resulting membrane was stable in distilled water, acidic, and basic media overnight. Moreover, the adsorption ability of nano fibrous membrane was studied over Cr^{6+}, Pb^{2+}, and Ni^{2+} ions. Kinetic parameters were estimated using the first-order and pseudo-second-order models. Kinetic study showed that adsorption rate was high. Therefore, chitosan/polyvinyl alcohol (PVA)/magnetic nano fibrous membrane can be a useful material for water treatment at moderate concentration of heavy metals.

Keywords: Chitosan; PVA; Magnetic nano particles; Electro spinning; Heavy metals adsorption

1. Introduction

Water pollution by heavy metals causes a major problem throughout the world and their removal from water resources is a real challenge [1,2]. Their toxicity, non-biodegradability and carcinogenicity are dangerous problems for human health and other living organisms [3] Ni^{2+}, Pb^{2+} and Cr^{6+} are common heavy metals that can be found in water due to rapid industrialization. Numerous techniques have been used for metal ions removal from aqueous solutions [4]. The most commonly used methods are coagulation/precipitation, liquid-liquid extraction, membrane separation and adsorption. Among these techniques, adsorption is greatly used as an economical and efficient method for removal of heavy metals from aqueous solutions [5], but in adsorption process, regeneration of adsorbent in one of the most difficulty. Recently, electro spinning is attracting the researcher's attention to overcome the problems and make them a suitable candidate for adsorption of heavy metals. This type of membrane offers excellent properties,

*Corresponding author.

such as tunable pore size, porosity and high surface to volume ratio [6,7]. In the last few decades, the feasibility of low-cost biomass application for removal of heavy metals has been studied, for example chitosan [8,9] and so on. Chitosan is one of the most accepted biopolymer which usually obtained from biomass through processing the shells of prawns, shrimp and crabs [10]. Chitosan has been widely applied as bio-sorbent for heavy metal removal and has two (–OH) side groups and one NH_2 group which may act as active functional groups for chelating metal ions [11]. However, there are some disadvantages with pure chitosan such as low mechanical strength and poor chemical resistance [12]. Mixing of two polymers has become a significant method for improvement these disadvantages and performance of polymer [13–15]. Poly vinyl alcohol (PVA) is a good candidate for blending with chitosan due to its excellent mechanical property and chemical resistance and also good biodegradability [16]. PVA makes specific intermolecular interactions (hydrogen bonds) with hydroxyl and amino groups of chitosan. Chitosan/PVA blend has received attention for removal of heavy metals due to its good mechanical and chemical properties [17]. Magnetic (Fe_3O_4) nano particles have been used as a promising filler to prepare several types of nano materials because of its high adsorption capability within short time [18,19]. To improve the adsorption capacity and recovery properties of chitosan/PVA polymer, magnetic nano particles have been added to blend for significant removal of heavy metals from water. The objectives of the present study were fabrication and characterization of PVA/chitosan/magnetic nano fibrous membrane using electro spinning technique. Moreover, its application for removal of heavy metals from aqueous media was investigated.

2. Experimental

2.1. Materials

Chitosan (Mw = 8.96 × 10^5 g/mol, DDA = 40%) and PVA (Mw = 60000, degree of hydrolysis = 89%) were obtained from SE Chemical Co. Ltd and Kuraray Co. Ltd. (Tokyo, Japan) respectively. $FeCl_3{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$ (96%) were purchased from GPR (USA). NaOH (99%) and Glutaraldehyde (Mw = 100·12) were from Merck (Germany) and R&M chemicals. $K_2Cr_2O_7$, $NiCl_2$ and $Pb(NO_3)_2$ were supplied by Hamburg Chemical. All aqueous solutions were prepared with deionized water.

2.2. Methodology

Experimental work was divided into two major parts: synthesis of magnetic nano particles using co-precipitation method, and fabrication of chitosan/PVA/magnetic electro spun nano fibrous membrane.

2.2.1. Synthesis of magnetic nanoparticles

For the synthesis of magnetic nano particles, measured amount of Fe^{3+} and Fe^{2+} with molar ratio adjusted to 2:1, were added to 50 ml of deionized water. 15 ml of fresh NaOH (2.0 M) was added to Fe^{3+} and Fe^{2+} suspension under continuous stirring and in a non-oxidizing oxygen-free environment. The final product was centrifuged, washed and kept at 100°C.

2.2.2. Solution preparation

First, PVA (8 wt.%) was dissolved in distilled water at 70°C. Then chitosan solution (7 wt.%) prepared separately with concentrated acetic acid was added to aqueous PVA. Chitosan solution was blended with aqueous PVA solution in weight ratios of 50:50, 60:40, 70:30, 80:20 and 90:10. These solutions were named as B_1, B_2, B_3, B_4, and B_5. All mixtures were stirred for 24 h.

2.2.3. Fabrication of chitosan/PVA and chitosan/PVA/magnetic nanofibrous membrane

Electro spinning schematic is presented in Fig. 1. It consists of a high voltage power supply 25 kV (LD Didactic GmbH, Germany), syringe pump NE-300 (New Era Pump Systems, NY, USA), and stationary collector.

Electro spinning of B_1, B_2, B_3, B_4, and B_5 solutions were performed under the following conditions: 19 gauge needles, 10 cm tip to collector distance, 0.1–0.4 m L h^{-1} feed rate, 12–18 kV voltage. The blend with 50:50 ratio (B_1) used for magnetic nano particles addition due to its defect free morphology that is shown in the results and discussion part. About 1 wt.% of magnetic nano particles was stirred with B_1 solution. Finally, electro spinning was performed under the same condition. The electro spun fibers were kept in a glass desiccator saturated with (50% aqueous solution) of glutaraldehyde vapor for 24 h.

2.3. Characterization

The morphological study of fabricated membrane and magnetic nano particles was done by using field emission scanning electron microscope (FESEM, JEOL JSM-7600F, Akishima, Japan) and transmission electron microscopy (Hitachi Ltd Tokyo, Japan). The elemental composition of nano fibrous membrane was analyzed by X-ray energy dispersive spectroscopy (EDS) (IE 300X, Oxford, UK).

Fourier transfer infrared (FTIR, Nicolet iS10, Thermo Scientific) was applied to determine the composite chemical structure and bonding among membrane materials. The

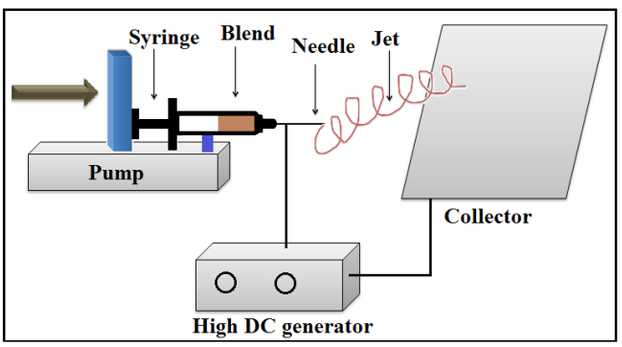

Fig. 1. Electro spinning set up schematic.

X-ray diffraction (XRD, PAN analytical Empyrean, USA) was conducted to observe the overall crystallinity of the magnetic nano particles and nano fibrous composite membrane. The tensile properties of samples were investigated by a tensile machine (Instron Universal Testing Machine model INSTRON 4302) with cross head speed of 5 mm/min. The reported results represented average results of five tests.

2.3.1. Swelling test

The swelling test was applied for durability determination of nano fibrous. In this research, basic (pH = 10), acidic media (pH = 3), and distilled water (pH = 7) were used for this purpose. Firstly nano fibrous membrane samples were weighted and then immersed in mentioned media overnight. Then, the samples dried at 105°C for 24 h and weighted. The swelling ratio (S_w) was measured using the following equation [20]:

$$S_w = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

2.3.2. Adsorption study

The adsorption behavior of chitosan/PVA/magnetic nano fibrous membrane was evaluated on Cr^{6+}, Pb^{2+}, and Ni^{2+}. About 0.1 g of membrane was immersed in 20 mL of $K_2Cr_2O_7$, $NiCl_2$ and $Pb(NO_3)_2$ solutions by using a magnetic stirrer. The initial concentration of heavy metals ranged between 25–250 mg/L. The pH of the solutions was not changed to prevent precipitation. The concentration of solutions was analyzed after different time intervals and measured by using flame atomic adsorption spectrometer (Thermo scientific, S series). The amount of heavy metals adsorbed by membrane was calculated by using the following equation:

$$q_t = \left(\frac{C_0 - C_t}{m}\right) V \quad (2)$$

where V is the volume of solution (L), and m is the membrane weight (g), C_0 and C_t are the initial and equilibrium heavy metals concentrations (g/L) respectively [21].

3. Results and discussion

3.1. Morphology study

Figs. 2A,B demonstrate TEM image and size distribution of magnetic nano particles. The mean diameter and standard deviation of spherical shape magnetic nano particles was about 7.89 ± 0.32 nm. The macroscopic appearance of the electro spun membranes is shown in Fig. 2C. It can be seen that the color of the nano fibrous membranes changes from white to brown as the magnetic nano particles loaded successfully. The surface morphology of the chitosan/PVA and chitosan/PVA/magnetic nano fibrous membranes are observed in Fig. 3. Defect-free nano fiber was obtained from the electro spinning of B_1 (50:50) solution. For B_2 and B_3, the significant changes in morphology were observed such as irregular shape and bead formation. It was clear that both the size and number of beads increase in B_4 and B_5.

The bead formation affected by some parameters including low viscosity, high surface tension, high applied voltage and low molecular weight.

It seems that the formation of beads is strongly influenced by the solution viscoelasticity. Beads and beaded fibers are high likely to be formed in low viscous solutions [6,22]. According to Table 1, the applied voltages for B_2, B_3, B_4, and B_5 solutions were higher than that of B_1, which might be the reason of beads formation with chitosan increasing content in the blend. Moreover, the protonation of chitosan amino group, leads to viscous solution and would be the reason of high voltage needed to get the stretched jet [23]. Based on findings presented in Fig. 3, uniform and most suitable fibers obtained from chitosan/PVA (50:50) ratio (B_1).

The morphology of electro spun chitosan/PVA/magnetic nano fibrous membrane was also studied using FESEM (Fig. 4A). The surface of membrane looks brighter due to the incorporation of magnetic nano particles in the nano fibrous. Magnetic nano particles were distributed uniformly over the nano fiber surface and is the reason of rough and porous surface fabrication [24]. The magnetic nano particles as a filler cause an increment in viscosity and viscoelastic force, which hamper the surface tension of the chitosan solution to be electro spun [6,24], consequently, the

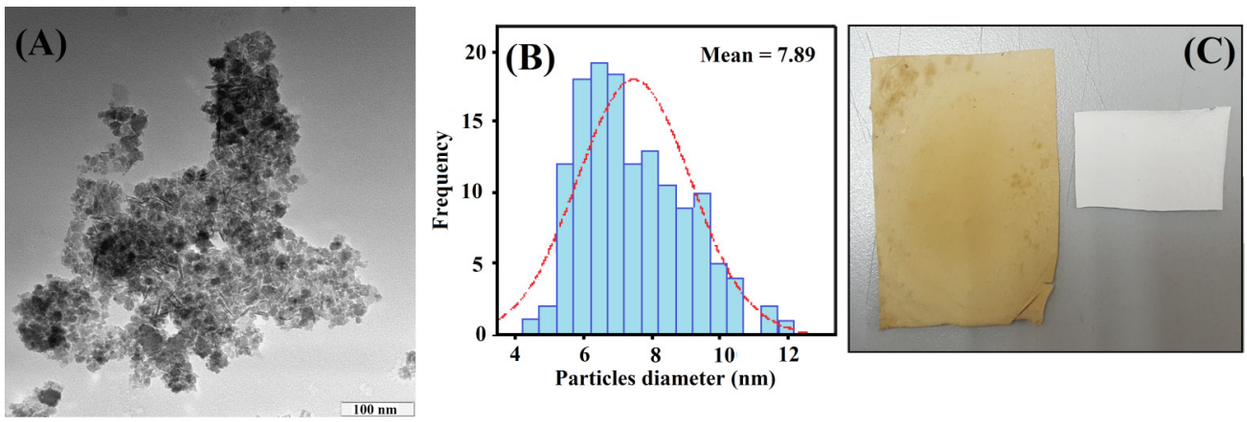

Fig. 2. TEM image (A), size distribution histogram of magnetic nanoparticle (B) and color of membranes (C).

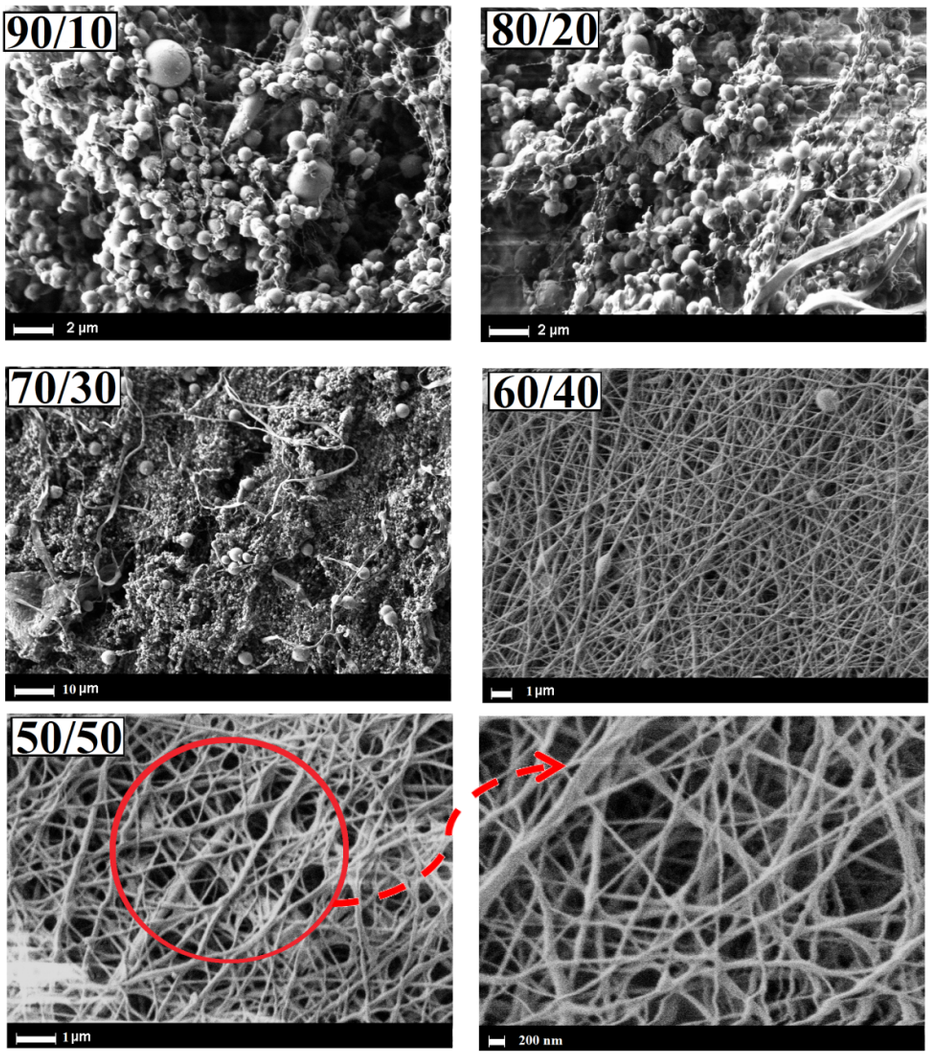

Fig. 3. (FESEM) image of nanofiber membrane with different ratio of PVA and chitosan.

Table 1
Applied conditions of the blended solutions

Sample	Product type	Flow rate (mL·h^{-1})	Voltage (kV)
B_1	Fibers	0.40	12
B_2	Fibers	0.30	13
B_3	Mostly particles	0.20	14
B_4	Particles	0.15	16
B_5	Particles	0.10	18

bead formation decreases [25]. A strong bonding has been made between Fe-O group with negative charges and protonated chitosan by an electrostatic interaction and chemical reaction through glutaraldehyde cross linking [26].

The elements on the surface of membrane were analyzed by EDS (Fig. 4B). EDS analysis was applied to confirm the presence of iron in the membrane. The EDS spectra of the membrane showed the peaks of O, C, N and Fe which were four major constituents of chitosan/PVA/magnetic nano fibrous membrane, confirming the existence of PVA, chitosan and magnetic nano particles.

A comparison between Fig. 4A and Figs. 5A–C shows the change in the morphology of membrane after heavy metals adsorption. It can be seen that the membrane structure is a little deformed after the heavy metals adsorption.

3.2. XRD analysis

Fig. 6 shows the XRD patterns of chitosan/PVA/magnetic nano fibrous membrane. A significant peak at approximately 19.3, in pure PVA is due to the occurrence of strong inter- and intra-molecular hydrogen bonding [22]. Six characteristic peaks of magnetic nano particles appeared at the (2θ = 30.20, 35.58, 42.95, 53.83, 57.42, and 62.93) which were corresponding to the (220), (311), (400), (422), (511) and (440) crystal planes of pure

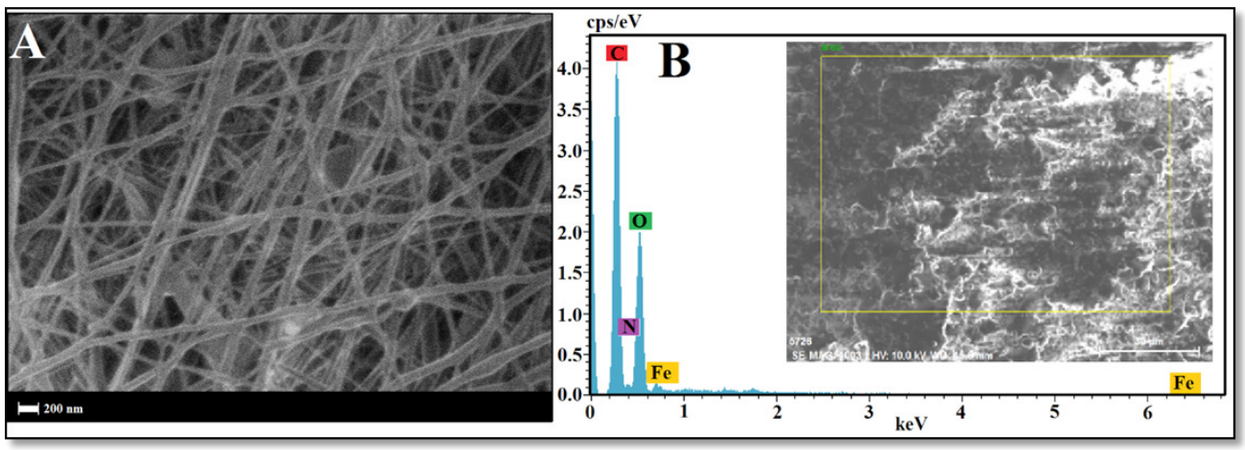

Fig. 4. FESEM image (A) and EDS spectra (B) of chitosan/PVA/magnetic nanofiber membrane.

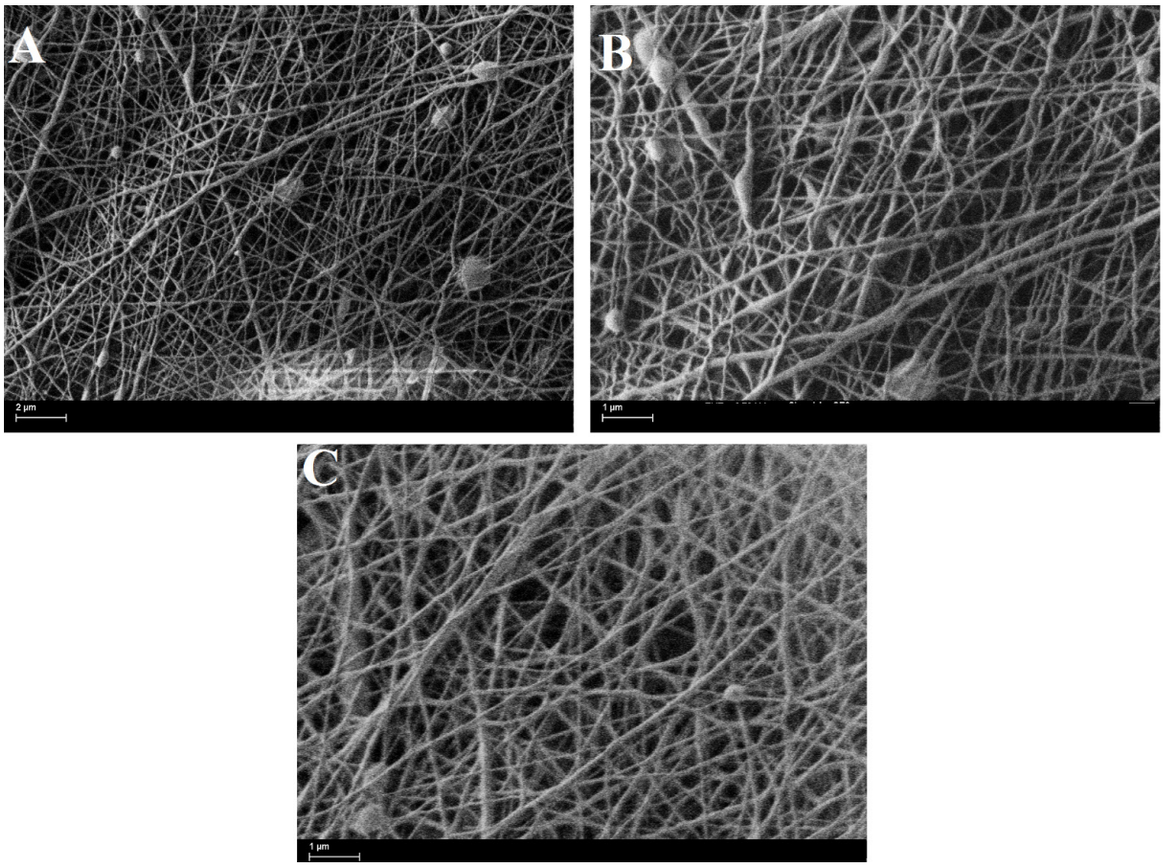

Fig. 5. FESEM images of membrane after adsorption of Pb^{2+} (A), Ni^{2+} (B), and Cr^{6+} (C).

magnetic nano particles with a spinel structure, respectively [8]. Moreover, the chitosan peaks around 10° and 20° and PVA peaks around 19.3° and 39° became weak in the membrane. This result indicated the magnetic nano particles have been incorporated successfully in the m embrane without damaging the crystal structure of nano particles.

3.3. FTIR

To determine the mechanism of bindings, FTIR spectra of the naked PVA, chitosan/PVA, chitosan/PVA cross linked and chitosan/PVA/magnetic nano fibrous membrane were examined as shown in Fig. 7. The broad band from 3500 to 3200 cm^{-1} revealed the existence of $–NH_2$ and –

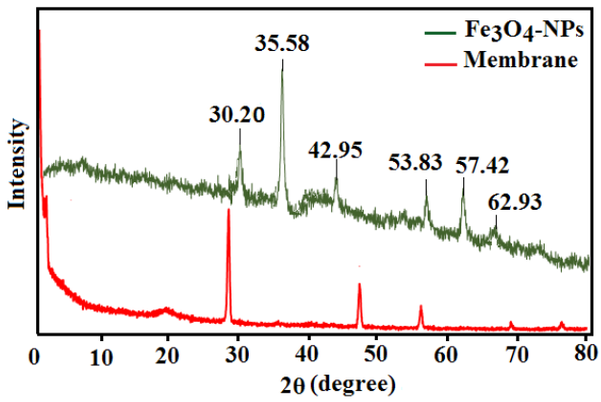

Fig. 6. X-ray diffraction (XRD) spectra of magnetic nano particles and chitosan/PVA/magnetic nano fibrous membrane.

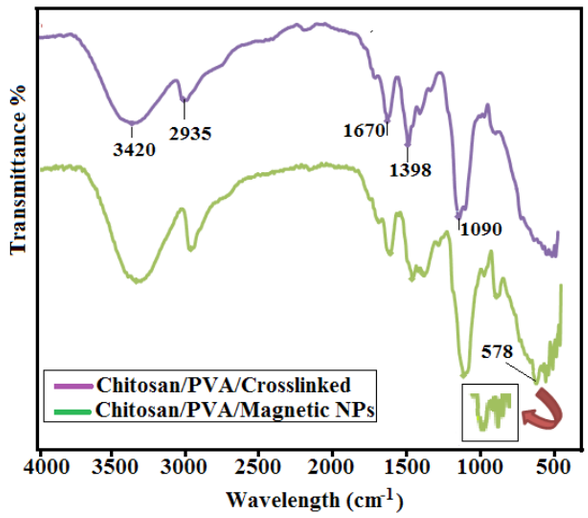

Fig. 7. FTIR spectra of chitosan/PVA cross linked, chitosan/PVA/magnetic NPs membrane.

OH stretching vibrations [27]. The peak at 2935 cm^{-1} was related to the stretching of –CH– group [28]. The peak at 1670 cm^{-1} assigned to the carbonyl stretching. The peak at 1398 cm^{-1} corresponded to –NH deformation vibration. The adsorption band at 1090 cm^{-1} indicated the stretching vibration of the C=O group [27,29]. The new peak appeared at 578 cm^{-1}, which is related to Fe–O group and indicates that the magnetic nano particles was coated by chitosan [29,30] . It could be seen that all related peaks of chitosan/PVA cross linked were also present in the spectrum of membrane. This result indicated that chitosan/PVA was coated on magnetic nano particles and the membrane was prepared successfully.

3.4. Swelling test

Amine groups of chitosan make it hydrophilic and cross linking improves the swelling property of membranes and enhance their perm-selectivity and stability [31]. Swelling test was carried out for overnight in distilled water, acidic and basic media on chitosan/PVA/magnetic nano fibrous membrane. Experiments were repeated two times. All media showed no changing in weight and no aggregation. Cross linking should be necessary to reinforce the chemical stability of membrane [32].

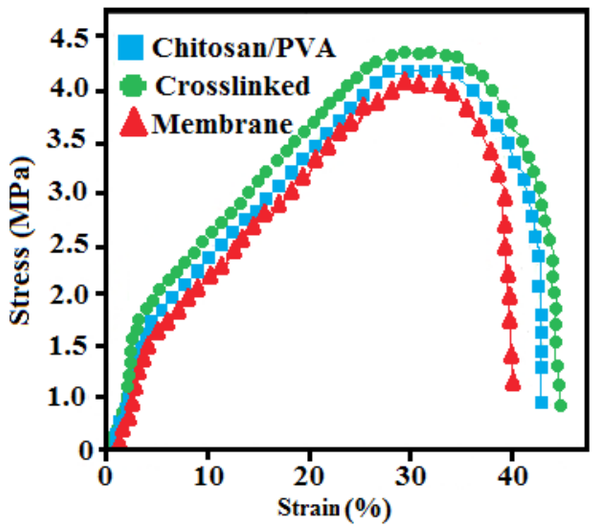

Fig. 8. Typical stress–strain curves of the chitosan/PVA, chitosan/PVA cross linked and chitosan/PVA/magnetic nano fibrous membrane.

3.5. Mechanical properties

Fig. 8 shows typical stress–strain curves of membranes. It was observed that by glutaraldehyde cross linking, the chitosan/PVA membrane became rigid with less flexibility due to covalently chains linkage [33], and its ultimate tensile strain decreased. The result was similar to the effect of cross linking on mechanical properties of PLGA–chitosan/PVA and chitosan/collagen blends [34,35]. Based on obtained results, glutaraldehyde cross linking improved tensile strength and decreases tensile strain of the membrane.

Moreover, Fig. 8 made it clear that the chitosan/PVA magnetic nano fibrous membrane exhibited no significant difference on the average ultimate tensile stress and ultimate strain. These results are same as reported results in Wei et al., published research [36].

3.6. Adsorption study

3.6.1. Adsorption kinetics

The kinetic parameters are helpful for investigation the adsorption mechanism and also adsorption rate, which gives important information about the efficiency of adsorption. Two most commonly kinetic models, pseudo-first and second-order (Fig. 9), were used to analysis the experimental data to understand the dynamics of the adsorption process and their kinetic model equations are expressed as [37]:

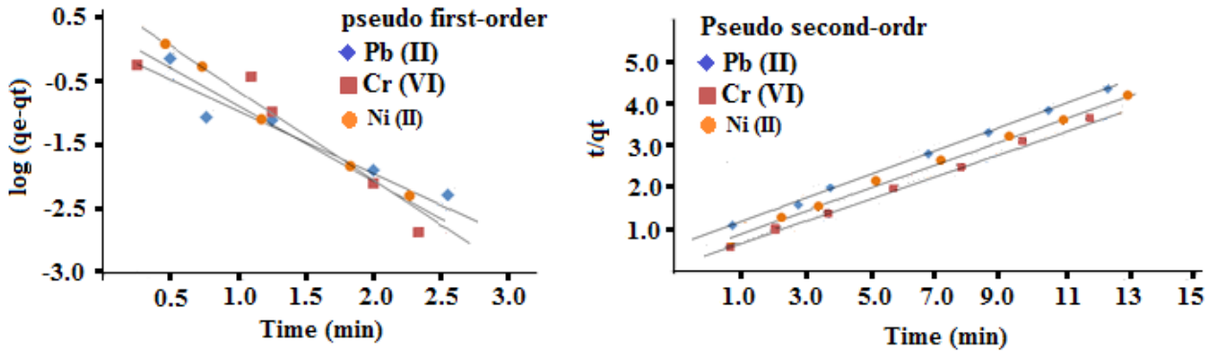

Fig. 9. Kinetic study of heavy metal ions.

Table 2
Kinetics parameters for adsorption of cations on membrane

	Pseudo first-order			Pseudo second-order		
Cation	q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2	R^2
Ni (II)	4.96	0.059	0.946	12.506	0.005	0.999
Pb (II)	1.01	3.994	0.755	25.65	0.002	0.997
Cr (VI)	6.69	0.076	0.366	15.50	0.001	0.995

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) \tag{4}$$

where k_1 is the pseudo-first-order rate constant of adsorption (h^{-1}); k_2 is the pseudo-second-order rate constant of adsorption (g/mg h); and q_e is the ion adsorption amounts at equilibrium and q_t is the ion adsorption amounts at any time, (mg/g). The slopes of the linear equations can be used for calculation the values of k_1 and k_2 [29]. The correlation coefficient (R^2) and rate constants of the kinetic models are listed in Table 2.

Based on the obtained R^2, the kinetic experimental data could be fitted better by pseudo second order adsorption and indicates that adsorption process was dependent on ion concentration, and chemical sorption involving valence forces through electron sharing or exchange between adsorbent and adsorbate was the rate-controlling step [38].

From Table 2, due to very low values of correlation coefficients (R^2), the pseudo-first-order model was not suitable to interpret the adsorption mechanism. In this model, (R^2) for heavy metal ions vary in the range of 0.36–0.94.

Chitosan has one amino group and two hydroxyl groups per unit of glucosamine [39]. It was assumed that the oxygen atom of the hydroxyl groups in both PVA and chitosan and nitrogen atom of amino group in chitosan acted as heavy metal ions adsorption sites. Oxygen and nitrogen atoms have lone pair of electrons which can be bind with positively charged ions through the sharing of electron pair. The nitrogen atoms can release lone pair electron easily and it makes them the main binding site to form stable metal complexes [40]. Moreover, magnetic nano particles have high surface area and increase the ability of membrane in heavy metal adsorption. It is well known that electrostatic attraction and coordination, between metal ions and adsorbent is the adsorption mechanism and magnetic nano particles plays significant role in this process [3].

3.6.2. Adsorption isotherms

The adsorption data were analyzed with the help of derived linear form of Langmuir isotherm and Freundlich isotherm models, expressed by the Eqns. (5) and (6), respectively. The adsorption isotherm models describe the interaction of adsorbate with adsorbents. Langmuir Isotherm uses to describe the adsorption on completely homogeneous surfaces with negligible interaction between adsorbed molecules. It is represented as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \tag{5}$$

where q_e is the equilibrium adsorption capacity of ions on the adsorbent (mg g^{-1}), C_e is the equilibrium ions concentration in solution (mg L^{-1}), q_m is the maximum capacity of the adsorbent (mg g^{-1}) and b is the Langmuir adsorption constant (mg L^{-1}) [41].

Freundlich isotherm can be applied for heterogeneous surfaces and multilayer sorption. It is expressed as:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

where K_F and n are the Freundlich constant (mg L^{-1}) and heterogeneity factor respectively. Meanwhile, equilibrium capacity q_e and C_e are defined as above [42].

Langmuir isotherm describes that intermolecular forces decrease rapidly with distance and thus lead to the coverage of adsorbent by mono layer of adsorbate. Moreover, it is expected that once an adsorbate ions occupy the adsorbent available sites, no more adsorption take place at that site [40,43]. On the other hand, in Freundlich model, it is assumed that the heterogeneous system and reversible adsorption and not restricted to the mono layer formation [44].

By plot of obtained data into linearized form of Langmuir and Freundlich isotherms, various R^2 and constant are presented in Table 3. Based on the R^2 values, the linear form

of the Langmuir isotherm appears most suitable model for the adsorption of heavy metal ions onto chitosan/PVA/magnetic nano fibrous membrane. The Langmuir isotherm of Ni^{2+}, $Pb^{2+}$and Cr^{6+} ions is shown in Fig. 10.

3.6.3. Effect of initial concentration of adsorbate

One of the most important parameter in adsorption process is the initial concentration of adsorbate. In this study, we have varied the initial concentration of the adsorbate from 25 to 250 mg/L. The batch experiments were carried out at room temperature by using 20 ml of heavy metals solutions and adsorbent dose of 0.1 g. Fig. 11 shows the effect of initial concentration on the removal of heavy metal ions. Chitosan/PVA/magnetic nano fibrous membrane was an effective adsorbent over a wide range of heavy metal ions. It is observed from this Fig. that the removal percentage of heavy metal ions decreased with the increment in the initial concentration of heavy metal ions. At higher concentration, the available adsorption sites on the chitosan/PVA/magnetic nano fibrous membrane are decreased [6,44].

The maximum removal of Pb^{2+} was 100% at 25 mg/L and lowest was 60% at 250 mg/L. The highly favourable active sites were involved in the removal process of Pb^{2+}. The maximum and minimum removal of Cr^{6+} was 98% and 39% at 25 and 250 mg/L respectively. According to this figure, the adsorption efficiency started to drop after reaching around 125 mg/L. In the case of Ni^{2+}, the maximum removal percentage was almost 100% at 25 mg/L and the

Table 3
Isotherm parameters for adsorption of cations on membrane

	Freundlich constants			Langmuir constants		
Cation	K_F (mg g^{-1})	n	R^2	q_m (mg g^{-1})	b	R^2
Ni (II)	1.22	3.52	0.93	4.34	0.294	0.98
Pb (II)	3.98	1.85	0.92	24.66	0.005	0.97
Cr (VI)	1.78	1.206	0.91	33.67	0.036	0.99

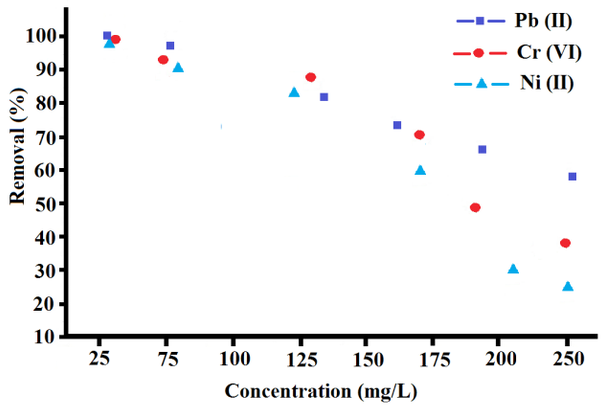

Fig. 11. Effect of initial concentration of heavy metals on removal percentage.

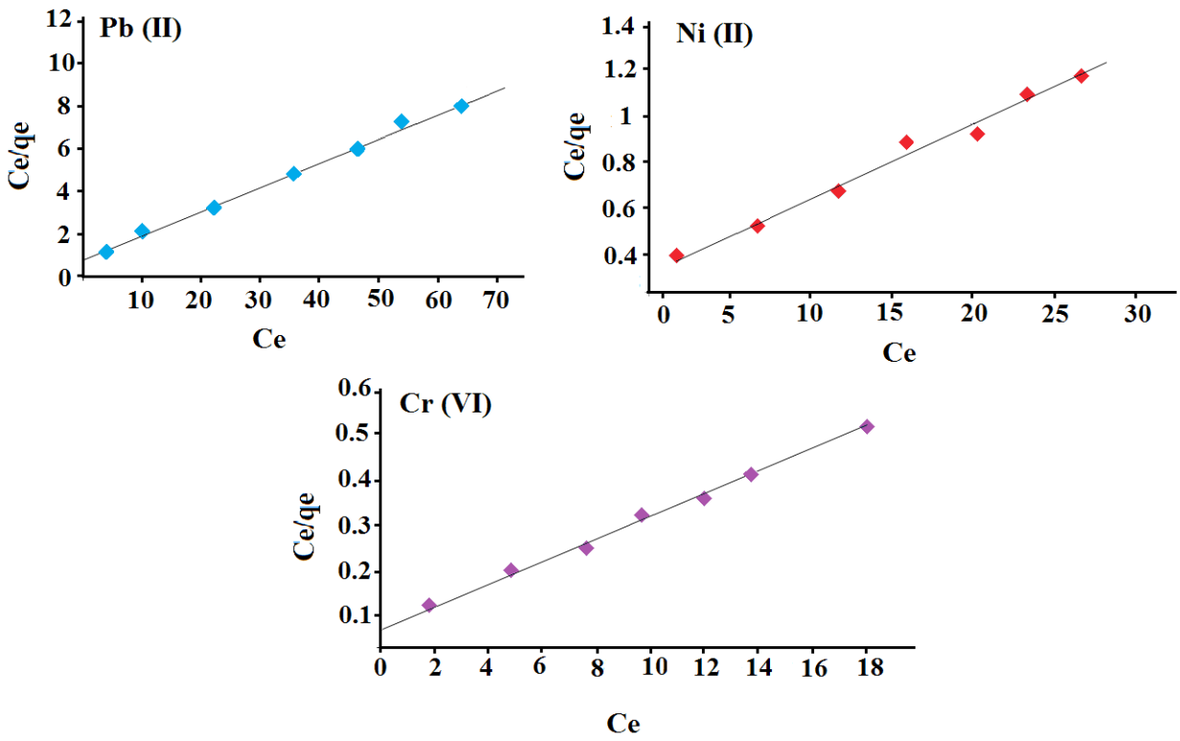

Fig. 10. Langmuir adsorption isotherm of chitosan/PVA/magnetic nanofibrous membrane.

lowest was 22% at 250 mg/L. The selectivity sequence of $Pb^{2+} > Cr^{6+} > Ni^{2+}$ adsorption was observed on nano fibrous membrane. The differences in the radius of Cr^{6+}, Ni^{2+} and Pb^{2+} ions have significant influence on adsorption efficiency. The heavy metal removal efficiency followed the decreasing order: $Pb^{2+} > Cr^{6+} > Ni^{2+}$. Since the radius of Pb^{2+} (1.32 Å) is noticeably bigger than Ni^{2+} (0.69 Å) and Cr (VI) (0.52 Å) and the hydration of Pb^{2+} is more difficult compared to Cr^{6+} and also forming a larger water layer on the surface. As a result, Ni^{2+} and Cr^{6+} are more moving in solution and would have a lesser tendency to adsorb on the membrane [3]. Moreover, charge density decreases with increasing the heavy metal ionic radius, so the availability of active sites to react with nano fibrous membranes for adsorption of heavy metals also decreases. This process leads to decreasing adsorption capacity of different heavy metal ions through increasing the ionic radius [6,45].

4. Conclusion

In this research, chitosan/PVA/magnetic electro spun nano fibrous membrane was successfully fabricated via electro spinning technique. The nano fibrous membrane was characterized with FESEM, XRD, EDX, FTIR spectroscopy, swelling test, and adsorption test. The adsorption capacity of nano fiber was studied over Cr^{6+}, Pb^{2+}, and Ni^{2+} ions in different initial concentrations. The resulting nano fibrous membrane showed stability in distilled water, acidic, and basic media overnight swelling experiment. Equilibrium isotherm data fitted well with Langmuir isotherm data. The heavy metal ions adsorption can be well described by the pseudo-second-order kinetic model. The adsorption rate was significantly high and the results showed the efficient adsorption at moderate heavy metal ions concentration. Finally the metals affinity to the nanofibrous membrane was found to be in the sequence of $Pb^{2+} > Cr^{6+} > Ni^{2+}$.

Acknowledgment

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