Removal of nickel and cadmium heavy metals using nanofiber membranes functionalized with (3-mercaptopropyl)trimethoxysilane (TMPTMS)

Saeed Reza Zahabi, Seyed Abdolkarim Hosseini Ravandi and Alireza Allafchian

ABSTRACT

Functionalized nanofibrous membranes have been produced via electrospinning with a polymer solution of 19% (w/w) of nylon 66 prepared in a formic acid/chloroform mixture (75:25 v/v). The optimum parameters of electrospinning, like voltage, flow rate, tip and collector distances, were achieved and produced nanofiber membranes with a thickness of 287 nm. Then the nanofiber membranes were functionalized by (3-mercaptopropyl)trimethoxysilane (TMPTMS) at various amounts. Three different initial concentrations of metal ions and three different levels of pH were chosen. The effect of filtration process parameters such as the initial concentration of metal solution, pH of the solution, and the amount of functionalizer trimethoxysilane (TMPTMS) on the adsorption was studied. In surveying filtration process parameters, the results showed that metal ion rejection increased by increasing the pH of the solution and decreased by increasing the initial concentration of the effluent. By increasing the amount of functionalizer, removal efficiency increased. The results showed that the maximum efficiency of absorption of cadmium and nickel were 93.0 and 97.6%, respectively, and the filtering mechanism of the membrane is the blocking pores type. The adsorption data of cadmium and nickel ions fitted particularly well with the Freundlich isotherm.

Key words | (3-mercaptopropyl)trimethoxysilane, adsorption, cadmium, heavy metals, membranes, nickel

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INTRODUCTION

With the rapid development of global industry and new technologies, environmental pollution threatens human health and unintentionally gives an unpleasant gift to society, which is wastewater. Especially in recent years, increasing amounts of heavy metal ions in wastewater and heavy metal pollution has become a very serious issue, and many researchers are trying to solve it using wastewater filtration (Lin *et al.* 2011; Chen & Wang 2014).

Heavy metal ions are widespread, typically in concentrations less than 1 mg/L in surface water resources, and they are stable and persistent environmental contaminants (Zolotov *et al.* 1987; Srivastava & Majumder 2008; Fu & Wang 2011). Heavy metals such as cadmium, nickel, chromium, cobalt, lead, copper and mercury are types of environmental pollutants that cause serious human diseases. The main effects of cadmium toxicity are on the lungs, kidneys and bones. Cadmium reduces resistance to bacteria and viruses and may cause increased bone fragility. In the same way, nickel causes similar problems such as allergies, cancer and respiratory disorders (Iqbal *et al.* 2007).

Finding a simple and low cost process to remove heavy metals from aqueous solutions is considered. In selecting a suitable removal method, it should completely evaluate the

doi: 10.2166/wh.2016.267

method efficiency, access to equipment, construction and energy costs, and consider environmental issues.

Nanofibrous membranes have some benefits such as low energy consumption, mass transfer, low volume, they do not occupy much space, variations in size and shape, high efficiency, low pressure drop, ease of use, low need for additives and solvents and ease of handling on an industrial scale, so they play a key role in wastewater removal technology (Fane 1996; Fane *et al.* 2005; Chegoonian *et al.* 2012).

Depending on the performance, the membrane separation process has different types, one of which uses nanofibrous materials. Fibers with a diameter of less than 1 micrometer are generally classified in the nanofiber category (Subbiah *et al.* 2005). Nanofibers have unique properties such as high porosity, high surface to volume ratio and the ability to functionalize the surface (Huang *et al.* 2003). Among all the surface functionalizers, (3-mercaptopropyl)-trimethoxysilane (TMPTMS), which is an organosilane, has a high absorption capacity for heavy metal ions, especially cadmium and nickel.

In recent years several researchers (Yang *et al.* 2010; Irani *et al.* 2011; Abbasizadeh *et al.* 2013) have worked on the removal of heavy metal ions from water and wastewater by using a TMPTMS functionalizer with different polymers.

The aim of this work is to use TMPTMS as the functionalizer and nylon as the nanofiber to improve the adsorption capacity and decontaminate wastewater containing Ni and Cd ions. In order to achieve this, nylon 66, which has good interaction with TMPTMS, was chosen and the electrospinning parameters were almost optimized. In addition, the adsorption isotherms were investigated.

METHODS

Materials

Ethanol, CH_3COOH, $CHCl_3$, NaOH, HCl, Nickel(II) nitrate and cadmium nitrate were supplied by Merck (Germany). TMPTMS was obtained from Sigma Aldrich (USA). Solid state polymerized PA66 (SSP PA66) was purchased from Zanjan Tire Cord Co. (Iran). Ultrapure water was used in the experiments.

Methods

Preparation of nylon 66 solution

Nylon 66 granules were dissolved in a formic acid/chloroform mixture by volume ratio of 75:25 v/v at room temperature with vigorous stirring at a speed of 150–200 rpm for at least 24 hours to prepare 19 wt.% nylon 66 solution.

The concentrations of polymer solution play an important role in the fiber formation during the electrospinning process. As the concentration is very low, electrospray occurs instead of electrospinning owing to the low viscosity and high surface tension of the solution (Deitzel *et al.* 2001). Also, in low concentration the web production rate and thickness is low. As the concentration increases slightly, a mixture of beads will be obtained. When the concentration is suitable, smooth nanofibers can be obtained (Eda & Shivkumar 2007). In this article we selected a solution by 19 wt% of nylon 66.

Electrospinning of nylon 66

The prepared nylon solution was added to the syringe, which was then placed on the pump. The jet of polymer solution with a constant feed rate (0.314 mL/h) under 12.5 kV voltage was collected on the rotary drum in the form of a nanofiber web. The duration of electrospinning was 16 hours, and the distance between the syringe needle and collector was 15 cm. All of the above electrospinning parameters were almost optimized after many experiments. Prior to use, the electrospun nanofibers were placed in a vacuum at room temperature (25 °C) to remove any trace of solvent.

Surface modification of nylon nanofibers with mercapto

There are several methods to functionalize the nanofiber surface. In this study, to produce three types of functionalizer concentration a mixture of three levels of TMPTMS solution (0.8, 1.7, 2.5 mL), water (8.1 mL), ethanol (5.2 mL) and 15 μL HCl in the molar ratio of 4:200:50:0.1 was prepared. The mixtures were then sonicated for 1.5 h and the solution sprayed on the surface of the nanofiber and dried for 24 h at room temperature. This mercapto-modified membrane has -SH functional groups, and it

causes chemical bonding to occur between fibers and heavy metals (Huang *et al.* 2014).

Membrane processing

Due to the low strength of nanofibers and the pressure effect during the filtration process, there is a need to build a platform in the membrane. Moreover, a support layer for nanofibers was utilized, as without it, the nanofiber layers were easily separated from the surface of the polyurethane mesh.

Filtration processing

In this study, two kinds of heavy metals, cadmium and nickel (Merck, Germany), were chosen. Three different initial concentrations of metal ions with values of 20, 50 and 80 ppm were used. Deionized water was used in the preparation of all solutions, and the filtration process was conducted at three different pH levels of 3, 5, and 7.

The surface area of the membrane was $12 \times 8\ cm^2$. The membrane process was operated in a recirculation mode. The feed stream was pumped to the membrane module and both the permeate and concentrate streams flowed back to the feed vessel during experiments. Aqueous solution flowed over the surface of the membrane in a cross flow mode to minimize the accumulation of heavy metal ions on the membrane. Figure 1 shows the filtration process schematically.

Before starting the experiments, the filtration set-up was washed with distilled water. After the filtration experiments, concentrations of Cd and Ni were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Perkin Elmer, USA). Filtration efficiency was determined by implementing the conventional definition of membrane rejection as follows:

$$Rejection = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t are the component concentration in the feed and permeate, respectively. In this research, the metal removal efficiency was measured for 60 minutes.

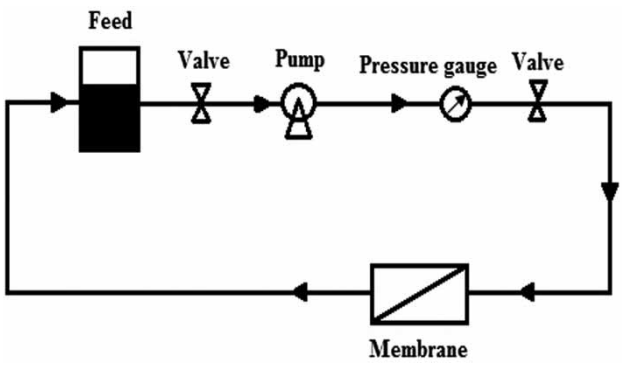

Figure 1 | Schematic representation of filtration process (Basiri *et al.* 2011).

Taguchi orthogonal design

Taguchi's techniques have been used widely in engineering design. The main importance of Taguchi's techniques is the use of parameter design, which is an engineering method for product or process design that focuses on determining the parameter (factor) settings producing the best levels of a quality characteristic (performance measure) with minimum variation (Taguchi 1993; Kumar Karna & Sahai 2012).

In this study, according to the multiplicity of factors that influence the filtration process and their interactions with each other, routine testing is expensive and time consuming. Hence, the Taguchi design was used to optimize process parameters. To analyze the results, a statistical measure of robustness called the signal-to-noise (S/N) ratio is used in the Taguchi method. Minitab (version 16) gives three different S/N ratios depending on the goal of the experiment including: larger is better, nominal is the best, and smaller is better. In all cases, we want to maximize the S/N ratio. In this work, the target was to maximize the efficiency of the filtration. So three main factors were chosen: (1) initial concentrations of metal ions, (2) solution pH, and (3) amount of functionalizer (TMPTMS). The L9 orthogonal array was chosen according to Taguchi's methodology. These factors were studied at three levels, as shown in Table 1.

RESULT AND DISCUSSION

Membrane properties

To observe the structure of nylon 66 nanofiber membrane, a field emission scanning electron microscope was used.

Table 1 | Experimental factor and their levels for Taguchi method

Sample	Initial pollutant concentration (ppm)	Amount of functionalizer (mL)	Solution pH
1	20	0.8	3
2	20	1.67	5
3	20	2.5	7
4	50	0.8	5
5	50	1.67	7
6	50	2.5	3
7	80	0.8	7
8	80	1.67	3
9	80	2.5	5

Then, 100 diameter of nanofiber was measured by the Digimizer software and the results are shown in Figure 2. The average diameter of the nanofibers obtained was 287 nm with a CV% of 69/22.

Attenuated total reflectance-Fourier transform infrared spectroscopy analysis

To prove the presence of functional groups after functionalizing of nanofiber membranes, and to determine the components, attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was used. The peaks in the graph of the spectrum were analyzed by OMNIC software. IR spectra of raw nylon 66 nanofibers and the modified nanofibers are shown in Figure 3. The IR spectrum of the raw nylon 66 nanofibers shows a broad bond at around 3,302.4 cm^{-1}, which was assigned to N–H stretching. This included 3,080.8 cm^{-1} (C–H asymmetric stretching), 2,928.5 and 2,860.8 cm^{-1} ($C–H_2$ asymmetric stretching), 1,733.4 cm^{-1} (C = O stretching), 1,642.2 cm^{-1} (Amid I bond), 1,542.1 cm^{-1} (Amid II bond) and 935.7 cm^{-1} (C–C).

The new peaks after the functionalization of nylon 66 by mercaptopropyltrimethoxysilane at 2560 (–SH) and 1,047.6, 1,112.3, 1,250.7 and 2,866.7 cm^{-1} ($Si–O–CH_3$) were added to the diagram. This showed that there was an interaction between nylon 66 and mercaptopropyltrimethoxysilane, and the membranes were functionalized.

The effect of time on filtration efficiency

In order to optimize the time of filtration, the applied pressure was 1.5 bar and the filtration process was conducted for a period of 120 minutes. As seen in Figure 4, the greatest part of metal removal occurred during the first 60 minutes. After this time, the thickness of the layer which was formed on the membrane surface became constant and filtration came to a steady state. Based on the achieved results, for the rest of the experiments an interval of 60 min was chosen.

Filtration process parameters

Effect of pH

The effect of pH is the most important parameter in the process of adsorption. The influence of this parameter is due to the interaction between nanofiber with heavy metal ions, hydrogen and hydroxide ions. Also, pH is effective on

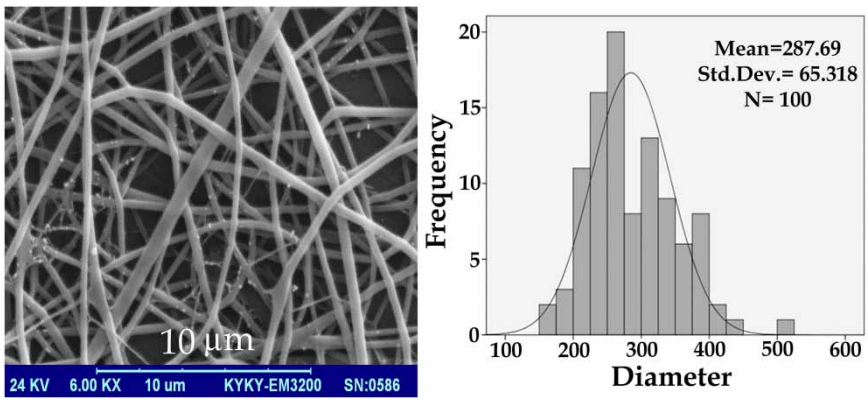

Figure 2 | Structure of nylon 66 nanofibers with the concentration of 19% with magnification of 6,000, and the histogram and normal curve.

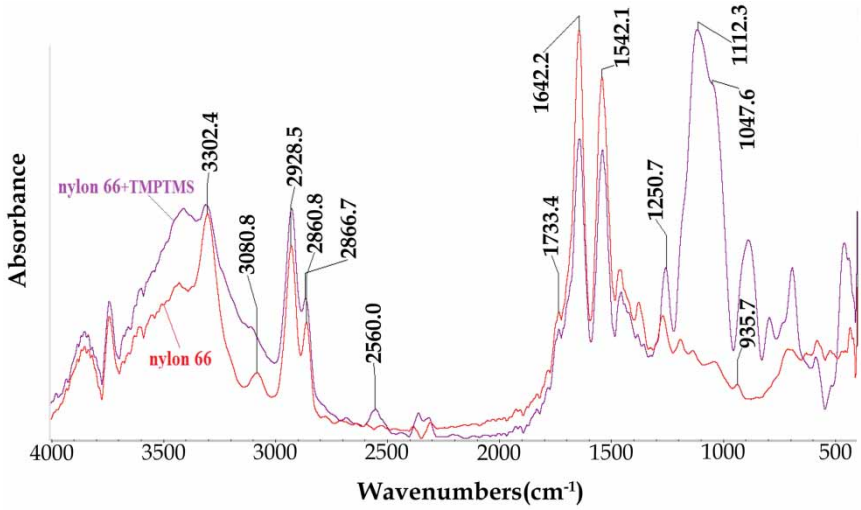

Figure 3 | FTIR spectra of nylon 66 and functionalized nylon 66/TMPTMS nanofibers.

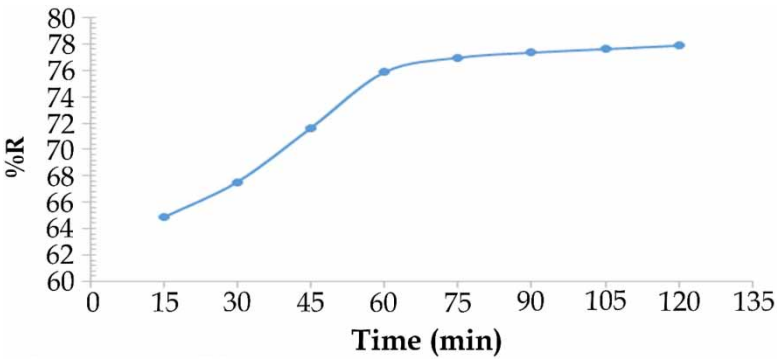

Figure 4 | The effect of time on the removal of heavy metals from the waste solutions in the filtration process.

chemical properties of metal solution, the activity of functional groups and ionic competition (Yan & Viraraghavan 2003). pH can influence the adsorption process, and change the surface charge of a membrane.

To investigate the effect of pH on filtration efficiency, different values were adjusted to minimize the precipitation of metal ions. In a pH range above 7, precipitation occurred in the cadmium and nickel solutions, so the experiments were not conducted beyond a pH of 7 (Montazer-Rahmati *et al.* 2011).

The effect of pH on the sorption of metal ions is shown in Figure 5. As can be seen, the adsorption capacity of cadmium and nickel onto the nanofiber is increased when raising the pH value from 3 to 7. The low values of cadmium and nickel adsorption capacity at lower pH values can be attributed to the partial protonation of the sulfone groups, which hinders the interactions between the adsorbent and metal ions. Also, at low pH values the surface of the sorbent would be closely associated with H_3O^+, which hinders the access of metal ions to surface functional groups such as −SH. As the pH increases from 3 to 7, the protonation of functional groups of electrospun nanofibers is reduced, which results in the active sites becoming increasingly ionized and the competition between hydrogen ion and metal ions decreasing, so the metal ions are adsorbed more (Shahram Forouz *et al.* 2016).

Effect of initial pollutant concentration

Experiments were carried out in different initial cadmium and nickel ion concentrations ranging from 20 to 80 mg/L. The

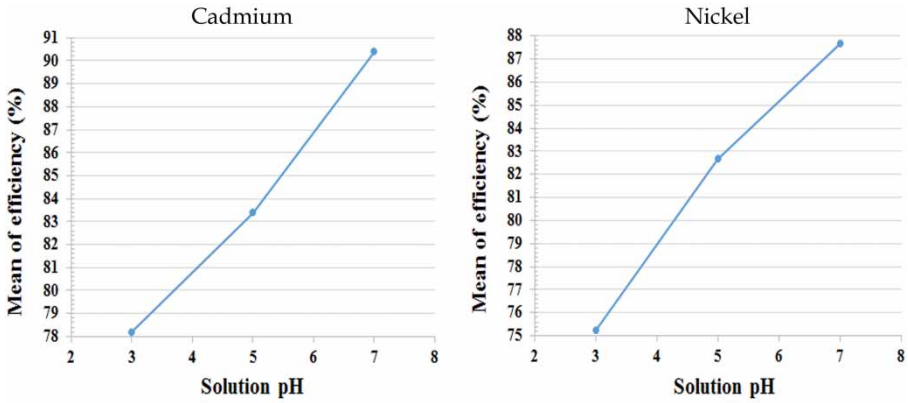

Figure 5 | Effect of pH on mean of efficiency for removal of Cd (left) and Ni (right).

initial metal ion concentration was one of the most important factors that determined the equilibrium concentration. The effect of Cd and Ni concentration on the efficiency of removal by varying the initial ion concentration (20, 50 and 80 mg/L) for the optimum value of time and pH is shown in Figure 6. As can be seen, the percentage removal decreased with an increase in Cd and Ni concentration. At low concentrations, metals are adsorbed by specific active sites, while at higher concentrations the lower adsorption yield is due to the saturation of adsorption sites. The decrease in percentage adsorption may be attributed to a lack of sufficient surface area to accommodate much more metal available in the solution. This appears to be due to the increase in the number of heavy metal ions competing for the available active sites on the surface (El-Sayed *et al.* 2010). Also, this could be attributed to the surface binding of low-affinity surface sites as high-affinity ones began to reach saturation, thereby leading to the reduction of efficiency (Omraei *et al.* 2011).

Effect of the amount of functionalizer

To study the effect of TMPTMS content in the nanofiber adsorbent on metal ion sorption, nylon 66 nanofibers were functionalized with different amounts of TMPTMS. According to Figure 7, it can be seen that by increasing the amount of functionalizer, efficiency is increased. By increasing the amount of functionalizer, functional groups that are created on the surface increase and are more able to absorb metal ions. Also, this increase is due to a more uniform surface and more regular pore structure (Abbasizadeh *et al.* 2013).

Study of membrane adsorption isotherm

The adsorption isotherm is also an equation relating to the amount of solute adsorbed onto the solid and the

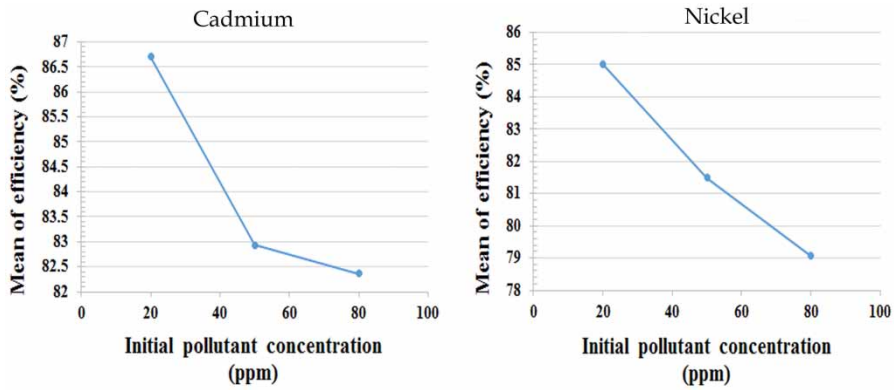

Figure 6 | Effect of initial pollutant concentration on mean of efficiency for removal of Cd (left) and Ni (right).

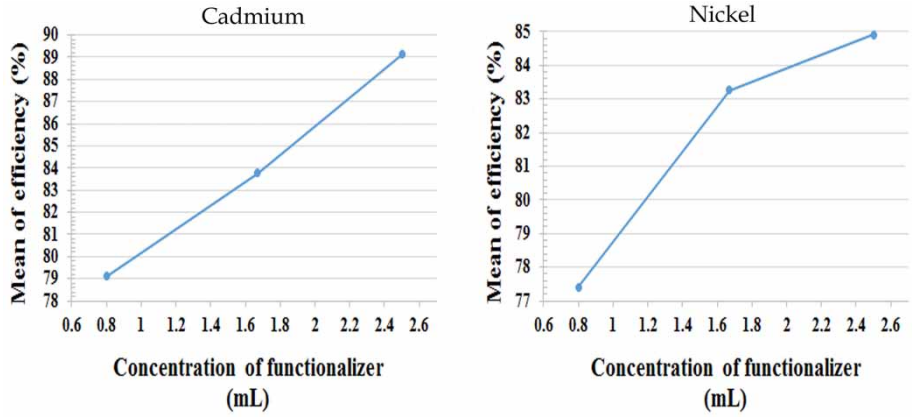

Figure 7 | Effect of amount of functionalizer on mean of efficiency for removal of Cd (left) and Ni (right).

equilibrium concentration of the solute in solution at a given temperature.

An adsorption isotherm describes the equilibrium of the sorption of a material at a surface at constant temperature. It represents the amount of material bound at the surface as a function of the material present in the gas phase and/or in the solution. To investigate the sorption isotherms empirical models are often used, but this kind of model does not consider the processing parameters. They are obtained from measured data by means of regression analysis. The most frequently used isotherms are the Langmuir and Freundlich isotherms. Langmuir and Freundlich isotherm models are frequently used for describing adsorption of metal ions by different materials. The Freundlich isotherm is an empirical equation and the Langmuir isotherm has a rational basis. Both the Langmuir and Freundlich isotherms can be applicable for the equilibrium data of adsorbents from many materials, suggesting that either monolayer or multilayer adsorption could occur on the surface, depending on the type of adsorbents.

The Langmuir model assumes that sorption takes place on the homogeneous surface of the adsorbent and a saturation monolayer is formed (Gopal & Elango 2007). The Langmuir model estimates the maximum sorption capacity corresponding to complete monolayer coverage on the adsorbent surface. This model assumes that the surface is homogeneous and the energy of sorption is constant (Zargaran *et al.* 2010).

The Langmuir model is based on five assumptions:

1. The surface containing adsorbing sites is perfectly flat without corrugations.
2. The gas adsorbs into an immobile state.
3. All sites are equivalent.
4. Each site can hold one molecule of A.
5. There are no interactions between adsorbed molecules with adjacent sites.

The linear form of the Langmuir isotherm model is given in the following equation (Vu *et al.* 2013):

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m b}\right) + \left(\frac{1}{q_m}\right) C_e \tag{2}$$

where C_e (mg/L) is the equilibrium concentration of the metal ions, q_e (mg/g) is the amount adsorbed at equilibrium, q_m (mg/g) is the parameter related to maximum sorption capacity, and b is the Langmuir constant related to the energy of adsorption (Zhou *et al.* 2009).

The Freundlich isotherm is the most important multisite adsorption isotherm for rough surfaces. This model assumes that the surface is heterogeneous and the energy of sorption is not constant.

The Freundlich isotherm is an empirical equation based on sorption on a heterogeneous surface with nonuniform energies of active sites. The linear form of the Freundlich model can be expressed as follows (Li *et al.* 2012):

$$Lnq_e = Lnk + \left(\frac{1}{n}\right) LnC_e \tag{3}$$

where q_e (mg/g) is the mass of coating on the nanofiber at equilibrium in mg/g, C_e (mg/L) is the equilibrium concentration of the metal ions, k (mg/g) and $1/n$ are Freundlich constants related to the sorption capacity and intensity of the adsorption, respectively (Zhou *et al.* 2009).

In this investigation, the sorption isotherms were conducted in six various initial concentrations of cadmium and nickel solutions (20, 35, 50, 65, 80 and 100 mg/L). The concentration of Cd and Ni ions before and after equilibrium sorption was determined by use of an ICP-OES. In the filtering operation time of 60 minutes, the remaining amount of adsorbed ions (C_e) was determined. The applied membrane weight after drying in an oven for 2 h was determined and then the Q_e values, which is the mass of coating on the nanofiber, were calculated according to Equation (4). The results of the adsorption isotherm are shown in Figures 8 and 9.

$$Q_e = \frac{C_0 - C_e}{W} \times V \tag{4}$$

where C_0 and C_e (mg/L), respectively, are the initial and equilibrium concentration of metal ions, respectively; V and W are the liquid volume (L) and the weight of dried used adsorbent (g).

The results were fitted with the Freundlich model and adsorption equations are as follows:

$$q = K_f \times C_e^{1/n}$$

$$q = 1,269 \times C_e^{0.8389}$$

$$q = 956 \times C_e^{0.6508}$$

Table 2 shows the Freundlich model parameters.

By comparing the correlation coefficients, it was found that the Freundlich isotherm model ($R^2 = 0.9988$ for Cd and $R^2 = 0.9986$ for Ni) fitted the equilibrium data onto the functionalized nanofiber membrane better than the Langmuir isotherm model ($R^2 = 0.9771$ for Cd and $R^2 = 0.9814$ for Ni). The maximum sorption capacities obtained from the Freundlich model for Cd and Ni were 956 and 1,269 mg/g, respectively.

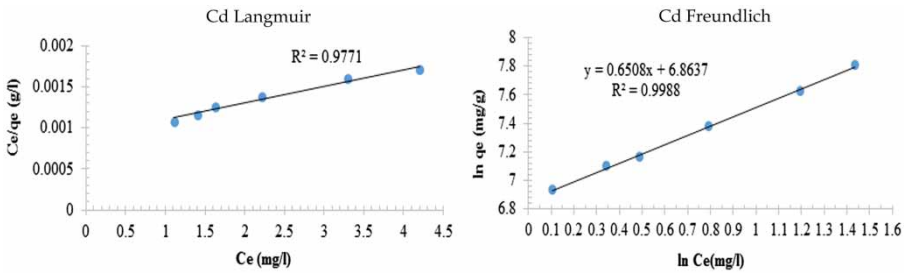

Figure 8 | Langmuir and Freundlich isotherm for adsorption of Cd by nylon 66 nanofiber membranes.

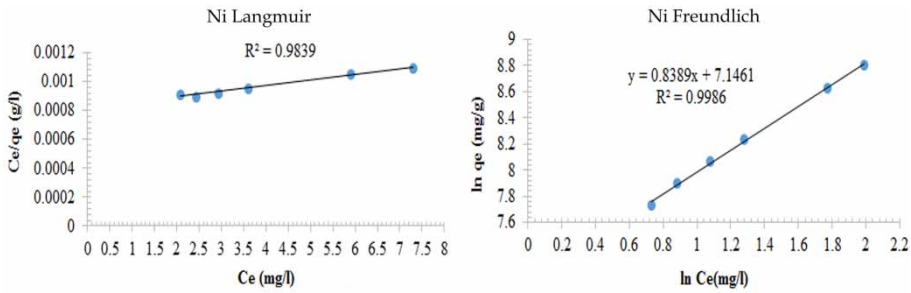

Figure 9 | Langmuir and Freundlich isotherm for adsorption of Ni by nylon 66 nanofiber membranes.

Table 2 | Freundlich parameters for Cd and Ni sorption onto the nylon 66 nanofiber membrane

Metal	K_f (mg/g)	1/*n* (L/mg)	R^2
Cadmium	956	0.6508	0.9988
Nickel	1,269	0.8389	0.9986

CONCLUSIONS

Nylon 66 nanofiber membranes were produced using the electrospinning technique; subsequently, they were functionalized with TMPTMS and as an adsorbent, the potential of the prepared nanofiber for the removal of cadmium and nickel from aqueous solution was investigated. FTIR spectra were obtained to confirm the presence of TMPTMS on the surface of the membranes. The effects of the adsorption process parameters such as the initial concentration of the metal solution, the pH of the solution, and the amount of functionalizer (TMPTMS) were investigated for the removal of cadmium and nickel from aqueous solutions. Based on the results, as the pH of solution and amount of functionalizer increased, the metal ion rejection increased. With an increasing initial concentration of effluent, removal efficiency decreased. The prepared functionalized nanofiber membranes showed a good ability to adsorb cadmium and nickel from aqueous media. The maximum rejection of Cd and Ni are found to be 93 and 97.6%, respectively.

Among various isotherm models applied, the Freundlich isotherm model established a strong correlation with the experimental data, which indicated that the surface was heterogeneous and the adsorption was multilayer. The maximum sorption capacities obtained from the Freundlich model for Cd and Ni were 956 and 1,269 mg/g.

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First received 2 November 2015; accepted in revised form 24 February 2016. Available online 28 March 2016