Original paper

Preparation of aldehydic electrospun PAN mats for ammonia removal from wastewater

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ARTICLE INFO

ABSTRACT

Novel electrospun polyacrylonitrile (PAN) nanofiber mats and PAN fabric were chemically modified by dissolved anhydrous stannous chloride diethyl ether saturated with hydrogen chloride to contain aldehyde groups on their surfaces, which are suitable for ammonium adsorption due to their high adsorption affinity for NH_4^+ ion. Scanning electron microscopy (SEM), and Fourier-transform infrared spectra (FT-IR) were employed to characterize the prepared adsorbents. FT-IR spectra of these adsorbents confirmed that aldehyde groups are successfully formed on the surface of these chemically modified adsorbents. The aldehydic electrospun PAN nanofiber mats and aldehydic PAN fabric were assessed for their chelating property with NH_4^+ ion from aqueous solution. The effects of contact time on the amounts of ammonium adsorbed into the prepared adsorbents were also studied. Results revealed that ammonium removal increased by increasing contact time which finally reached equilibrium at about 3.5 h and 4 h for aldehydic electrospun PAN nanofiber mats and aldehydic PAN fabric, respectively. The adsorption performance of these prepared adsorbents for ammonium adsorption with initial ammonium concentration of 300 ppm via isotherm studies was investigated. The maximum ammonium removal efficiency (% R) was 48.33 and 70 for aldehydic electrospun PAN nanofiber mats and PAN fabric, respectively. Results indicated that the adsorption of ammonium by both prepared adsorbents followed Langmuir isotherm.

1. Introduction

Nowadays due to the rapid population growth and development of agriculture and industrial activity, concerns in both waters-care regions and development countries have raised. It seems that the reuse of treated water is the most suitable solution for the future sustainable water cycle control (Radjenović et al. 2009).

Nitrogen is a fundamental nutrient for all the life forms. It forms a basic building block of animal and plant proteins. Although it is a fundamental nutrient, too much nitrogen can be toxic. The presence of extra amount of nitrogen in the environment has drastically disordered the natural nutrient cycle between living organisms and the solid, water and atmosphere. Nitrous oxide, nitric oxide, nitrate or ammonia/ammonium are the usual forms of nitrogen that are soluble in water, so it can exist in drinking and grounded water (Rožić et al. 2000). The extent of nitrogen contamination in water supply has raised due to the discharge of industrial and domestic wastes to the environment. The increase of nitrogen concentrations in domestic wastewater is becoming significant among the pollutants. The ammonia and ammonium ions are the most prevalent encountered nitrogenous compounds in wastewater, causes accelerated eutrophication of lakes and rivers, dissolved oxygen reduction, fish toxicity in receiving water, undesired odors and several diseases (Balci. 2004; Du et al. 2005). The word ammonia derived from the name of the old Egyptian God Ammon and had been used chemically since 1799 (Lewis. 1993). Up to now, a number of biological and physiochemical methods have been used for ammonia removal from wastewater, including air stripping (Liao et al.

1995) chemical precipitation (Li et al. 1999), ion exchange (Koon and Kaufman. 1975), and biological nitrification-denitrification (Kuai and Verstraete. 1998). Adsorption has been identified as a new economically feasible and environmentally friendly method as compared to the other methods of ammonia removal from wastewater that have been received significant attention (Liu et al. 2010). Polymer fibers with diameters in the range of micrometers (e.g. 10-100 μm) to submicron or nanometers (e.g. 10×10^{-3}-100×10^{-3} μm) are of great interest to be developed as efficient adsorbent because of flexibility in surface modification, very high surface area to volume ratio, and better mechanical performance such as better stiffness and tensile strength as compared to any other known forms of the material (Huang et al. 2003). These prominent properties made the polymer nanofibers to be a good candidate for many significant applications such as filtration (Tsai et al. 2002), wound dressing (Jin et al. 2002), medical prosthesis (Laurencin et al. 1999), and adsorbent (Lee et al. 2010). Several methods including drawing (Joachim. 1998), template synthesis (Feng et al. 2002), self-assembly (Liu et al. 1999), phase separation (Ma and Zhang. 1999), electrospinning (Deitzel et al. 2001), and others have been used for polymeric nanofiber production in recent years. However, the electrospinning technique seems to be the only method that could be used for mass production of one-by-one continuous nanofibers from various polymers (Fong and Reneker. 2001). Polyacrylonitrile (PAN) nanofibers have been widely modified to contain adsorbent groups for contamination removal from wastewater. Besides, PAN can be easily prepared into nano-scale fibrous material by electrospinning method (Kampalanowat and Supaphol. 2010). The purpose of the current

contribution was to synthetize aldehydic electrospun PAN nanofiber mat and PAN fabric as NH_4^+ ions adsorbents from the reaction between electrospun PAN nanofibers mat or PAN fabric and stannous chloride suspended in dry ether in the saturated dry hydrogen chloride surroundings. Scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FT-IR) were used to characterize the aldehydic electrospun PAN nanofibers mat or PAN fabric. Adsorption of NH_4^+ ions by prepared aldehydic electrospun PAN nanofiber mat and PAN fabric was also examined by using NH_4^+ aqueous solutions. Adsorption performance of prepared adsorbents for ammonium removal was investigated by isotherm studies.

2. Materials and methods
2.1. Materials

Industrial Polyacrylonitrile (PAN) powder, used as the raw material for preparing the base PAN solution which was later fabricated into PAN fiber mats by electrospinning, and PAN fabric were received from Iran Polyacryle Co. The weight average molecular weight (M_w) and the number average molecular weight (M_n) of the purchased PAN were 100000 g/mol and 70000 g/mol, respectively. Dimethylformamide (DMF; ~99.98 % purity) was purchased from Merck Co. was used as a solvent. Tin (II) chloride (stannous chloride, $SnCl_2$ ~99.98 % purity), hydrogen chloride (HCL ~35-37 % purity), Barium chloride ($BaCl_2$ 99.98 % purity), Diethyl ether ($C_2H_5)_2O$, ammonia solution (25 %) and Nessler's reagent were purchased from Merck Co. Also, deionized water was used for functionalization reaction and batch adsorption experiments. Throughout the studies all chemicals were used without further purification.

2.2. Electrospun PAN nanofibers preparation

A schematic description of electrospinning setup is shown in Fig. 1. The key components of the electrospinning system including the DC high voltage power supply, a syringe pump with controllable feed rate, polymer solution, grounded collector and nozzle. A syringe, mounted in a pump was employed as a storage for electrospinning source solution (Tang et al. 2009).

In electrospinning process, polymer solution or melt is loaded to a syringe connected to a nozzle. Then, under the application of an electric field between the nozzle tip and a collector, a droplet of polymer solution is formed at the nozzle tip. As the intensity of the electric field is increased, charge repulsion on the drop surface at the end of the nozzle tip increases and changes the hemispherical shape of a drop in a conical shape which is known as a Taylor cone. Eventually, if the applied voltage reaches a critical value, a jet of polymer solution initiates from the Taylor cone towards the grounded collector. This critical value is strongly related to the surface tension of the polymer solution. In the other word, the higher applied voltage is required for jet initiation at higher surface tension (Lee et al. 2003). During the jet traveling towards the grounded collector, solvent evaporates and polymer fibers in the form of nonwoven mats are deposited on the collector. At the nozzle tip to collector distance, the jet undergoes frequently whipping, which stretches the fiber and considerably reduces fiber diameter (Shenoy et al. 2005). The morphology of the obtained fibers is influenced by several factors including solution properties, processing and ambient conditions (Ding et al. 2002). In this study, the 13 wt. % solution of PAN in DMF was prepared at room temperature under constant mixing for about 4 h. The prepared solution was loaded into a syringe and electrospun under fixed electric field of 22 kV and nozzle tip to collector distance of 9 cm, using DC high voltage power supply, onto an aluminum (AL) sheet wrapped around a rotating drum, which was used as a collector. Each of the electrospun fiber mats were placed in vacuo at room temperature to remove further DMF from them as possible.

2.3. Aldehydic modification of electrospun PAN nanofiber mats and PAN fabric

Aldehydic electrospun PAN nanofiber mats were prepared in similar way to that reported by Stephen (1925). The basis of this new method is the conversion of nitrile group into an aldehyde with the same number of carbon atoms. In this method, anhydrous stannous chloride powder was dissolved in diethyl ether saturated with hydrogen chloride as the most proper reducing agent. The reaction and structure of obtained aldehydic PAN is shown in Fig. 2. Briefly, 4.2 gr powdered anhydrous stannous and 100 ml diethyl ether were suspended thoroughly in a round-bottomed 250 ml flask which was then saturated with hydrogen chloride. After about 1 hour, the mixture was separated into two layers, the lower viscous layer consisting of stannous chloride dissolved in ethereal hydrogen chloride. Then, about 0.88 gr of electrospun PAN nanofiber mats was added to the mixture with vigorous shaking and then was refluxed for 5 h. After the reaction, the mixture containing electrospun PAN nanofiber mats was filtered and fiber mats were placed into 500 ml glass chamber containing 100 °C water for 1 h. Afterwards, the obtained fiber mats were washed with hot deionized water and then dried in vacuo at room temperature. For comparative purpose, aldehydic PAN fabric was also synthesized from PAN fabric at the same condition was used in the preparation of aldehydic electrospun PAN nanofiber mats.
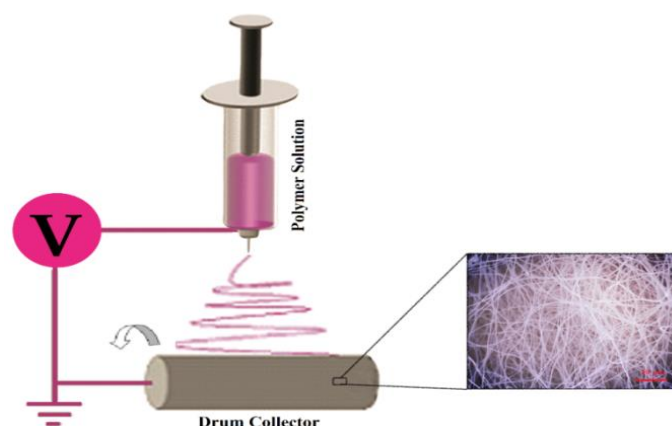

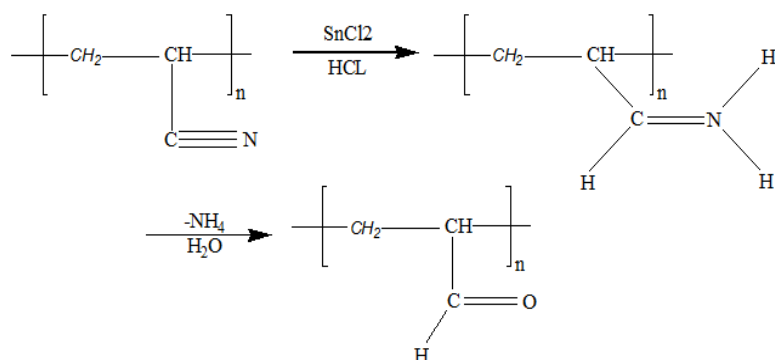**Fig. 1.** A schematic diagram of electrospinning setup.

Fig. 2. The reaction and structure of obtained aldehyde PAN.

2.4. Characterization

Morphologies of both aldehydic electrospun PAN nanofiber mats and aldehydic PAN fabric were observed by Seron-AIC2300c scanning electron microscope (SEM). Each sample was coated with layer of gold to the SEM observation. The average fiber diameters of electrospun nanofiber mats were determined by measuring 100 random fibers from the SEM images using Digimizer software. The electrospun PAN nanofiber mats, aldehydic electrospun PAN nanofiber mats and aldehydic PAN fabric were also characterized using Fourier-transform infrared spectra (FT-IR) that were recorded between 400 and 4000 cm^{-1} with KBr pallets at room temperature (Bruker Alpha, Germany).

2.5. Batch adsorption experiment

Aldehydic electrospun PAN nanofiber mats and aldehydic PAN fabric were individually placed in a 100 ml conical flask containing 50 ml solution of ammonium aqueous solution. The standard solution (1000 mg/L) of ammonium was prepared through dissolving a sufficient amount of ammonium in 1000 ml deionized water. Each flask was shaken in a thermostatic shaker (Pars Azma, IN12), operating at 30 $^{\circ}$C and 120 rpm for a certain time. Then, the adsorbents were separated by using 0.5 μm microporous membrane filters. Nessler's reagent colorimetric method was used to determine the concentration of ammonium in the aqueous solution after batch adsorption process. To study the effect of contact time, 6 batch experiments with the initial concentration of 300 ppm were done where samples were shaken from 1.5 to 4.5 h. The removal efficiency and adsorption capacity of prepared adsorbents for ammonium ion adsorption was computed from the following equations, respectively.

$$R \% = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \qquad (1)$$

$$q = \frac{(C_0 - C_e)V}{M} \qquad (2)$$

where, R % is the removal percentage and q (mg/g) is the ammonia adsorption capacity by the adsorbent. C_0 and C_e (mg/l) are the initial and final NH_4^+ ion concentration in the testing solution, V (L) is the volume of testing solution and also M (g) is the weight of the adsorbent.

3. Results and discussion
3.1. Characterization of prepared adsorbent

Morphologies of prepared aldehydic electrospun PAN nanofiber mats and electrospun PAN nanofiber mats were observed by SEM and the results are illustrated in Fig. 3. It is clear that aldehydic electrospun PAN nanofiber mats showed identical morphology as compared to those of electrospun PAN nanofiber mats. The average fiber diameter of PAN nanofiber mats and aldehydic PAN nanofiber mats were 341.26 ± 55 nm and 345.32 ± 60 nm, respectively, indicating that the diameter of PAN nanofiber mats after aldehydic modification was essentially similar to that of PAN nanofiber mats. The FT-IR spectra of electrospun PAN and aldehydic electrospun PAN nanofiber mats and aldehydic PAN fabric are shown in Fig. 4. The FT-IR spectrum of electrospun PAN nanofiber mats showed adsorption peak of 1728.90 cm^{-1} and 1250 cm^{-1}, corresponding to the stretching vibration of carbonyl and ether groups of the methyl acrylate monomers. The frequency peak at 2244.54 cm^{-1} is related to the nitrile group (Saeed et al. 2008). The spectra of aldehydic electrospun PAN nanofiber mats showed new adsorption bands at 1732.33 cm^{-1}, 2924.56 cm^{-1} and 1633.00 cm^{-1} which are related to the C=O, C–C–H, and H–C=O groups in aldehyde, respectively. The intensity of nitrile peak in FT-IR spectra of aldehydic electrospun PAN nanofiber mats at frequency of 2244.85 cm^{-1} decreased due to the conversion of the nitrile to aldehyde group. In the case of aldehydic PAN fabric the FT-IR spectra exhibited new adsorption peak at frequencies of 2857.43 cm^{-1}, 1629.64 cm^{-1}, and 1740.03 cm^{-1} which attributes to the stretching vibration of O=C–H, C–H, and C=O in aldehyde, respectively. The adsorbing frequency peak at 1372 cm^{-1} belongs to the vibration of C–H alkane groups in the structure of aldehydic PAN fabric. The peak related to nitrile group of aldehydic PAN fabric at 2245.03 cm^{-1} also decreased in its intensity due to the conversion of nitrile to aldehyde groups. Moreover, the intensity of the adsorbing peak at 1740.03 cm^{-1} and 2857.43 cm^{-1} which are related to the aldehyde groups in prepared PAN fabric was greater than adsorbing frequency of aldehyde (1732.33 cm^{-1} and 29.24.55 cm^{-1}) in aldehydic PAN nanofiber mats.
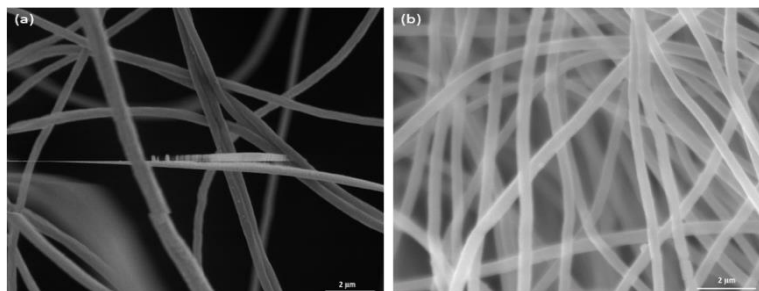

Fig. 3. SEM images of: (a) electrospun PAN nanofiber mats; (b) aldehydic electrospun PAN nanofiber mats.

3.2. Effect of contact time

Fig. 5 shows the ammonium removal efficiency (R %) and ammonium adsorption capacity (mg/g) of aldehydic electrospun PAN nanofiber mats and aldehydic PAN fabric from a 300 ppm aqueous solution of NH_4^+ as a function of time. It can be seen from the Fig. 5 that the ammonium removal efficiency (R %) of aldehydic electrospun PAN nanofibers with the maximum value of 48.33 % in all the ranges of contact time was lower than aldehydic PAN fabric. These results can be attributed to the greater amounts of unreacted nitrile group on the surface of aldehydic electrospun PAN nanofiber mats than aldehydic PAN fabric (see FT-IR spectra) that had weak interactions with ammonium ion. Therefore, considerably higher amounts of ammonium ions could be adsorbed on the surface of aldehydic PAN fabric with higher conversion of nitrile to aldehyde group. Also, it can be seen from

the Fig. 5 that at the first step of ammonium batch adsorption process, ammonium removal efficiency (R %) and ammonium adsorption capacity increased by increasing contact time, but thereafter the rate considerably leveled off and eventually reached equilibrium within 3.5 h and 4 h for aldehydic electrospun PAN nanofiber mats and aldehydic PAN fabric, respectively. This observed trend of ammonium removal from aqueous solution might be because of the fact that, at the initial step of adsorption process, due to the great number of vacant adsorbent sites and high concentration of NH_4^+ ion in aqueous solution of ammonium adsorption was swift. Thereafter, the ammonium adsorption rate decreased considerably and finally reached equilibrium because of the decrees in ammonium ion concentration in testing solution as well as adsorption sites reduction due to depletion. Our observation confirmed the past studies (Deng et al. 2003).
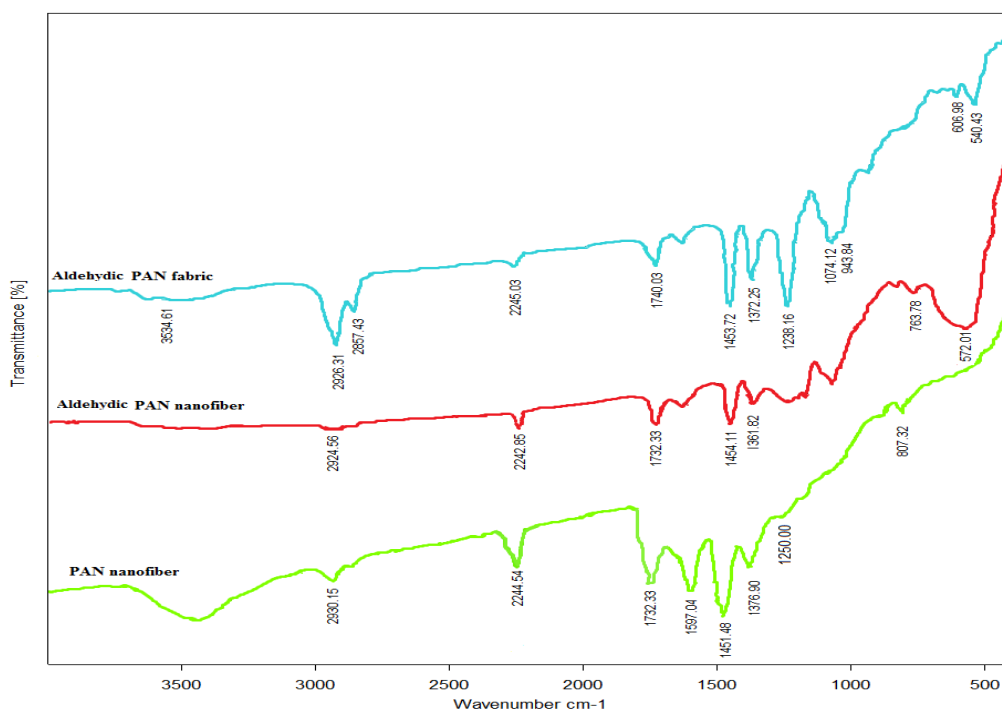

Fig. 4. FT-IR spectra of electrospun PAN nanofiber mats, aldehydic electrospun PAN nanofiber mats, and aldehydic PAN fabric.
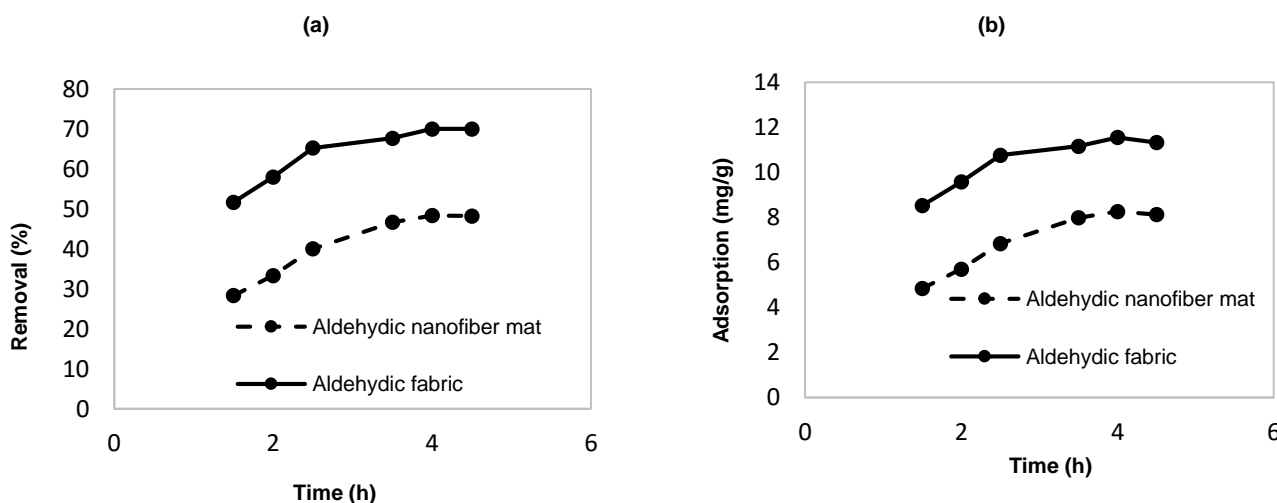

Fig. 5. (a) Ammonium removal efficiency (R %); (b) ammonium adsorption capacity (mg/g) of aldehydic electrospun PAN nanofiber mats and aldehydic PAN fabric.

3.3. Adsorption equilibrium isotherm

The experimental ammonium adsorption equilibrium data was analyzed using Langmuir isotherm model that can be written as follows:

$$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{Kl\ qm} \tag{3}$$

where, q_e is the equilibrium amount of NH_4^+ adsorbed on the aldehydic electrospun PAN nanofiber mats and aldehydic PAN fabric (mg/g), C_e is the equilibrium NH_4^+ concentration in the testing solution (mg/l). q_m and K_L are the Longmuir constants related to the maximal adsorption capacities of the NH_4^+ on the adsorbent and binding energy,

respectively. The value of q_m were calculated from the slope of the plot of C_e/q_e versus C_e (the inverse value of slope), whereas that of K_L can be calculated from the intercept of the plot [29]. The values of these parameters that were taken from the plot shown in Fig. 6, are summarized in Table 1. The linear plot confirmed that the NH_4^+ adsorption on the prepared adsorbents followed the Langmuir isotherm. The basic assumption of the Langmuir theory is that adsorption takes place on a homogeneous, flat surface of an adsorbent (Mall et al. 2006). The results showed that the adsorption of NH_4^+ on the aldehydic PAN fabric was greater than aldehydic electrospun PAN nanofiber mats that had been prepared at the same condition (see Table 1). This should be the result of the higher pore size of fabric and higher conversion of nitrile to aldehyde group in aldehydic PAN fabric.

Table 1. Langmuir constants for NH_4^+ on aldehydic PAN nanofiber mats and aldehydic PAN fabric.

Adsorbent	Langmuir model		
	q_m (mg/g)	K_L (L/mg)	r^2
Aldehyde electrospun PAN nanofiber	2.39	0.051	0.981
Aldehyde PAN fabric	5.98	0.022	0.994
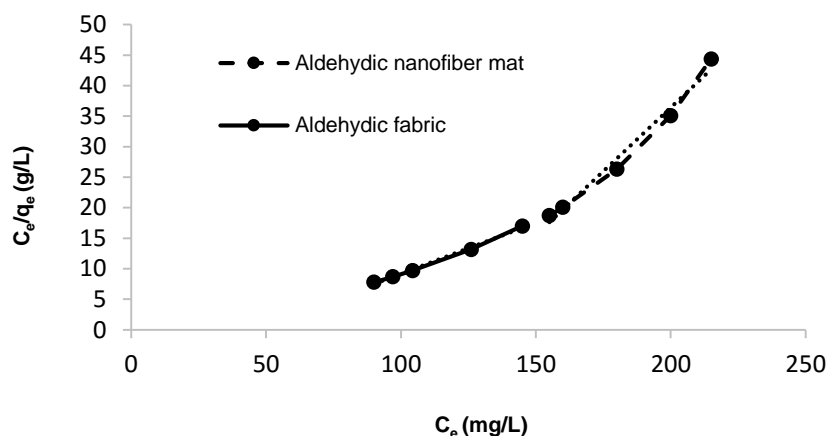
Fig. 6. Langmuir plot of aldehydic electrospun PAN nanofiber mats and aldehydic PAN fabric.

4. Conclusion

PAN nanofiber mats were prepared from 13 wt. % solution of PAN in DMF using the electrospinning technique at 20 kV and 9 cm nozzle tip to collector distance. Subsequently, the obtained electrospun PAN nanofiber mats were modified by dissolved anhydrous stannous chloride diethyl ether saturated with hydrogen chloride to produce aldehydic electrospun PAN nanofiber mats. Aldehydic PAN fabric also synthesized from PAN fabric at same condition was used in the preparation of aldehydic electrospun PAN nanofiber mats. FT-IR spectra were used to confirm the aldehydic modification of PAN nanofiber mats and fabric surface. The scanning electron microscopy (SEM) was employed to characterize the morphology of obtained fiber mats. The aldehydic electrospun PAN nanofiber mats and Aldehydic

PAN fabric were applied as adsorbents to ammonium adsorption. The initial concentration of ammonium in testing solution was 300 ppm. The contact time posed a strong effect on the ammonium removal of the prepared adsorbents. On the other word, the ammonium removal was found to increase with contact time increase and finally reached equilibrium within 3.5 and 4 h for aldehydic electrospun PAN nanofiber mats and Aldehydic PAN fabric, respectively. The ammonium removal efficiency (R %) of aldehydic electrospun PAN nanofiber mats in all the ranges of contact time was lower than aldehydic PAN fabric. The maximum ammonium removal efficiency (R %) was 48.33 and 70 % for Aldehydic electrospun PAN nanofiber mats and PAN fabric, respectively. The adsorbent of ammonium by both prepared adsorbents was fitted well with Langmuir equation.

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