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ORIGINAL ARTICLE

On the Hydrogen Cyanide Removal from Air Using Metal loaded Polyacrylonitrile Composite Nanofibers

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KEYWORDS

Metal loaded nanofiber;
Nanofibrous filter media;
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Experimental design

ABSTRACT: The present study highlights the potential application of electrospun polyacrylonitrile/metal salts (CrO_3, $CuCO_3$) nanofibrous filter media impregnated with TEDA (PAN-M-TEDA) as an efficient adsorbent for hydrogen cyanide removal from air. The PAN-M-TEDA nanofiber before and after adsorption of hydrogen cyanide was characterized with Fourier transforms infrared microscopy (FTIR). The concentration of hydrogen cyanide passes through the samples was determined by measuring the absorption of hydrogen cyanide in the solution containing indicator via UV-Vis spectroscopy. The results showed that introducing metal salts to PAN nanofiber along with their impregnation with TEDA, significantly increases the adsorption capacity of nanofibrous filter media. The adsorption of hydrogen cyanide over PAN-M-TEDA nanofiber was also studied as a function of thickness, PAN concentration and TEDA concentration by response surface methodology (RSM) based on central composite design. It is found that the highest adsorption capacity can be achieved at thickness 28.42 mm, PAN concentration 16.19 w/v % and TEDA concentration 14.80 w/v %.

INTRODUCTION

Hydrogen cyanide (HCN) is one of the most common and very toxic gases, which is commonly released to the environment from various sources including chemical processing, vehicle exhaust emissions, petroleum refineries, and coal gasification. HCN vapors could enter to the human body by breathing and absorption through skin and consequently induce some health and environmental hazards. Several methodologies have been developed to remove HCN from air, including catalytic hydrolysis, oxidation, and adsorption. Among them, adsorption process, as a particularly attractive method for direct removal of HCN, has attracted much research interest [1-5].

Different types of adsorbent have been investigated in recent years for removal of HCN and other toxic gases from air. Seredych et al. [6] used an activated carbon as

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an adsorbent for HCN and found that the adsorbed value in dry air was only 0.5 mg/g. According to the literature, impregnation of activated carbons with metal oxides (e.g., copper, chromium, cobalt, zinc, molybdenum) and/or organic compound (e.g., triethylenediamine) [7,8] could enhance the adsorption capacity and removal of toxic gas (e.g., cyanogen and hydrogen cyanide). The adsorption of HCN gas by metal (Cu, Co, or Zn) loaded zeolites (ZSM-5 and Y zeolite) were investigated by Ning et al. [5]. They found that the HCN adsorption capacity was enhanced significantly when Cu-loaded zeolite was used. In another study, Sullivan et al. [9] compared the HCN adsorption capacity of activated carbon nanofiber and commercially available activated carbon fiber cloth. They found that activated carbon nanofiber, due to the more accessibility of its internal micro-pores to HCN, results in faster adsorption kinetics and 4-20 times greater HCN adsorption capacity than its commercially microfiber counterpart.

The high specific surface area, high porosity along with small pore sizes, flexibility, and superior mechanical properties of electrospun nanofiber make them good candidate for many practical applications in filter media, scaffolds and fuel cells for bio-medical, energy applications, as a sorbent for solid phase extraction and also removal of pollutants like HCN from air [10-16]. To the best of author knowledge, application of metal loaded polyacrylonitrile (PAN) nanofiber for hydrogen cyanide removal from air, has never been studied. Moreover, according to the literature, there has not been a previous report regarding the utilization of response surface methodology (RSM) for optimization and statistical prediction of HCN removal from air. Hence, in this work, electrospun PAN nanofibers were loaded with metals (Cu, Cr) and impregnated with triethylenediamine (TEDA) to act as chemical adsorbents. Furthermore, the effect of three main parameters, including the thickness of filter media, PAN solution concentration and TEDA concentration on adsorption of HCN have been investigated through RSM based on central composite design (CCD).

MATERIALS AND METHODS

Materials

Polyacrylonitrile (PAN) with a weight-average molecular weight (Mw) of 100,000 Daltons was purchased from Polyacryle Co. (Iran). Sulfuric acid (98%), potassium cyanide (KCN), sodium carbonate (Na_2CO_3), ninhydrin, triethylenediamine (TEDA), chromium trioxide (CrO_3, 99%), copper carbonate ($CuCO_3$), ethanol (99.9%), and *N*-*N*, dimethylformamide (DMF) were obtained from Merck Co. (Germany) and were used without any further purification. Reticulated polyurethane (PU) foam was purchased from Jalafoam Co. (Tehran, Iran) and used as a substrate.

Electrospinning and preparation of composite nanofibers

The polymer solution (10 % w/v) was prepared by dissolving PAN powder in DMF via magnetic stirrer for 24 hours and used for electrospinning of PAN nanofiber. To produce metal loaded PAN composite nanofibers, 0.8 g $CuCO_3$ and 0.4 CrO_3 were added to the 10 ml of PAN solution (10 % w/v) and stirred for 24 hours before electrospinning. Then, the prepared solutions were placed into a 5 ml plastic syringe with an 18 gauge (diameter=0.12 mm) needle tip as a nozzle for electrospinning. A syringe pump fed polymer solutions to the needle tip at a flow rate of 1 ml/h. The electrospinning device used in this experiment was produced by Fanavaran Nano-Meghyas Co. (Iran). The metallic needle was connected to a positive high voltage and the collector (PU porous membrane) was connected to the ground. The distance between the needle tip and the grounded collector was set at 10 cm and the applied voltage were 14 and 16 kV for PAN and metal loaded PAN compo-

site nanofibers, respectively. All electrospinning experiments were carried out at room temperature.

The electrospun metal loaded PAN composite nanofiber was impregnated with TEDA (15 % w/v) for 15 min and was dried in an oven at 30 °C.

Filtration process

First, hydrogen cyanide was generated by the dropwise addition of sulfuric acid to potassium cyanide. The generated vapor was introduced directly into condenser and finally, the aqueous hydrogen cyanide was collected and stored in a freezer.

$$HCN + Na_2CO_3 \rightarrow Na^+ + CN^- + NaHCO_3$$

The fabricated nanofibrous media, i.e., PAN nanofiber (PAN), metal loaded PAN nanofiber (PAN-M), and TEDA impregnated metal loaded nanofiber (PAN-M-TEDA), were placed into a 1 cm diameter plastic syringe. Adsorption test apparatus is shown in Figure 1. Gas stream containing 4 µl HCN and N_2, as a carrier gas, was introduced into the flowmeter and syringe tube containing electrospun filter medias. The outlet gas was introduced into a 70 ml stirring solution of sodium carbonate (Na_2CO_3, 2%). HCN was rapidly hydrolyzed in base to cyanide ion according to the following reaction. The samples were taken for measurement of HCN concentration in every 2 min to 16 min.

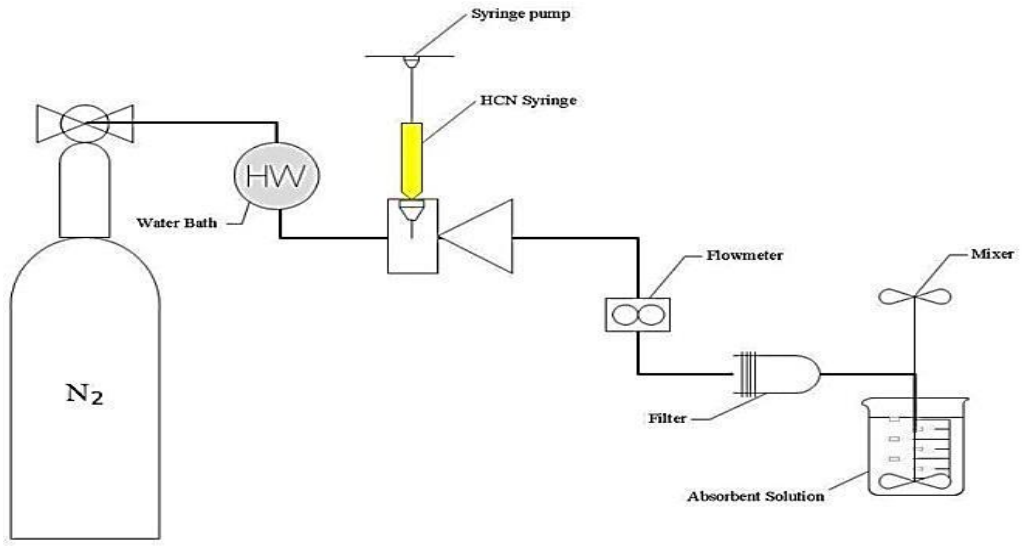

Figure 1. Schematic representation of filtration process.

Measurement and characterization

The morphology of composite nanofibers was investigated by scanning electron microscope (SEM, XL30, Philips, Netherlands) after gold coating using a sputter coater. Fourier transform infrared (FT-IR) measurement was recorded with a PerkinElmer Spectrum 400 in the wave number range of 500-4000 cm^{-1}. Ultraviolet-visible (UV–Vis) absorption were obtained using a UV-160A spectrophotometer (Shimadzu, Japan). 0.5 ml solution containing indicator (ninhydrin, 1%) was added to the sample before UV–Vis spectroscopy. After 15 min, the absorption of HCN from solution was measured at λ=485 nm.

Experimental design

In this work, the experimental design based on central composite design (CCD) was used to explore the optimum conditions through response surface methodology (RSM). The effect of adsorbent thickness (mm), PAN concentration (w/v%), and TEDA concentration (w/v %) on removal of HCN were investigated. The experiment was performed for at least three levels (coded as -1, 0, and +1) of each factor to fit a quadratic model. The experimental parameters and their levels are given in Table 1. The coded values were calculated according to the following equation:

$$X_i = \frac{\xi_i - [\xi_{Hi} + \xi_{Li}]/2}{[\xi_{Hi} - \xi_{Li}]/2} \quad (1)$$

where, ξ_{Hi} and ξ_{Li} refer to the high and low levels of the variables ξ_i (i= 1,2,3), respectively. The behavior of the system is explained by the following quadratic polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=2}^{3} \beta_{ij} X_i X_j \quad (2)$$

where, Y is the predicted response, X_i and X_j are the independent variables, β_0 is constant coefficient, and β_i, β_{ii}, β_{ij} are coefficients estimated from the regression [17,18]. In this work, the experimental design was applied to the experimental data using Design-expert statistical software program (Version 8.0.3).

RESULTS AND DISCUSSION

Characterization of composite nanofibers

SEM images and EDX spectra of PAN-M and PAN-M-TEDA nanofibers are illustrated in Figure 2. As can be seen, the metal loaded nanofibers (Figure 2a) were highly uniform and smooth without beads. The SEM image of PAN-M-TEDA nanofibers (Figure 2b) shows that the TEDA impregnated nanofibers were fused together or fused onto the PU membrane collector resulting in the ribbon-like morphologies. The EDX spectrum of metal loaded nanofibers demonstrates the existence of major elemental constitutes of composite nanofiber (Cr and Cu), from which it is clearly evidenced that layer of metal nanoparticles formed on the PAN nanofibers.

Table 1. Design of experiment (factors and levels).

Symbol	Parameters	Levels		
		-1	**0**	**1**
A	Thickness (mm)	15	24	33
B	PAN concentration (w/v %)	10	15	20
C	TEDA concentration (w/v %)	5	10	15

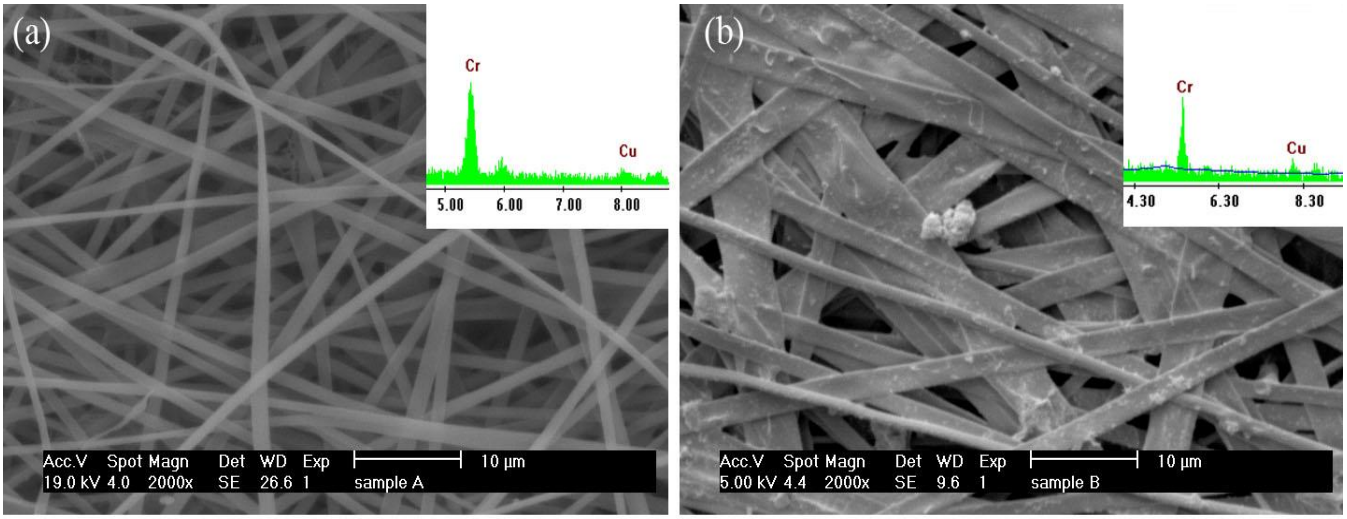

Figure 2. SEM images and EDX spectra of (a) PAN-M and (b) PAN-M-TEDA nanofibers.

FTIR spectra of PAN, PAN-M-TEDA and PAN-M-TEDA-HCN nanofibers are shown in Figure 3. The peak at 2245 cm^{-1}, which appearing in all spectra, corresponds to the characteristic band of nitrile (-CN) group. The vibrations of the aliphatic CH groups (CH, CH_2, and CH_3) were observed at 2870-2931 cm^{-1}, 1450-1460 cm^{-1}, 1350-1380 cm^{-1}, and 1220-1270 cm^{-1}. The band at 1650 cm^{-1} attributes to stretching vibration of C=N [19]. The peaks at 780 cm^{-1} and 940 cm^{-1} are responsible for the amine group of TEDA, and metal oxide, respectively. The peak at 1055 cm^{-1} region is attributed to the formation of the HCN/amine complex (Figure 3d).

Filtration efficiency

Figure 4 shows the variation of absorption of HCN from solution as a function of time for PAN, PAN-M and PAN-M-TEDA nanofibrous filter media. As observed, the absorption of crossing HCN in sample solution for all nanofibrous filter media increased with increasing time. It is clear that the HCN was traced in solution after 4 min for PAN nanofibrous filter media, while it observed after 12 min for PAN-M-TEDA nanofibrous filter media. Furthermore, after 16 min, the absorption of HCN in solution for PAN nanofiber is 0.76, while it is only 0.03 for PAN-M-TEDA nanofiber media. It is noteworthy to note that loading metal salts to PAN nanofiber and impregnation with TEDA, leads to increase the capacity of PAN nanofibrous filter media about 96%. Moreover, the shelf-life of the filter increases from 4 min to 12 min by TEDA impregnation of metal loaded PAN nanofibers. Table 1 shows the concentration of crossing HCN through the nanofilter media observed in solution.

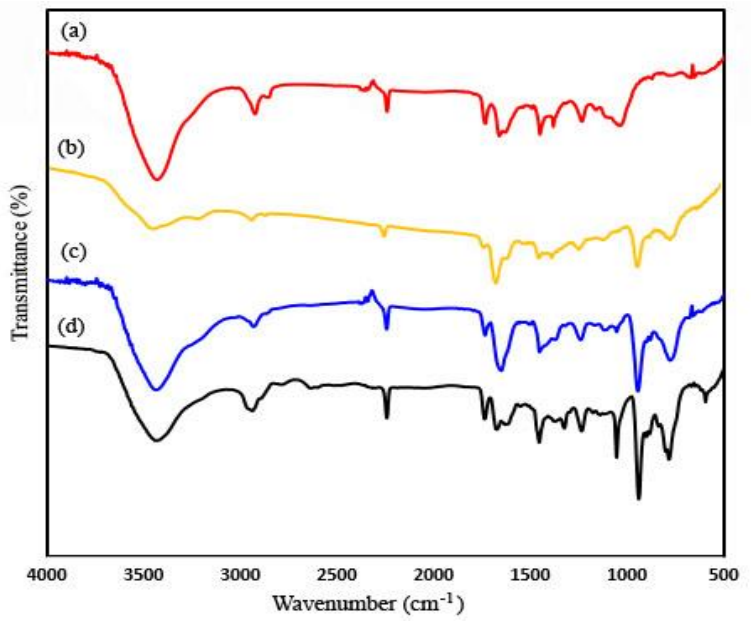

Figure 3. FTIR spectra of (a) PAN, (b) PAN-M, (c) PAN-M-TEDA and (d) PAN-M-TEDA-HCN nanofibers.

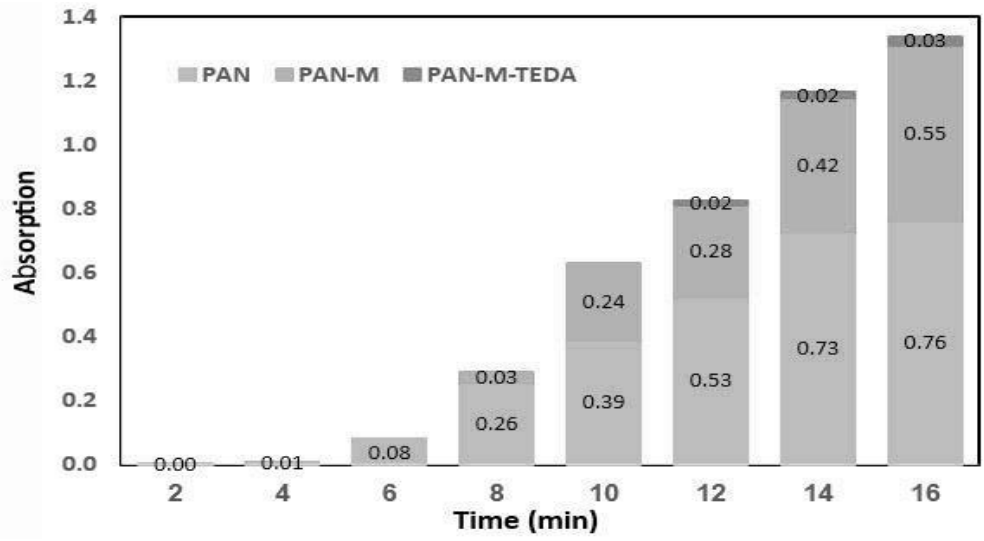

Figure 4. The variation of absorption of HCN from solution as a function of time for different nanofibrous filter media.

Table 2. Concentration of crossing HCN through the nanofilter media observed in solution.

Time (min)	Concentration of HCN in solution (µg/ml)		
	PAN	PAN-M	PAN-M-TEDA
2	0.05	0.00	0.00
4	0.12	0.00	0.00
6	1.15	0.00	0.00
8	3.90	0.52	0.00
10	6.10	3.80	0.00
12	8.52	4.61	0.27
14	12.23	7.01	0.33
16	13.28	9.57	0.47

The HCN adsorption capacity of nanofibrous filter media was calculated according to the following equation [5].

$$X = \frac{m_{HCN}}{m_{filter}} = \frac{V_{HCN} \times D_{HCN}}{m_{filter}} \qquad (3)$$

where, X (mg/g) is the adsorption capacity, m_{filter} (g) is the weight of nanofilter media, m_{HCN} (g) is the weight of HCN, V_{HCN} (μl) and D_{HCN} (g/ml) are the volume and density of HCN, respectively.

The adsorption capacity of PAN, PAN-M and PAN-M-TEDA nanofibrous filter media were obtained 13.14, 39.42, and 65.70 mg/g, respectively. It is found that the PAN-M-TEDA nanofibrous filter media exhibits the most HCN adsorption capacity, while the PAN nanofiber shows the least adsorption capacity. Increasing the HCN adsorption capacity of TEDA impregnated PAN-M nanofibers is attributed to the presence of amine groups as well as nitrile groups in PAN-M-TEDA nanofibrous filter media, which could efficiently adsorbacidic HCN. Indeed, the amine groups present on the opposite ends of the TEDA molecule enhance the adsorptive properties of PAN-M-TEDA nanofibers. Functionalization of PAN nanofibers with metal salts (Cr and Cu) has also significantly enhanced the adsorption of HCN.

Analysis of variance

The results of each experimental run for the absorption of HCN from solution are summarized in Table 3. Using the experimental data, regression equations has been developed for correlating the absorption and the input parameters (thickness, PAN concentration, and TEDA concentration). In this work statistical conclusions were obtained at the 95% confidence level. Using the 5% significance level, a factor is considered significant if the p-value is less than 0.05. By linear regression analysis of Eq. (2), the final mathematical model in terms of coded variables was obtained and was given in Eq. (3).

Table 3. Experimental design and results of the central composite design.

Run	Variables			Responses
	Thickness (mm)	PAN concentration (wt.%)	TEDA concentration (wt.%)	Absorption of HCN from solution
1	15	20	5	1.47
2	15	10	15	1.15
3	15	10	5	1.51
4	15	20	15	1.04
5	15	15	10	1.25
6	24	15	10	0.54
7	24	15	15	0.046
8	24	15	10	0.47
9	24	15	10	0.59
10	24	15	10	0.46
11	24	15	10	0.51
12	24	20	10	0.46
13	24	10	10	0.53
14	24	15	10	0.51
15	24	15	5	0.8
16	33	10	5	0.8
17	33	15	10	0.64
18	33	20	15	0.065
19	33	10	15	0.15
20	33	20	5	0.65

Absorption=+0.51-0.41*A-0.046*B-0.28*C-0.056*A*C+0.43*A^2-0.088*C^2

Table 4 shows the results of the second-order response surface model in the form of analysis of variance (ANOVA). It showed that the model was significant ($p < 0.0001$), which indicated that the model had a good agreement with the experimental results. The coefficient of variation (R^2) and adjusted R-squared (Adj-R^2) were found to be close to 1 (0.98 and 0.97, respectively) revealed high correlation between experimental and predicted values. This can be observed in Figure 5 by comparing the experimental value against the predicted response by the model. Adequate precision, which measures the signal to noise ratio, was 34.3 demonstrating that model is significant for process.

Table 4. ANOVA analysis for absorption of HCN from solution.

Source	Sum of squares	DF	Mean square	*F*-value	Prob > *F*	
Model	3.26	9	3.26	54.16	< 0.0001	Significant
A-Thickness	1.69	1	1.69	252.97	< 0.0001	
B-PAN concentration	0.021	1	0.021	3.09	0.1091	
C-TEDA concentration	0.77	1	0.77	115.38	< 0.0001	
AB	9.031E-004	1	9.031E-004	0.13	0.7210	
AC	0.025	1	0.025	3.70	0.0834	
BC	3.125E-006	1	3.125E-006	4.699E-004	0.9832	
A2	0.53	1	0.53	78.90	< 0.0001	
B2	3.811E-004	1	3.811E-004	0.057	0.8162	
C2	0.019	1	0.019	2.88	0.1204	
Residual	0.067	10	6.694E-003			
Lack of Fit	0.056	5	0.011	4.91	0.0528	Not significant
Pure error	0.011	5	2.267E-003			
Cor Total	3.33	19				
R-Squared = 0.9799						
Adj R-Squared = 0.9618						

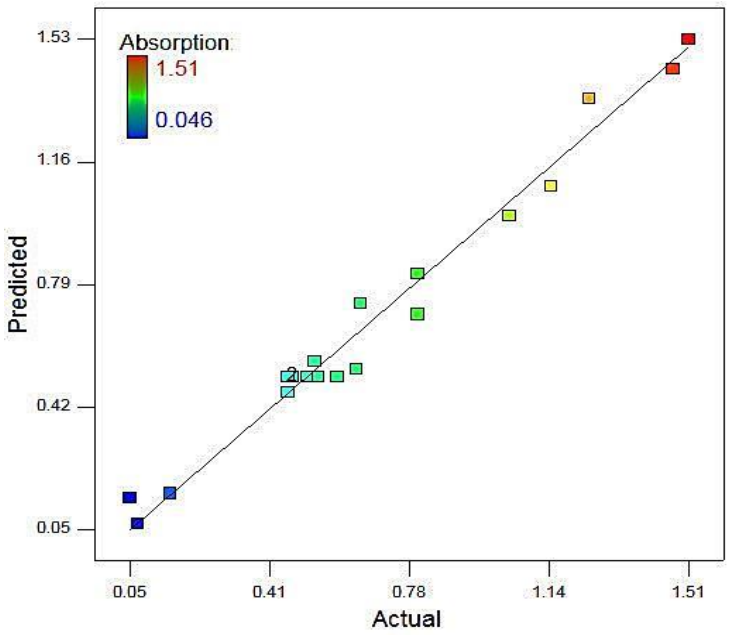

Figure 5. Comparison between the actual and predicted value of HCN absorption from solution.

Effects of significant parameters

Figure 6 shows the perturbation plot for the absorption model and illustrates the overall influence of each input parameter with a common point where all three input parameters meats to achieve maximum absorption. The X-axis represents the value of the factor in coded form. As can be seen, increasing the thickness and TEDA concentration both lead to decrease in absorption, demonstrating the higher performance of nanofibrous filter media. The PAN concentration did not have significant role in absorption. Increasing the thickness of nanofibrous filter media and TEDA concentration are the key considerations for decreasing the absorption and improving the yield of filtration.

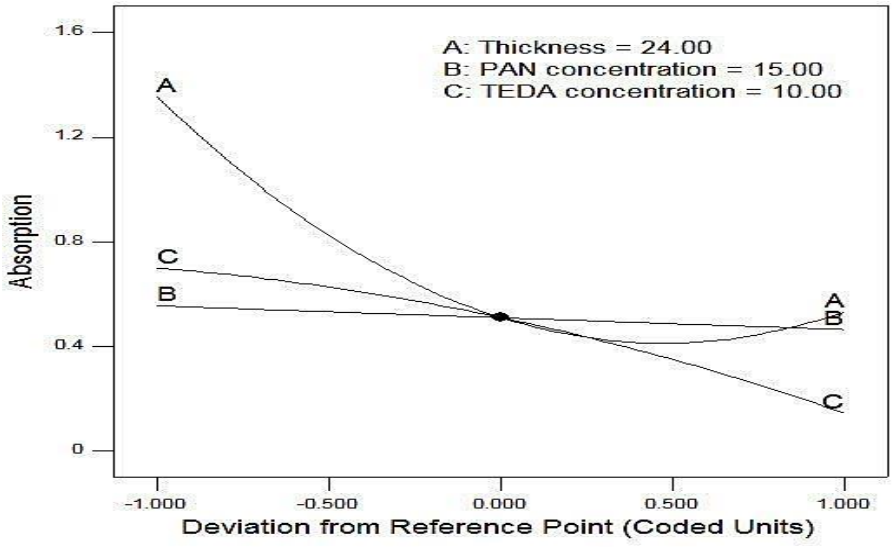

Figure 6. Perturbation curve for the absorption of HCN from solution.

The three-dimensional response surface curve and contour plot for absorption are illustrated in Figure 7. It illustrates the effect of thickness and TEDA concentration (PAN concentration = 15 w/v %) on absorption. It can be seen that absorption of HCN from solution decreases as the thickness of filter media is increased. For TEDA concentration of 10 w/v %, increasing the thickness from 15 to 30 mm lead to a 60% decrease in absorption of HCN from solution. By increasing the TEDA concentration up to 15 w/v %, the absorption decreased from 1.04 to 0.11, when the thickness increases from 15 to 30 mm. Moreover, increasing the TEDA concentration in constant thickness of filter media lead to a decrease in absorption of HCN from solution and consequently increase in the yield of filtration. As mentioned earlier, it is due to the increase in the content of amine groups in PAN-M-TEDA nanofibrous filter media by increasing the TEDA concentration. Consequently, it could enhance the adsorption of acidic HCN by PAN-M-TEDA nanofibrous filter media.

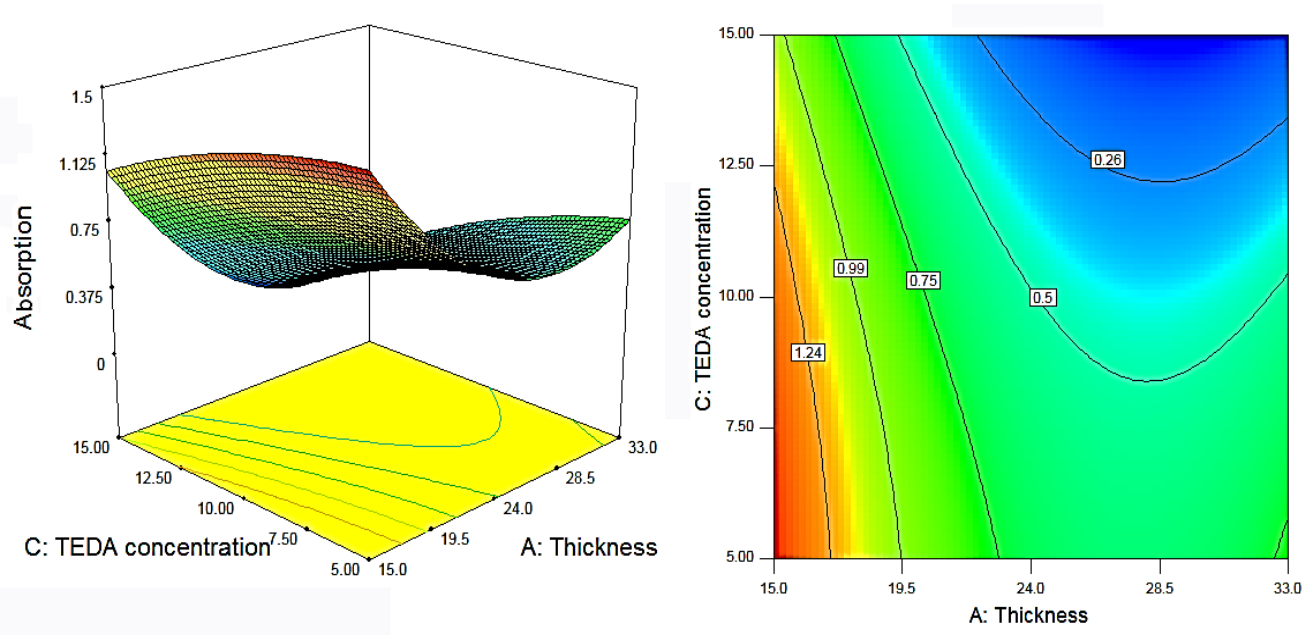

Figure 7. Response surface and contour plot for absorption of HCN from solution.

Optimization

The optimum conditions of input variables in the tested range for minimum absorption of HCN from solution and consequently efficient filtration of HCN from air were established from the RSM. The aim of optimization is to find a good set of conditions that will meet the favorite goal. The constraints of factors and response for the optimization of absorption are shown in Table 5. The optimum solutions have been derived for specified design space constraints for absorption of HCN. The minimum absorption of HCN from solution estimated by RSM equation was obtained at condition of thickness = 28.42 mm, PAN concentration = 16.19 w/v % and TEDA concentration = 14.80 w/v %. The obtained value of desirability (=1) shows that the estimated function may represent the experimental model and desired conditions. In order to confirm the predictive ability of the RSM model for response, a further experiment was carried out according to the optimized conditions. It was observed that the experimental value obtained was in good agreement with the value predicted from the model, with relatively 4% error between the predicted and the actual values.

Table 5. Constraints of factors and response for optimization.

Name	Goal	Lower Limit	Upper Limit	Weight	Importance
Thickness	Is in range	15	33	1	3
PAN concentration	Is in range	10	20	1	3
TEDA concentration	Is in range	5	15	1	3
Absorption of HCN from solution	Maximize	0.046	1.51	1	5

CONCLUSIONS

A novel metal loaded PAN nanofiber impregnated with TEDA (PAN-M-TEDA) has been presented as a potential adsorbent for the purity the air contaminated with hydrogen cyanide. The HCN passes through the filter medias and introduced to the solution containing indicator to measure its absorption via UV-Vis spectroscopy. The results showed that both the functionalization of PAN nanofiber with metal salts and impregnation with TEDA significantly increases the absorption of HCN from solution and consequently the adsorption capacity of nanofibrous filter media. The effect of sample thickness (mm), PAN concentration (w/v %), and TEDA concentration (w/v %) on the absorption of HCN from the adsorbent solution were investigated using response surface methodology (RSM) based on central composite design (CCD). The obtained results indicated that the thickness and TEDA concentration are two most important factors influencing the adsorption of HCN. The use of the response surface model showed that the highest adsorption capacity can be achieved at thickness 28.42 mm, PAN concentration 16.19 w/v % and TEDA concentration 14.80 w/v %.

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