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Development of a novel method for nitrate sorption: an application of Taguchi method

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ABSTRACT

The aim of this study is to investigate application of polypyrrole/polyaniline (PPy-PANI) nanofiber for the removal of nitrate (NO_3^-) from paper mill wastewater. The tests and their optimization results were based on the experiments design in three levels of variables using Taguchi method. The obtained data revealed that maximum removal efficiencies were ~86% (with 0.6 g, 30 min and 6 of adsorbent dose, contact time and pH respectively for PPy-PANI nanofiber). The results showed that in nitrate removal, the pH of the solution was the most effective parameter on the sorption process and the highest NO_3^- removal rate was achieved in near neutral condition. The contact time and adsorbent mass also had considerable effect (less than pH) on NO_3^- removal in the Taguchi method. The effect of temperature on the process was also found that the temperature had positive effect on the process. The calculated amounts of thermodynamic parameters such as $\Delta H°$ (15.09 Kj/mol), $\Delta S°$ (0.0681 Kj/mol·K) and $\Delta G°$ (–4.11, –4.73, –5.38 kj/mol) showed that the adsorption of NO_3^- onto nanofiber was feasible, spontaneous and endothermic.

Keywords: Polypyrrole/polyaniline; Nanofiber; Paper mill wastewater; Experiment design; Taguchi method

1. Introduction

The cellulose and paper industry is an almost global, being present in most developed and developing countries and is one of the most important environmental concerns [1]. One of the important pollution in paper mill wastewater is nitrate. Nitrate contamination of water resources can be originated from the extensive use of nitrogen fertilizers and improper treatment of industrial wastewater [2]. At high concentration of nitrate in human body, nitrates may be reduced to nitrites that combine with hemoglobin to form met-ha hemoglobin, which can be fatal to neonates [3]. In some industrial zones, nitrate is the problem of nuclear waste treatment, where it significantly increases the volume of waste and has a negative effect on cohesion after solidification [4]. A maximum concentration of 50 mg/L NO_3^- (15 mg/L NO_3^- for infants) for drinking water was permitted [5]. Elevated nitrate levels in water can be provided a favorite situation for the growth of algal species which bloom and deplete dissolved oxygen, killing other oxygen requiring aquatic species [6]. Nitrate is a highly soluble and stable ion in water. Therefore much attention has been recently paid to nitrate removal from water or the reduction of nitrates [7].

Among the several methods for nitrate removal from solutions such as evaporation, electro-coagulation, precipitation,ion exchange and membrane separation, adsorption proves to be an efficient and cost-effective method strongly recommended for low concentration. Many sorbents such as a mine-functionalized MCM-41 [8], Fe_3O_4/polyaniline nanocomposite [9], modified steel slag [10], $ZnCl_2$-modified coconut granular activated carbon [11] and low cost natural materials [12] were applied for nitrate sorption from solutions.

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Conducting polymers are widely used in various fields such as microelectronics, composite materials, optics and biosensors [13] and as adsorbent [14,15]. Recent decades, it has reported that conducting polymers such as polyaniline (PANI) and polypyrrole (PPy) has successfully been used for removal of ions from aqueous solution, water and wastewater [16]. Polymerization conditions, the type and size of the dopants incorporated during the polymerization process as well as on the ions present in the electrolyte solution strongly affect onto sorption capacities of conducting polymers [17]. Ghorbani et al. [18] used polyaniline and polypyrrole composites for treatment of paper mill wastewater; the composites showed considerable capacity for heavy metals, anions, color and COD (chemical oxygen demand) removal from paper mill wastewater. It was also reported that polypyrrole and polyaniline were successfully used fornitrate adsorption from aqueous solution by batch sorption method [19]. Polyacrylamide (PAM) was used as adsorbent for pulp and paper mill wastewater treatment. The effectiveness of the polyacrylamides was determined based on the reduction of turbidity, the sorption of total suspended solids (TSS) and the reduction of chemical oxygen demand (COD)[20].

The aim of this study was to investigate the NO_3^- sorption onto PPy-PANI nanofiber from paper mill waste water. These experiments were performed on a batch system. The tests and their optimization results were based on the experiments design in three levels of variables (pH, contact time and adsorbent dosage) using Taguchi methods. The effect of temperature on the NO_3^- removal and thermodynamic of sorption process were also investigated.

2.Materials and methods

2.1. Materials

Aniline (Merck) and pyrrole (Merck) were purified by vacuum distillation and stored in refrigerator prior to use. The pH of the solution was adjusted by adding 0.5 M HCl and 0.5 M NaOH solution. The $FeCl_3$ was purchased from Merck. Table 1 shows the characteristics of the wastewater (paper mill factory in sari, Iran). The concentration of nitrate was determined by ion chromatography.

Table 1
Textile wastewater characterization

Compound	Concentration in waste water before removal
Cu (mg/l)	4.5
Mg (mg/l)	300
Fe (mg/l)	1.5
Zn (mg/l)	16
Total N(NO_3^-, NO_2^-) (mg/l)	33
S^{-2} (mg/l)	21
SO_4^{-2} (mg/l)	155
Color (adsorbance at 600 nm)	0.3612
COD (mg/l)	2700

2.2. Instrumentation

In this study, to study the nanofiber surface, the scanning electron microscope (SEM) device model S3 400, Hitachi, Japan was used to identify the absorbent level. Before taking the SEM photographs from these two specimens, their surface was fitted with a gold plated sputter to guide these improved materials, which ultimately resulted in a higher-quality image and a thickness of 30 nm coated materials. The identification of functional groups was also done by Fourier transform infrared (FTIR) by FTIR spectrometer (Shimadzu 4100). To prepare the sample for testing, mix 1 mg of absorbent with 1000 mg of KBr uniformly, and then press them on a plate that is transparent under pressure of 2200 kg·cm^{-2} for 5 min. After this operation, the sample is ready for the FTIR test. The range of scan for specimens was between 5000–500 cm^{-1}. Ion chromatography (Dionex, ICS-90, Ion Chromatography System, USA) were used to measure the concentration of nitrate in the solutions. The mobile phase consisted of a mixture of 7.0 mM sodium carbonate (Na_2CO_3) and 2.0 mM sodium bicarbonate ($NaHCO_3$) delivered at the flow rate of 1.0 mL min^{-1}. AS40 Auto sampler (Dionex, USA) was assembled with a 10-mL injection loop. A separation column, IonPac® AS9-HC, 4.0 mm × 250 mm (Dionex, USA), a guard column, IonPac® AG9-HC, 4.0 mm × 50 mm (Dionex, USA), and membrane suppressor, AMMS III 4-mm were used. The Data acquisition was performed using a Chromeleon 6.5 (Dionex, USA). The nitrate detection limit was 0.01 mg/L.

2.3. Synthesis of the PPy-PANI nano fibers

PPy-PANI nanofibers were synthesized by in situ simultaneous polymerization of Py and ANI monomers at room temperature in presence of $FeCl_3$ oxidant. In a typical process, 6 g of $FeCl_3$ and 80 mL of distillated water were mixed together in a 250 mL conical flask. A mixture (0.8 mL) of Py and ANI monomers (0.4 mL each) was poured drop wise into the $FeCl_3$ solution under stirring. After 5 min stirring, polymerization reaction was performed without stirring for 6 h. To stop the reaction, 10 mL of acetone was added to the polymerization reaction. The formed PPy-PANI nanofibers were filtered and washed several times with distilled water and then for removal of oligomers, the filtered fiber was washed with acetone [21]. The nanofibers were then dried at oven.

2.4. Testing procedure

These experiments were performed using a stirrer in a batch system. After the initial filtration of the paper mill wastewater for removing suspended solid particles, the samples were ready for the NO_3^- sorption process. Experiments were done with 100 mL of solution (Initial concentration of NO_3^- in paper mill wastewater was 33 mg/L), the adsorbent was separated from the solution after each experiment through filtration, and the sample was prepared for analysis. The efficiency of NO_3^-, % Removal, was calculated as:

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final concentration (mg/L) respectively.

2.5. Statistical design of the experiment using the Taguchi method

In late 1940, Taguchi introduced new statistical concepts and later proved that these concepts are valuable tools in the field of control and quality improvement. Since then, many Japanese industrialists have used this method to improve product and process quality. The increasing quality of vehicles constructed by Japan is heavily linked to the widespread use of this method. In this research, the primitive and practical concepts of the Taguchi method are presented, with examples of various practical applications. Taguchi method is completely different from the typical and commonly used methods of engineering. Taguchi's methodology emphasizes designing quality when designing products and processes, while commonly used methods are based on inspection and quality control during or after the production process. Taguchi has used quite commonly used statistical tools in his quality improvement methods. But he has simplified these methods by identifying a set of powerful strategies for designing tests and analyzing results. Taguchi method has been very effective in improving the quality of Japan's products. Recently, Western industrialized nations have used Taguchi as a simple and effective way to improve products and improve the quality of their manufacturing processes. The Taguchi test design method has a wide range of applications in various industries. However, this method is usually applicable to "outsource" quality control. The Taguchi method creates two new and powerful elements: the first is that it is a systematic way to develop a product or to examine complex issues. Secondly, this method provides a tool for the cost-effective inspection of usable final options. Although the Taguchi method develops concepts of optimization through experimental design, his philosophy with considering the quality of the value and the procedure of new experiments were brand new. The power and generality of this method are more proper than the method itself [22]. Statistical design of the experiments and analysis of data was done using Minitab statistical software (version 17). For this design, three main factors of pH (A), contact time (B) and adsorbent mass (C) were evaluated at three levels. The interaction of AB, AC and BC parameters is not being considered and only the effect of the main parameters is being considered. In general, the range and amount of each of the variables used in this study for the removal of NO_3^- ion from paper mill wastewater using nanofiber are shown in Table (2).

Table 2
Experimental ranges and levels of the independent variables

Symbol	Factor	Level 1	Level 2	Level 3
A	pH	4	6	8
B	Contact time (min)	10	20	30
C	Adsorbent mass amount (g)	0.4	0.6	0.8

3. Results and discussion

3.1. Characterization of the adsorbents

Fig. 1 shows the SEM images of nanofiber. As can be seen, the spherical nanosize particle has been formed with an average size of 24 nm. The polymer nanofiber structure has come under scrutiny by means of the FTIR technique and is shown in Fig. 2. The characteristic IR peaks at 1513, 1430, 1082, and 957–825 cm^{-1} are attributed to the pyrrole ring stretching, conjugated C-N stretching, C-H stretching vibration, and C-H deformation, respectively [23]. The main characteristic peaks for PANI homo polymer are assigned as follows: the bands at 1568 and 1486 cm^{-1} correspond to quinine and benzene stretching ring deformation and the stretching bands at 1293, 1137 belong to C N and N=Q=N

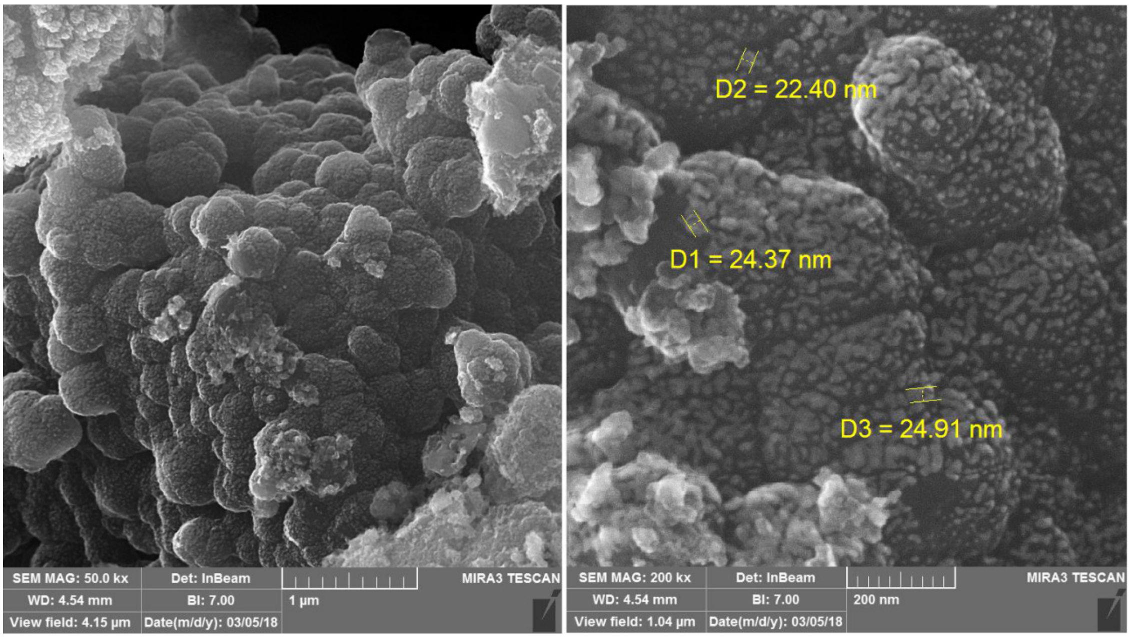

Fig. 1. Scanning electron micrographs (SEM) image of polymer nanofiber.

(Q denotes the quinoid rings) [24]. In the case of the PPy-PANI nanofibers, the observed peaks at 1565, 1447, 1047, and 930–837 cm^{-1} and 1621, 1490, 1209, 1128 cm^{-1} confirm the presence of both PPy and PANI in the synthesized nanofibers.

3.2. Results of Taguchi experiment design

3.2.1. Analysis of experimental data and performance prediction

In these experiments, the NO_3^- sorption from paper mill wastewater using the nanofiber and the effect of three variables of pH, contact time and adsorbent mass using the Taguchi method, in batch absorption tests were performed based on L9 array design with two repetitions. The percent of removal efficiency (% R) was selected as the test response. In all experiments, 100 ml of paper mill wastewater was used. In Table (3), the experimental design of these experiments and the response obtained from each experiment (Taguchi L9 array) for NO_3^- removal from paper mill wastewater are presented.

In the next step in Taguchi optimization, the effect of E_i (i = A, B, and C) has been calculated. For the E_i analysis, the average response (% of NO_3^- removal efficiency) for all levels of the factors (surface effect) must be calculated. Then the effect of the factor, which is a criterion for analyzing the impact of each of the factors on the response, can be obtained from the difference of the lowest average from the highest of it for each factor [25]. For example, to obtain the effect of Factor A, the removal of NO_3^- by a nanofiber is as follows:

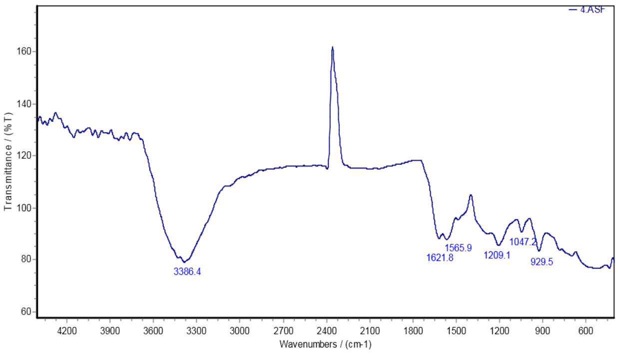

Fig. 2. FTIR spectrum of polymer nanofiber.

Step 1: Calculate the mean of responses at all three levels of factor A.

$$\overline{A_1} = \frac{45.15 + 63.39 + 71.47 + 46.63 + 63.11 + 69.90}{6} = 59.94 \qquad (2)$$

As the same way, we can calculate the mean of responses for factor A at two other levels.

Step Two: The difference of the highest response means from its lowest for factor A.

$$\overline{E_A} = \left(\overline{A_i}\right)_{\max} - \left(\overline{A_i}\right)_{\min} \qquad (3)$$

Furthermore, the effect of other factors can also be calculated in the same way. Table 4 shows the effect of factors on NO_3^- sorption. Based on these tables, the factor A, the pH of the solution, has the most effect on the NO_3^- removal efficiency. After that, contact time and the amount of adsorbent mass are respectively in second and third place of the effectiveness. In the future study, the more efficient the removal (%) is, the more ideal the process will be. A quantitative diagram of the effect of the main factors for the removal of NO_3^- from paper mill wastewater is shown using nanofiber in Fig. 3. According to these forms and information given in

Table 4
The effects of factors and their rankings for NO_3^- removal

Factor			Level
C	B	A	
55.85	57.09	59.94	1
67.37	63.91	81.72	2
67.01	69.23	48.57	3
11.52	12.14	33.15	E_i
3	2	1	*Effectiveness Rank*

Table 3
Variables and results from Taguchi experimental design for removing NO_3^- using nanofiber

Number	Variable by encoding surfaces			NO_3^- removal results (%)	
	pH	Contact time (min)	The amount of adsorbent mass (g)	Experimental results of the first experiment	Experimental results of the second experiment
1	1	1	1	45.15	46.63
2	1	2	2	63.39	63.11
3	1	3	3	71.47	69.90
4	2	1	2	81.58	79.79
5	2	2	3	86.15	85.14
6	2	3	1	79.78	77.87
7	3	1	3	46.04	43.34
8	3	2	1	43.52	42.16
9	3	3	2	58.57	57.78

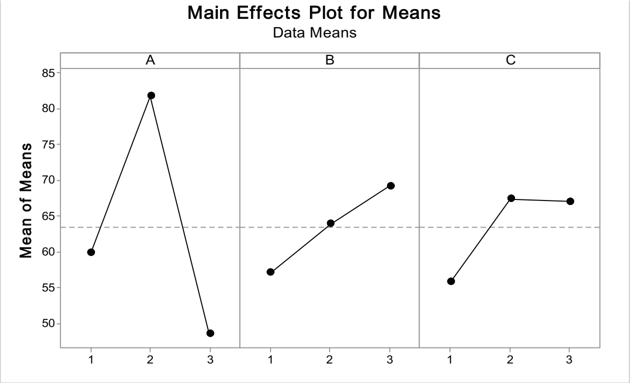

Fig. 3. Diagram effects of main factors of NO_3^- absorption by the adsorbent.

Table 5, it can be concluded that the combination of A_3, B_3, and C_3 has the greatest effect on increasing the removal efficiency of NO_3^- from paper mill wastewater by adsorbent. According to the results obtained from the diagrams of the main factors for NO_3^- sorption from paper mill wastewater, the optimal conditions were predicted as follows:

3.2.2. Statistical analysis of variance of Taguchi method

In addition to analyzing the effect of factors, statistical analysis (ANOVA) shows which factor has a meaningful significance. Variance analysis is a method used for the average comparison of two or more groups [26]. The results of ANOVA analysis for absorbing of NO_3^- are presented in Table 6 and the effects of the three main factors in the design are presented briefly. Also, due to the fact that with 9 experiments, the effect of the interaction of factors cannot be investigated, the effect of interactions between AB, AC, and BC has been discarded. Based on the design of ANOVA, the more P value of the investigated factor is smaller (close to zero), the more effective it is. In the same condition (P-number is equal), the sum of squares (SS) will be decisive, so the larger the SS number, the more effective it will be. As can be seen, the results of ANOVA analysis for absorbing NO_3^- from wastewater by the nano fiber are consistent with the results of the analysis of the effect of the factor considered in the previous section.

The last step in the Taguchi statistical analysis is predicting the response of the optimal situation. After determining the optimal combination of factors and their levels by analyzing ANOVA and analyzing the effect of the agent, we can predict the optimal response from the following relationship [27,28]:

$$R_{pred} = \bar{R} + \left(\bar{A}_3 - \bar{R}\right) + \left(\bar{B}_3 - \bar{R}\right) + \left(\bar{C}_3 - \bar{R}\right) \tag{4}$$

R_{perd} is the predicted removal efficiency in the optimal relationship, and $\bar{R}$ is the average of the responses in 18 experiments, which is 63.41 for NO_3^- adsorption. The predicted answer by the software is 91.5 to absorb NO_3^-. A confirmation experiment for optimal conditions was repeated for both adsorbents and the removal efficiency for NO_3^- was 85.87. The error percentage of the repeated experiment is calculated as:

Table 5
Optimal levels of the studied factors to achieve maximum NO_3^- removal efficiency

Surface value for NO_3^-	Level	Controllable factors
6	2	pH
30	3	Contact time (min)
0.6	2	Absorbent mass (g)

Table 6
Analysis of variance for the process of NO_3^- removal using the nanofiber

P Amount	F amount	Sum Square	Degree of freedom	Factor
0.005	181.65	1702.5	2	A
0.04	23.7143	222.2	2	B
0.035	27.45	257.24	2	C
–	–	9.37	2	Residual error
–	–	2191.31	8	Total

$$\%Error = \left|\frac{R_{\exp} - R_{pred}}{R_{\exp}}\right| \times 100 \tag{5}$$

where R_{exp} is the removal efficiency obtained from the confirmation experiment and R_{perd} is the optimum absorption capacity predicted by the Taguchi method. The repetition of the experiment had an error about 6.56 for NO_3^-, indicating its repeatability.

3.3. Effect of three main factors

As described above, three factors, pH, contact time (min) and adsorbent mass (g) were considered as the main factors for NO_3^- removal by the adsorbent.

3.3.1. Effect of pH parameter on responses

The pH solution is one of the most important factor for sorption process. The inherent value of the optimal pH value in the treatment system can have a significant influence both on the design and construction costs of the facility and on the system, and then on the maintenance and operation of the system. As shown in Table 4, the maximum effect on the removal efficiency of NO_3^- from paper mill wastewater by the adsorbent is the pH parameter (with a lower P–value). Fig. 3 shows the effect of pH parameter (factor A) on the NO_3^- removal efficiency using nanofiber adsorbent. As can be seen, increasing the pH leads to an increase in the NO_3^- adsorption amount. This increase gradually reached a maximum value sharply at pH 6 and then decreased. An increase in basic property of polymer due to the decrease in Cl^- exchange on the sites in polymers. Nitrate removal using PPy and PANI based on the ion exchange of PPy/PANI nanofiber. The rate of nitrite sorption seems to be dependent on the molecular weight (MW) of the polymer and the level of polymer oxidation. Higher molecular weight and highly doped polymer possess more anions or counter ions available for exchanging. However, importance of some other reasons such as strong interactions of NO_3^- ion with the amine and imine groups in the polymers and also the redox reactions between the electro active adsorbate (NO_3^- ion) and adsorbent (PPy) cannot be ignored. More investigation is needed for the achievement of precise conclusions [7,29]. Thus, all future sorption experiments in this research were conducted at initial pH value of 6.0.

3.3.2. The effect of the contact time parameter on responses

Contact time is the other variable which its effects on the system responses and its overall effect on the adsorption process and studied absorbents are one of the goals of this research. The contact time is the other variable which its effects on the system responses and its overall effect on the adsorption process and studied absorbents are one of the goals of this research. In any filtration system based on a discontinuous process, the contact time can have a significant effect on the overall system efficiency and therefore the total purge capacity of the system. In fact, it can be said that any part of the system's time and its sensitivity to deviation will, directly and indirectly, affect all costs and benefits. It should be noted that the contact time in the absorption process is an equilibrium parameter. This means, this variable has an optimal and equilibrium point, which at this point does not have a significant effect on absorption. As a result, the accurate study of this variable can be very important and necessary. Fig. 3 shows the influence of the contact time variable (factor B) on the removal efficiency of NO_3^- from the paper mill waste water by the nanofiber. As can be seen in these figure, with increasing contact time, the removal efficiency of NO_3^- increases. In justifying this phenomenon, it can be said that at the beginning of the reaction, with increasing contact time, the absorbed particles have more chance of penetrating into the adsorbent and occupy active adsorbing sites, but when the process reaches the equilibrium, adsorbent would be saturated and increasing the contact time has no effect on sorption efficiency.

3.3.3. The effect of amount of adsorbent material on the responses

The operating parameter or the next system variable that has been studied is the amount of adsorbent material in the wastewater samples. The adsorption process takes place on the surfaces and structures of the adsorbent material, so the availability of the absorb-able surface will have a significant effect on the removal efficiency. Like all other operating parameters, this item is also, directly and indirectly, related to processes and costs and other issues related to the purification system. The amount of adsorbent material is perhaps the most important determinant of choice with not choosing that material in an absorption process-based system, because the cost of procuring and as well as using this substance, if necessary, washed or disposed of it can be economical or completely uneconomic. As a result, this parameter must be carefully studied. Fig. 3 shows the effect of increasing the amount of adsorbent material on the removal efficiency of NO_3^- from waste water by the nanofiber. As can be seen in these graphs, with the increase in the amount of adsorbent material, the removal efficiency of NO_3^- increases, and after reaching its equilibrium value, it is almost constant, and the increase in the amount of adsorbent does not affect the removal efficiency of the NO_3^-. Meanwhile, the graphs of the interaction of the amount of adsorbent substance with the two previous variables were presented and analyzed in the previous forms.

3.4. Effect of temperature on the NO_3^- sorption

The sorption studies were conducted at 20–40°C, pH 6 and an adsorbent dosage of 0.6 g in a 100 mL wastewater solution to examine the thermodynamics of adsorption. The equilibrium contact time for adsorption was kept constant at 30 min. The adsorption percentage increased with the rise in temperature from 20 to 40°C. Results suggested that the adsorption process has an endothermic nature. Table 7 explains the effect of temperature on the removal efficiency. To determine the changes in Gibbs free energy (ΔG), heat of adsorption (ΔH) and entropy (ΔS) of the adsorption of NO_3^- from wastewater, the Table 7 data were used.

3.4.1. Effect of temperature on thermodynamics parameter on NO_3^-

Different thermodynamic parameters such as the enthalpy change ΔH, free energy change ΔG and entropy change ΔS were calculated using the Eqs. (6)–(8) in order to study the thermodynamics of adsorption of NO_3^- on polymer nanofiber. Using the following equations, the thermodynamic parameters ΔH, ΔS and ΔG for NO_3^- on polymer nanofiber system were calculated as follows [30,31]:

$$K_c = \frac{F_e}{1 - F_e} \tag{6}$$

$$\log K_c = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{7}$$

$$\Delta G = -RT \ln K_c \tag{8}$$

where F_e is the fraction of NO_3^- sorbed at equilibrium. The values of these parameters are given in Table 8. It shows that the enthalpy change ΔH is positive (endothermic) because of the increase in adsorption on successive increase in temperature. The negative ΔG values revealed that the nature of sorption is thermodynamically feasible and spontaneous. The positive value of ΔS indicates the increased randomness at the solid–solution interface during the fixation of the ion on the active sites of the sorbent.

Table 7
The effect of temperature on the NO_3^- removal efficiency.

Temperature (°C)	Removal efficiency of NO_3^- (%)
20	84.38
30	86.75
40	88.79

Table 8
Thermodynamic parameter for adsorption of NO_3^- onto sorbent.

$\Delta H \left(\frac{Kj}{mol}\right)$	$\Delta S \left(\frac{Kj}{mol \cdot k}\right)$	T(°C)	$\Delta G \left(\frac{kj}{mol}\right)$	R^2
15.09	0.0681	20	–4.11	1
		30	–4.73	
		40	–5.38	

4. Conclusions

The polymer nanofiber showed considerable potential for the removal of NO_3^- from paper mill waste water. The Taguchi was used as a most effective method to optimize the removal efficiency of NO_3^-. In the near neutral condition, NO_3^- removal is more than acid and alkaline soluble conditions. After pH, contact time and adsorbent mass, respectively, had the most effect on NO_3^- removal efficiency. Thermodynamic studies are indicative of a negative ΔG and positive ΔS and ΔH. Results showed that the sorption has an endothermic nature. The negative ΔG values suggested that the sorption has a thermodynamically feasible and spontaneous nature. The positive value of ΔS indicates that there is an increased randomness at the solid–solution interface during the fixation of the ion on the sites of the sorbent.

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