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Development of a novel method for Copper sorption: An application of Taguchi Method

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ABSTRACT

The aim of this study is to investigate the application of polypyrrole/ polyaniline (PPy/PANI) nanofiber for Cu (II) sorption 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 results showed that in Copper removal tests, the pH of the solution was the most effective parameter of the sorption process and the highest Copper removal rate was achieved in acid conditions. The adsorbent mass and contact time also had considerable effect (less than pH) on Copper removal in the Taguchi method. The effect of temperature on the sorption process was also studied and results showed that the temperature improved the Copper sorption. The adsorption percentage increased with the rise in temperature from 20 to 40 °C .The calculated amounts of thermodynamic parameters such as ΔH°(55.33KJ/mol) , ΔS°(0.209KJ/molK) and ΔG°(-7.4 ,-8.87,-11.31KJ/mol) showed that the adsorption of Copper on to nanofiber was feasible spontaneous and endothermic.

Keywords: *Experiment Design, Nano Fiber; Paper Mill Wastewater; Polypyrrole/Polyaniline; Taguchi Method*

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INTRODUCTION

Heavy metals come from several industries such as mining and smelting, paper industry, industrial activities, municipal wastes, the printing and photographic industries and sewage sludge [1-3]. The effluents of cellulose and paper industry, including heavy metals such as copper), are one of the important environmental concerns [3, 4]. Copper is one of the most toxic heavy metals, has attracted much attention due to its toxicity and impact on the public health and sometimes death, particularly in children [2, 5, 6]. Excessive amounts of Copper in the body also cause a lot of harm, resulting in a headache, decreased blood sugar, increased heart rate and nausea. The excess Copper in the brain and the liver damages the kidneys and prevents the production of urine. Copper poisoning leads to anemia and loss of hair in women. The high amount of Copper interferes the production of digestive enzymes. Copper poisoning associated with overactivity of children and learning disabilities such as reading and writing disorders, attention deficit disorder, and ear infections. Other symptoms of copper poisoning associated with psychology include symptoms of autism (such as depression, hallucinations, insomnia, paranoia, personality changes, insanity) and schizophrenia symptoms (such as high irritability, lack of awareness and understanding of the senses

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and time). Among the various techniques used for heavy metals removal from aqueous phase such as evaporation, electroplating, precipitation, ion exchange and membrane separation, adsorption can be introduced as an efficient and cost-effective technique especially for low concentration. Many sorbents such as polyethyleneimin emethylene phosphonic acid [7], acrylic acid grafted poly(ethylene terephthalate) fibers [8], Fe_3O_4/poly(L-glutamic acid) (P-L-Glu) magnetic microspheres [9], biomaterials [10, 11], fiber membranes [12], ion exchange [13, 14] and low cost natural materials [15] were used for heavy metal from aqueous phase.

Conducting polymers are widely used in various fields such as microelectronics, composite materials, optics and biosensors [16] and as adsorbent [17, 18]. In recent decades, it has reported that conducting polymers such as polyaniline (PANI) and polypyrrole (PPy) has successfully been used for removal of heavy metals from aqueous solution, water and wastewater [19]. 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 [20]. Ghorbani et al [21] used polyaniline and polypyrrole composites for treatment of paper mill wastewater; the composites showed a considerable capacity for heavy metals, anions, color and COD (chemical oxygen demand) removed from paper mill wastewater. It was also reported that polypyrrole/perlite composite was successfully used for Copper removal from wood and paper industry wastewater [22]. 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) [23]. The aim of this study was to investigate the Copper sorption onto PPy-PANI nano fiber from paper mill wastewater. 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 copper removal and thermodynamic of sorption process were also investigated.

MATERIALS AND METHODS

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 wastewater, Sari, Iran).

Synthesis of the PPy-PANI nano fibers

PPy-PANI nano fibers 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 dropwise 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 nano fibers were filtered and washed several times with distilled water and then for removal of oligomers, the filtered fiber was washed with acetone [24]. The nano fibers were then dried at oven.

Analytical Method

In this study, to study the nano fiber surface, the Scanning Electron Microscope (SEM) device model S3400, Hitachi, Japan was used to identify the absorbent level. Before taking the SEM photographs of 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

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($NO3^{-1}$, $NO2^{-1}$) (mg/l)	33
S-2 (mg/l)	21
$SO4^{-2}$ (mg/l)	155
Color (adsorbance at 600 nm)	0.3612
COD (mg/l)	2700

prepare the sample for testing, mix 1 milligrams of absorbent with 1000 milligrams of KBr uniformly, and then press them on a plate that is transparent under pressure of 2200 kg.cm^{-2} for 5 minutes. After this operation, the sample is ready for the FTIR test. The range of scan for specimens was between 3900-500 cm^{-1}.

Sorption Procedure

The sorption experiments with using a mixer were performed in a batch system. The required concentrations of copper solutions were obtained by paper mill wastewater. The total volume of the solutions was 100 mL and after each experiment, the solution was filtered and then adsorbent was prepared for analysis. The removal efficiency of Cu(II) was calculated as:

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

Where C_i and C_f are the initial and final concentration (mg L^{-1}) respectively.

Statistical design of the experiment using the Taguchi method

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 estimated 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 variable used in this study for the Copper ion removal from paper mill wastewater using nano fiber are indicated in Table (2).

RESULTS AND DISCUSSIONS

Characterization of the adsorbents

Fig. 1 shows the SEM images of nanofiber. As shown in Fig. 1, the morphology of nanofiber was porous. As can be seen, the spherical nanosized particle has been formed with an average size of 24 nm. The nanofiber structure was examined 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 [26]. 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 (Q denotes the quinoid rings) [27]. In the case of the PPy-PANI nanofibers, the

Table 2. Experimental ranges and levels of the independent variables

Symbol	Factor	Level1	Level2	Level3
A	pH	2	4	6
B	Contact time (min)	8	12	16
C	Adsorbent mass amount (g)	0.2	0.4	0.6

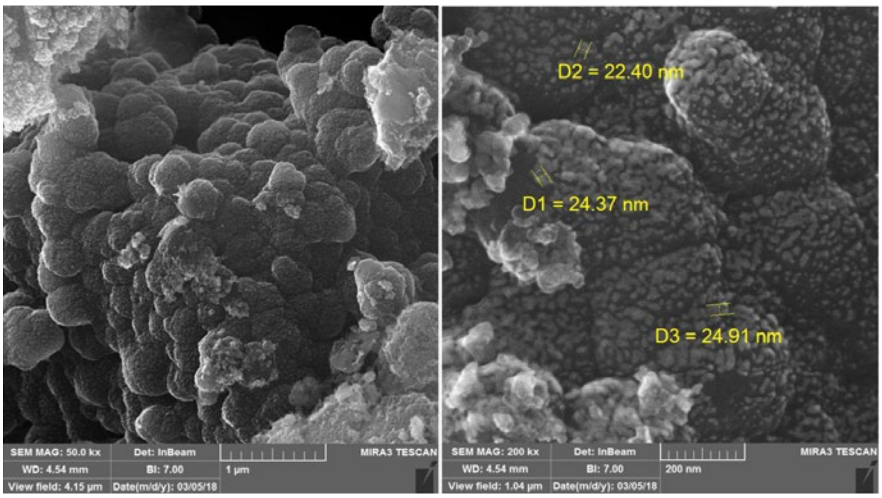

Fig. 1. Scanning electron micrographs (SEM) image of polymer nano fiber.

Table 3. Variables and results from Taguchi experimental design for removing copper using nano fiber.

Number	Variable by encoding surfaces			Copper 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	35.67	36.72
2	1	2	2	44.13	45.78
3	1	3	3	47.79	48.01
4	2	1	2	71.14	73.17
5	2	2	3	76.17	76.65
6	2	3	1	68.57	69.17
7	3	1	3	89.14	91.12
8	3	2	1	84.56	85.21
9	3	3	2	95.16	93.13

observed peaks at 1541, 1447, 1039, and 930–837 cm^{-1} and 1568, 1490, 1276, 1128 cm^{-1} confirm the presence of both PPy and PANI in the synthesized nanofibers.

Results of Taguchi experimental design

The results of designing the Copper adsorption experiment using nanofiber are:

Analysis of experimental data and performance prediction

In these experiments, the removal of copper from aqueous solution using the nanofiber and the effect of the three variables of pH, contact time and adsorbent mass using the Taguchi method, in the batch sorption system were performed based on L9 array design with two repetitions. The 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 copper 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 copper removal efficiency) for all levels of the factors (surface effect) should 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 [28]. For example, to obtain the effect of Factor A, the removal of Copper by a nanofiber can be calculated as:

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

$$\overline{A_1} = \frac{35.67+36.72+44.13+45.78+47.79+48.01}{6} = 43.02 \quad (2)$$

Table 4. The Effects of Factors and Their Rankings for Copper Removal

Factor C	Factor B	Factor A	*Level*
63.32	66.16	43.02	1
70.42	68.75	72.48	2
71.48	70.31	89.72	3
8.16	4.15	46.70	E_i
2	3	1	*Effectiveness Rank*

Table 5. Optimal levels of the studied factors to achieve maximum copper removal efficiency

Surface value for copper	Level	Controllable Factors
6	3	pH
16	3	Contact Time (min)
0.6	3	Absorbent Mass (g)

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.

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

Furthermore, the effect of other factors can also be calculated in the same way. Table 4 shows the effect of factors on Copper removal. Based on this table, the factor A, the pH of the solution, has the highest effectiveness on the Copper removal efficiency. After that, the amount of adsorbent mass and contact time 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 in the removal of Copper from paper mill wastewater is shown using nanofiber in Fig. 3. According to these forms and information given in 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

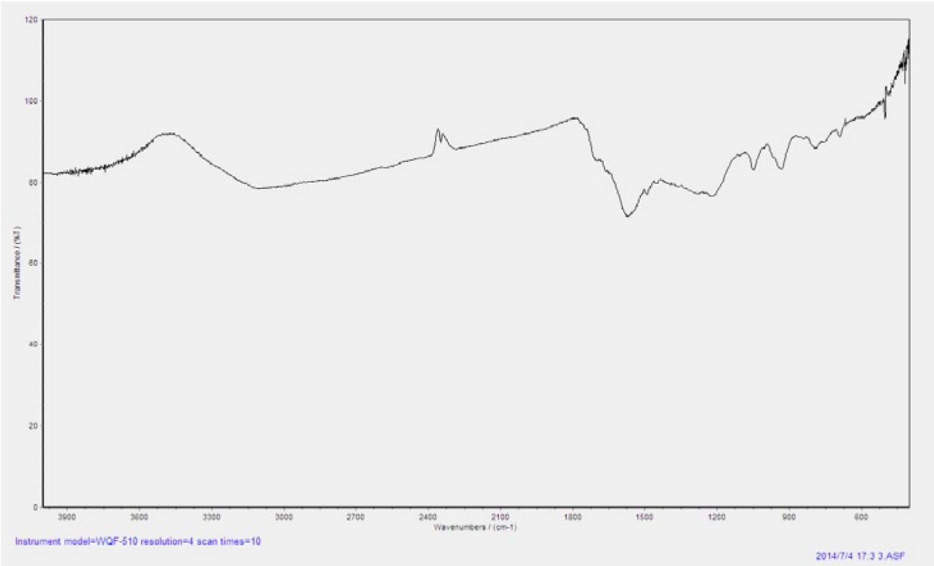

Fig. 2. FTIR spectrum of polymer nano fiber.

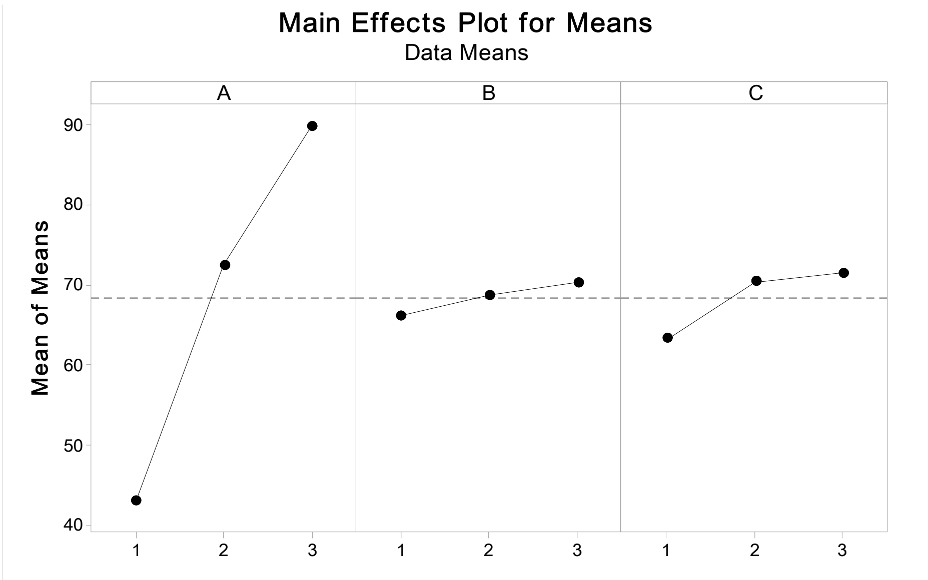

Fig. 3. Diagram effects of main factors of copper absorption by the adsorbent

efficiency of Copper from paper mill wastewater by adsorbent. According to the results obtained from the diagrams of the main factors for copper removal from paper mill wastewater, the optimal conditions were predicted as follows:

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 [29]. The results of ANOVA analysis for sorption of copper are presented in Table 6 and the effects of the three main factors in the design are briefly presented. Meanwhile, 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 was discarded. Based on the design of ANOVA, the more the P value of the investigated factor is smaller

Table 6. Analysis of variance for the process of copper removal using the nano fiber.

P Amount	F amount	Sum Square	Degree Of Freedom	Factor
0.0001	2497.70	3346.47	2	A
0.048	19.63	26.31	2	B
0.011	88.22	118.20	2	C
-	-	1.34	2	Residual Error
-	-	3492.31	8	Total

(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 sorption of Copper from wastewater by the nanofiber were 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 [30, 31]:

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

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 68.41 for Copper adsorption. The predicted answer of the software is 94.69 to adsorb Copper. A confirmation experiment for optimal conditions was repeated for both adsorbents and the removal efficiency for copper was 95.78. The error percentage of the repeated experiment is calculated as:

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

In which R_{exp} is the removal efficiency obtained from the confirmation experiment and R_{perd} is the optimum adsorption capacity predicted by the Taguchi method. The repetition of the experiment had an error about 1.14 for Copper, indicating its repeatability. Comparison to study of Ferrah et al (efficiency=85.69) that used polyethyleniminemethylene phosphonic acid[7], removal of Copper from paper mill wastewater by PPY/PANI in our study was higher. Removal of Copper by PPY/PANI nanofiber was more effective compare to PPY or PANI alone [21]

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 Copper removal by the adsorbent.

Effect of pH Parameter on Responses

The pH solution is one of the most important factors in sorption process. The inherent value of the optimal pH value in the filtration system can have a significant impact 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 a result of the accurate study of this parameter, it is important to study the optimal point of the purification process or the sorption process in this study and its efficiency and the effect of deviation from this point, if necessary, in practice or sensitivity analysis of the parameter. At high pH values, de-doping process occurred in PPY/PANIand then desorption of Cu(II) became the predominant process. No measurable Cu(II) sorption was observed when the treatment media was neutral or alkaline. Under alkaline conditions (pH>7), the polymer (PPy/PANI)became completely undoped and the polymer changed into its deprotonated emeraldine base form, with no counter anions in the polymer to be exchanged with Cu(II) ion in the solution.

As shown in Table 4, the maximum effect on the removal efficiency of Copper 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 Copper removal efficiency using nanofiber. As can be seen, increasing the pH leads to increase the Cu(II) adsorption. This increase gradually reached a maximum value sharply at pH 6. Working over pH=6.0 was avoided to prevent the possible precipitation of Copper. It can be concluded that, at low pH values, the concentration of H^+ ions increases, and thus an intense competition occur between H^+ ions and Cu (II) ions for the sorption on binding sites of the nanofiber. As a result, H^+ ions could either occupy the binding sites or protonate functional groups on nanofiber, i.e. metal-binding sites. Because of protonation, the amount of positively charged sites increases, the corresponding electrostatic repulsion restricts the adsorption of positively charged copper ions. Thus, the sorption capacity of Copper ions reduced at pH 2.0. On the other hand, as the pH values increased, the negative charge density on the surface of nanofiber also increased due to deprotonation of the metal binding sites. This in turn enhances the affinity toward positively charged Cu(II) ions and leads to the improved adsorption of metal ions [32, 33]. Thus, all future sorption experiments in this research were conducted on initial pH value of 6.0.

The effect of the contact time parameter on responses

Contact time is the other parameter which study of its effects on the system responses and its overall effect on the adsorption process is one of the goals of this research. In any filtration system based on a batch 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 sorption 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 Copper from the paper mill wastewater by the nanofiber. As can be seen in this figure, with increasing contact time, the removal efficiency of Copper increases. To demonstrate 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 occupying active sorbing sites, but when the process reaches the equilibrium, adsorbent would be saturated and increasing the contact time has no effect on sorption efficiency.

The effect of amount of adsorbent material on the responses

The other operating parameter has been studied is the amount of adsorbent in sorption process. The sorption process takes place on the surfaces and structures of the adsorbent material, so the availability of the surface will have a considerable 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 treatment system. The amount of adsorbent 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 copper from wastewater by the nanofiber. As can be seen, with the increase in the amount of adsorbent, the removal efficiency of Copper increases, and after reaching to equilibrium, it is almost constant, and the increase in the amount of adsorbent does not affect the removal efficiency of the Copper. Meanwhile, the graphs of the interaction of the amount of an adsorbent substance with the two previous variables were presented and analyzed in the previous forms.

Effect of Temperature on the Copper sorption

The sorption studies were conducted at 20–40 ºC, 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 16 min. The adsorption percentage increased with the rise in temperature from 20 to 40 °C. By increasing the temperature, the higher rate of evaporation will happen in the aqueous solution. More evaporation will change the volume of the aqueous solution that make a considerable error for determination of the pollutant concentration in aqueous phase. So, we have to determine of the temperature in the range of the 20- 40 ºC for reducing the volume change during the thermodynamic study.

Results suggested that the adsorption process has an endothermic nature. Table 7 indicates 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

Table 7. The effect of temperature on the removal efficiency.

Temperature (°C)	Removal efficiency of copper (%)
20	95.43
30	97.13
40	98.72

Table 8. Thermodynamic parameter for adsorption of Cu (II) onto sorbent.

$\Delta H(\frac{Kj}{mol})$	$\Delta S(\frac{Kj}{mol.k})$	T(°C)	$\Delta G(\frac{kj}{mol})$	R^2
54.33	0.209	20	-7.4	0.9778
		30	-8.87	
		40	-11.31	

adsorption of Copper from wastewater, the data of Table 7 were used.

Effect of Temperature on Thermodynamics Parameter on Cu(II)

Thermodynamic parameters such as the enthalpy change ΔH, free energy change ΔG and entropy change ΔS were calculated using the equations (6-8) in order to study the thermodynamics of adsorption of Cu(II) on nanofiber. Using the following equations, the thermodynamic parameters ΔH, ΔS and ΔG for Cu (II) on nanofiber system were calculated as follows [34]:

$$K_c = \frac{F_e}{1-F_e} \quad (6)$$

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

$$\Delta G = -RT \ln K_c \quad (8)$$

Where F_e is the fraction of Cu(II) sorbed at equilibrium. The values of these parameters are presented in Table 8. It indicates that the enthalpy change ΔH is positive (endothermic) because of the increase in Copper removal on the successive increase in temperature. The negative ΔG values revealed that the nature of adsorption is spontaneous and thermodynamically feasible. 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.

CONCLUSIONS

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

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1.C.Tizaoui,S.D. Rachmawati, and N. Hilal, Chem. Eng. J., **209**, 334-344 (2012).
2.S. Wang,L. Li and Z. Zhu, J. Hazard. Mater, **139**, 254-259 (2007).
3.Z. Khazheeva, S. Urbazaeva, N. Bodoev, L. Radnaeva, and Y.O. Kalinin, Water. Resour., **31**, 64-67 (2004).
4.S. Khansorthong, andM. Hunsom, Chem. Eng. J., **151**, 228-234 (2009).
5.L.C Zhou,Y.F Li,X. Bai and G.H. Zhao, , J. Hazard. Mater., **167**, 1106-1113 (2009).
6.M. Sarioglu, U.A.A. Güler, and N. Beyazit, Desalination, **239**, 167-174 (2009).
7.N. Ferrah,O. Abderrahim ,M.A Didi and D. Villemin, Desalination., **269**, 17-24 (2011).
8.M. Karakışla, J. Appl. Polym. Sci., **87**, 1216-1220 (2003).
9.H. Wang, Y. Liu, Z. Deng and S. Han, J. Appl. Polym. Sci., **133**, 43730 (2016).
10.N. Rahbar, H. Yazdanpanah,Z. Ramezani,M.R Shushizadeh, M. Enayat and M. Mansourzadeh, Water. Environ. J., Vol. pp (2017).
11.M. Mukhopadhyay, S. Noronha, and G. Suraishkumar, Bioresource Technol., **98**, 1781-1787 (2007).
12.C. Liu and R. Bai, J. Membrane. Sci., **284**, 313-322 (2006).
13.S.J. Kim, Y.G. Park and H. Moon, Korean. J. Chem. Eng., **15**, 417-422 (1998).
14.A.L Chen,G.Z. Qiu,Z.w. Zhao, P.M. Sun and R.L. Yu, T. Nonferr. Metal. Soc., **19**, 253-258 (2009).
15.H. Nadaroglu, E. Kalkan, andN. Demir, Desalination, **251**, 90-95 (2010).
16.M. Nishizawa, T. Matsue and I.Uchida, Sensor. Actuat. B-Chem., **13**, 53-56 (1993).
17. B.Saoudi, N. Jammul, M.L Abel, M.M Chehimi, and G. Dodin, Synthetic. Met., **87**, 97-103 (1997).
18.X. Zhangand R. Bai, Langmuir, **19**, 10703-10709 (2003).
19.S. Deng, and Y.P Ting, Environ. Sci. Technol., **39**, 8490-8496 (2005).
20.C. Weidlich, K.M. Mangold and K. Jüttner, Electrochim. Acta., **47**, 741-745 (2001).
21.M. Ghorbani, H. Esfandian, N. Taghipour and R. Katal,

Desalination., **263**, 279-284 (2010).
22.A. Naghizadeh,S.J. Mousavi, E. Derakhshani,M. Kamranifar and S.M Sharifi, Korean. J. Chem. Eng., **35**, 662-670 (2018).
23.S. Wong,T. Teng, A. Ahmad,A. Zuhairi andG. Najafpour, J. Hazard. Mater., **135**, 378-388 (2006).
24.M. Bhaumik,A. Maity,V. Srinivasu, and M.S. Onyango, Chem. Eng. J., **181**, 323-333 (2012).
25.J. Antony, D. Perry, C. Wang, and M. Kumar, Assembly. Autom., **26**, 18-24 (2006).
26.A. Maity and S. Sinha Ray, Macromol. Rapid. Comm., **29**, 1582-1587 (2008).
27.P. Xu, X. Han, C. Wang, B. Zhang, X. Wang and H.L Wang, Macromol. Rapid. Comm., **29**, 1392-1397 (2008).
28.M. Edrissi and R.Norouzbeigi, Chinese. J. Chem., **26**, 1401-1406 (2008).
29.A.K. Das,S. Saha, A. Pal and S.K. Maji, J. ENVIRON. SCI. Heal. A., **44**, 896-905 (2009).
30.R.K. Roy, Design of experiments using the Taguchi approach: 16 steps to product and process improvement, John Wiley & Sons, (2001).
31.C. Wang,H. Wu and S.L. Chung, J. Porous. Mat., **13**, 307-314 (2006).
32.B. Alizadeh, M. Ghorbani and M.A. Salehi, J. Mol. Liq., **220**, 142-149 (2016).
33.S.A. Kosa, G. Al-Zhrani and M.A Salam, Chem. Eng. J., **181**, 159-168 (2012).
34.R. Zahedi,R. Dabbagh, H. Ghafourian and A. Behbahanini, Water. Resour., **42**, 690-698 (2015).