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Fabrication of PES/NaX nanocomposite nanofibrous adsorbent for the removal of Cu^{2+}, Co^{2+} and Fe^{2+} from aqueous solutions

Mohsen Hasanizadeh[a], Abdolreza Aroujalian[a,b,*], Ahmadreza Raisi[a,b]

[a]*Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran, emails: aroujali@aut.ac.ir (A. Aroujalian), mohsenhasanizade@yahoo.com (M. Hasanizadeh), raisia@aut.ac.ir (A. Raisi)*
[b]*Food Process Engineering and Biotechnology Research Center, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran*

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ABSTRACT

In this work, the potential of the prepared polyethersulfone (PES)/NaX nanocomposite nanofibrous adsorbents for the removal of Cu^{2+}, Co^{2+} and Fe^{2+} from aqueous solution were investigated. For this purpose, PES/polyacrylonitrile/polyvinylpyrrolidone/NaX (PES/NaX) nanocomposite nanofibers were prepared using the electrospinning process. The prepared nanocomposite nanofibers were characterized by scanning electron microscopy analysis. The effect of different parameters such as zeolite concentration, the dosage of adsorbent, pH, contact time, and the initial concentration of Cu^{2+}, Co^{2+} and Fe^{2+} ions as well as temperature on the efficiency of adsorption were studied in a batch system. The adsorption results showed that the affinity of PES/NaX nanocomposite nanofibrous adsorbent for the removal of metal ions was on the agenda $Cu^{2+} > Co^{2+} > Fe^{2+}$. The kinetic data of metal ions were analyzed by pseudo-first-order, pseudo-second-order and double-exponential kinetic models. Isotherm models namely Freundlich, Langmuir, Redlich–Peterson and Temkin were applied to explain the equilibrium data of metal ions. The maximum monolayer sorption capacities of Cu^{2+}, Co^{2+} and Fe^{2+} were estimated to be 783.3, 654.4 and 642 (mg/g) in an equilibrium time of 60 min and temperature of 45°C. Evaluation of thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) indicated that the nature of metal ions sorption onto the PES/NaX nanocomposite nanofibrous adsorbent was feasible and endothermic. The reusability of the PES/NaX nanocomposite nanofibrous adsorbent was also evaluated after four adsorption–desorption cycles as well.

Keywords: PES/NaX; Nanocomposite; Nanofibers; Heavy metal; Adsorption

1. Introduction

Removal of heavy metal ions from wastewater is a very important factor for environmental considerations which is strongly related to the human's health [1]. Several methods including chemical precipitation [2], reverse osmosis [3], ion exchange [4], chemical reduction [5], membrane separation [6], solid phase extraction [7] and sorption [8] have been used for the removal of heavy metal ions from aqueous solutions [9]. The adsorption method could be considered as a highly efficient and widely used process compared with other techniques. This is because of the high efficiency, easy handling, availability of different adsorbents, the low-cost, flexibility, simplicity, moderate operational conditions and economic feasibility for removing the heavy metal ions from aqueous solutions [10,11]. Surface area, structure and functional groups on the adsorbent surface are the most important physical and chemical properties of adsorbents, respectively. The chemical nature and polarity of the adsorbent surface can influence the attractive forces between the adsorbent and adsorbate as well [10]. The nanofibers prepared by the electrospinning process have unique properties such as high specific surface area, small pore size and high porosity with

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[*] Corresponding author.

fine pores [12]. These properties have increased the appeal of the electrospun nanofibrous among the researchers for use as adsorbents in removal of heavy metal ions [13,14]. In recent years, researchers have used nanofibrous adsorbents such as polyvinyl alcohol/cellulose nanofibers [15], polyethersulfone (PES)/polyacrylonitrile (PAN)/polyvinylpyrrolidone (PVP)/SiO_2 composite nanofibers [16], polypyrrole–polyaniline nanofibers [17], PVP/SiO_2 [18] and PAN-oxime [19] nanofibrous adsorbents for the removal of heavy metal ions.

Zeolite has been widely used in industrial processes such as purification of heavy metal ions from wastewater. The presence of functional groups such as silanol as well as the ion-exchange properties, selective adsorbent, hydrophilic affinities and higher surface area make an increment on the adsorption efficiency of this adsorbent exponentially [20]. At the other extreme, due to their unique properties, such as high surface area, high porosity and negative functional groups, nanozeolites have a high efficiency in the heavy metal removal processes [21].

Many researchers have widely used natural and synthesized zeolites for the removal of heavy metal ions from wastewater. Nevertheless, NaX nanozeolites have been used in a few of them [22].

In the present work, initially, the NaX nanozeolites were synthesized by the microwave heating method [23]. Then, the PES/NaX nanocomposite nanofibrous adsorbent was prepared by the electrospinning process and the potential of the prepared adsorbent for adsorption of copper, cobalt and iron from aqueous solutions were investigated. The effects of various parameters including zeolite concentrations, the dosage of adsorbent, pH of solutions, contact times, initial concentrations and temperature on the sorption process were investigated. Also, the equilibrium thermodynamic and kinetic model parameters for copper, cobalt and iron sorption using PES/NaX nanocomposite nanofibrous adsorbent were investigated.

2. Materials and methods

2.1. Material

The commercial PES with a molecular weight of 58,000 g/mol was provided from BASF (Ludwigshafen, Germany). PAN powder with a molecular weight of 60,000 g/mol was purchased from Polyacryl Co. (Isfahan, Iran). *N,N*-Dimethylformamide (DMF) and NaOH were prepared from Merck Co. (Darmstadt, Germany). PVP (K90, molecular weight 360,000 g/mol), Fumed silica (7 nm) and $NaAlO_2$ were supplied from Sigma-Aldrich (MO, USA). HNO_3 and HCl were provided by Sigma-Aldrich. The solutions of Cu^{2+}, Co^{2+} and Fe^{2+} ions were prepared by dissolving a certain amount of copper, cobalt and iron nitrates (Sigma-Aldrich, USA) in laboratory deionized water.

2.2. Synthesis of NaX nanozeolites

The NaX nanozeolites were synthesized according to the microwave method described previously [23]. Briefly, aluminosilicate gel was made by mixing freshly prepared aluminate and silicate solutions together with the molar ratio of 5.5 Na_2O:1.0 Al_2O_3:4.0 SiO_2:190 H_2O. The gel was continually stirred at room temperature for 24 h. Then, microwave heating was applied at a 900 W power and temperature of 90°C for 3 h. Finally, the products were washed with deionized water by centrifugation at 600 rpm until the pH value reached under 8, and were finally dried at room temperature for 24 h.

2.3. Preparation of PES/NaX solution

2 wt% PAN and 2 wt% PVP were dissolved in DMF and were stirred at a temperature of 80°C for 24 h. Then, 16 wt% PES was dissolved in the solution and continually stirred at the same condition. Finally, the PES/PAN/PVP/NaX composite mixtures were prepared by mixing of nanozeolites in PES/PAN/PVP solutions in different weight ratios of 0%, 1%, 2%, 3% and 4% which are listed in Table 1.

2.4. Electrospinning process

The prepared solution was spinning via an electrospun apparatus for 8 h (Nanomeghias Fanavaran, Iran). The solution was injected in a constant rate of 8 μL/min by a needle using a syringe pump. A 16.5 kV voltage was applied for electrospinning of PES/NaX solution on an aluminum sheet located on the collector which was 14 cm farther from the nozzle. The prepared PES/NaX nanocomposite nanofiber adsorbent was heated in an oven at 160°C for 1 h. This adsorbent had a thickness of 60 μm.

2.5. Characterization of nanofibers

The morphology of the top surface and cross-section of the electrospun nanofibrous mats were analyzed using a scanning electron microscopy (KYKY-EM3200 SEM, China). The equilibrium concentration of heavy metal ions in the adsorption medium was measured using an atomic adsorption spectroscopy apparatus (AAS, Varian SpectrAA-300, Varian, California).

2.6. Determination of mean fiber diameter and porosity

The mean diameter of nanofibers was obtained using ImageJ software.

The bulk porosity (ε) of the prepared nanofibers absorbent was estimated by Eq. (1):

$$\varepsilon = \frac{W_w - W_d}{\rho_w v_w} \tag{1}$$

Table 1
The nomenclature and characterizations of prepared adsorbents

Adsorbent	Zeolite concentration (wt%)	Mean fiber diameter (nm)	Porosity (%)
M0	0	544	81
M1	1	–	89
M2	2	720	91
M3	3	–	93
M4	4	1,069	93

where W_w and W_d are the absorbent weight (g) in wet and dry states, respectively. ρ_w is density of water at the room temperature and v_w is the volume of the adsorbent in the wet state. The porosity values were determined from the averages of three measurements.

2.7. Batch adsorption experiments

The influences of the adsorption experimental parameters such as nanozeolite concentration, pH, time, initial metal ions concentration and temperature, on the removal of Cu^{2+}, Co^{2+} and Fe^{2+} ions were studied in a batch system. The concentrations of the metal ions in the solutions were determined by an atomic absorption spectrometer. Batch adsorption experiments were carried out by embedding 50 mg of PES/NaX nanocomposite nanofibers in flasks including 100 mL of solutions over 60 min at 298 K by magnetic stirring. The adsorption capacities (q_e (mg/g)) of metal ions were calculated by Eq. (2):

$$q_e = \frac{(C_0 - C_e)V}{1000M} \tag{2}$$

where C_0 and C_e are the initial and equilibrium heavy metal ion concentrations in the liquid phase (mg/L), respectively. V is the volume of the solution (mL) and M is the mass of nanofiber composite (g).

The influence of zeolite concentration in the adsorbent on the Cu(II), Co(II) and Fe(II) sorption was investigated at the range of 0%–4%. Also, the effect of pH solution on the Cu(II), Co(II) and Fe(II) sorption was studied in the range of 2–7 at the optimum zeolite concentration. The initial pH of the solution was adjusted with 0.1 M HCl and/or 0.1 M NaOH. For determining the effect of contact time on Cu(II), Co(II) and Fe(II) sorption, the experiments were done at optimum zeolite concentration (2 wt%), pH and 25°C at definite time intervals. For examining the effect of initial Cu(II), Co(II) and Fe(II) concentration and temperature, the experiments were carried out with an initial Cu(II), Co(II) and Fe(II) concentration range of 50–1,000 mg/L at three different temperatures of 298, 308 and 318 K at optimum pH.

The kinetic, isotherm and thermodynamic parameters were obtained by nonlinear regression using MATLAB software.

For regeneration of nanofiber nanocomposite adsorbent, the adsorbent was rapidly washed with 1 mol/L HNO_3 solution, and then washed several times with deionized water. Subsequently, the nanofiber nanocomposite adsorbents were dried in a vacuum oven at 80°C.

2.8. Determination of the point of the zero charge (pH_{pzc})

The pH_{pzc} for the PES/NaX nanocomposite nanofibers was determined by the following method. 50 mL of 0.1 M NaCl was transferred in a series of flasks. The pH of the solutions was adjusted in the range of 2–7 by adding 0.1 M HNO_3 or/and 0.1 M NaOH solutions. Then, 0.1 g adsorbent was added to the solution. After that, the solutions were shaken for 4 d at 25°C. Finally, the pH of the solutions was measured. pH_{pzc} was reported at a pH in which the initial pH equals the final pH. A similar method is applied by Hameed et al. [24] for determining pH_{pzc}.

3. Results and discussion

3.1. Characterization of nanofibers

The SEM images of synthesized NaX nanozeolite and PES/NaX nanocomposite nanofibers with different weight ratios (0%, 2% and 4%) are shown in Fig. 1. As shown in Fig. 1(a), the particle size distribution of synthesized NaX nanozeolite was uniform with narrow size distribution. Also, the average size of NaX particles was 43 nm. The effect of zeolite concentration on the morphology of electrospun PES/zeolite nanofibers with 0, 2 and 4 wt% is shown in Figs. 1(b)–(d). The pure PES nanofibers were smooth and uniform with an average diameter of 544 nm. Furthermore, the fiber diameter and porosity of the electrospun PES/NaX

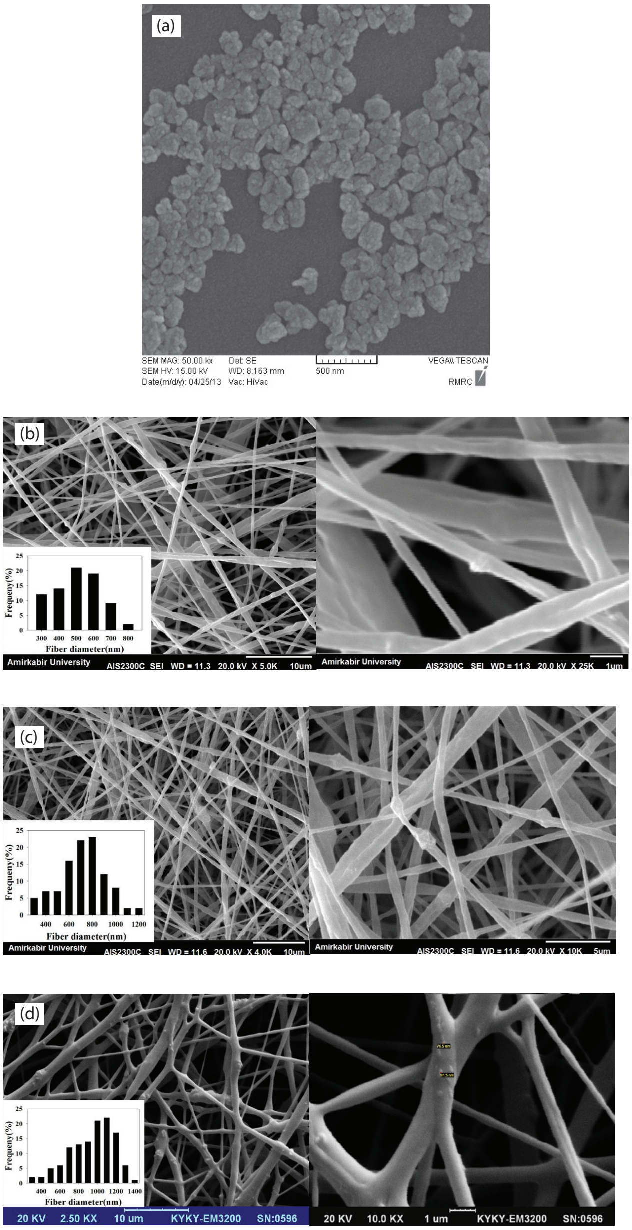

Fig. 1. The SEM image of nanocomposite nanofiber adsorbent (a) zeolite, (b) without zeolite, (c) 2% zeolite and (d) 4% zeolite.

nanocomposite nanofibers was gradually increased by the loading of nanozeolite up to 4% (Table 1). This can be due to the existence of the NaX nanoparticles in the PES fibers. The PES has a negative zeta potential and the NaX nanoparticles have negative charge on their surface, so adding NaX nanoparticles creates a reduction in the zeta potential of the PES/NaX electrospinning solution. This means that the presence of NaX nanoparticles can enrich the negative charge in the PES/NaX solution and as a result an increase in the diameter of fibers may be done. Also, adding the NaX nanoparticles in the solution will increase the viscosity of the electrospinning solution, and consequently the fiber diameter will be increased as well. For 4 wt% NaX nanoparticles in PES/NaX nanocomposite nanofibers, the agglomeration of nanoparticles was observed by loading a further increase in nanozeolites concentration into the PES nanofibers.

3.2. Effect of zeolite concentration on the adsorption of metal ions

The effect of nanozeolite concentration on the adsorption of Cu^{2+}, Co^{2+} and Fe^{2+} ions from aqueous solutions for initial metal concentrations of 100 mg/L, adsorbent dosage of 0.5 g/L, initial pH of solutions for Cu^{2+} (pH = 6), Co^{2+} (pH = 6) and Fe^{2+} (pH = 3) and contact time of 1 h is shown in Fig. 2. It can be seen that as the nanozeolite concentration is increased up to 2 wt%, the adsorption capacities of Cu^{2+}, Co^{2+} and Fe^{2+} are also increased. A further increment in nanozeolite concentrations in the nanofibers from 2 to 4 wt% leads to a decrement in the adsorption capacity of the nanofibrous adsorbent for three metal ions. Increasing adsorption capacity by increasing nanozeolite concentrations up to 2 wt% could be described by the good distribution of nanozeolites into the nanofibers. Furthermore, the affinity of the nanofibrous adsorbent for metal ions can be due to existing functional silanol groups in the nanozeolites which have a good ability to absorb metal ions. The decrement in adsorption capacities of metal ions in nanozeolite concentrations from 2 to 4 wt% could be ascribed to the aggregation and coagulation of nanozeolite particles which decreased the available sites of the adsorbent for the adsorption of metal ions (Fig. 1). Therefore, the nanozeolite concentration of 2 wt% was selected as an optimum value of experiments. Thus, all specimens prepared based on 2 wt% nanozeolite concentration for future works.

3.3. Effect of pH on adsorption of metal ions

The pH of the solution in the adsorption process is a very important parameter, which influences the metal adsorption by protonation/deprotonation of the functional groups of the adsorbent. The influence of pH on the sorption of Cu^{2+}, Co^{2+} and Fe^{2+} ions onto the PES/NaX nanocomposite nanofibrous adsorbent is shown in Fig. 3. Also, the calculations show that the pH_{pzc} value of PES/NaX nanocomposite nanofiber is 3.15. When the pH_{pzc} value is low, the more copper, cobalt and iron ions will be attracted to the active sites on the surface of the adsorbents. This indicates that as the pH value of the solution increases, the adsorption of metal ions will also increase. In fact, as the pH values of the solutions increase from 2 to 6 for copper and cobalt and from 2 to 3 for iron, the removal efficiency of metal ions enhanced remarkably and then decreased slowly at pH values >6. The lower adsorption capacities of metal ions at lower pH values could be attributed to the protonation of the sulfur atom of the –SH group which reduced the ability of adsorption of Cu^{2+}, Co^{2+} and Fe^{2+} ions from the solutions. As the pH increases from 2 to 6 for copper and cobalt, and from 2 to 3 for iron, because of its low pH_{pzc}, the protonation of functional groups of the adsorbent reduces. Consequently, the active sites will be ionized increasingly and the copper, cobalt and iron ions will be adsorbed accordingly. Furthermore, at a lower pH, the competition of H^+ with the metal ions in the solutions for the sorption sites of the nanofiber adsorbent resulted in a decrement in adsorption capacities of metal ions. The adsorption capacities of copper and cobalt reached a maximum (180.8 and 157.2 mg/g, respectively) when the pH value was 6. Nevertheless, this value was equal to 110.2 mg/g for the ion at a pH value of 3. In these values of pH, no metal hydroxide precipitate and sulfur atoms protonated group –SH occurs and thus three metal ion adsorption capacities decreased with increasing the pH value. The positive charge density of surface sites and the functional groups with the deprotonation process were decreased by increasing the pH value which leads to a decrement in the repulsion between the adsorbent surface and metal ions. Subsequently, an increment in the adsorption capacities of copper, cobalt and iron took place into the nanofibrous adsorbent. This result is due to the lower pH_{pzc}. Due to the formation of hydroxylated complexes, the adsorption capacity of metal ions was decreased by increasing pH value. This behavior can be justified by precipitation

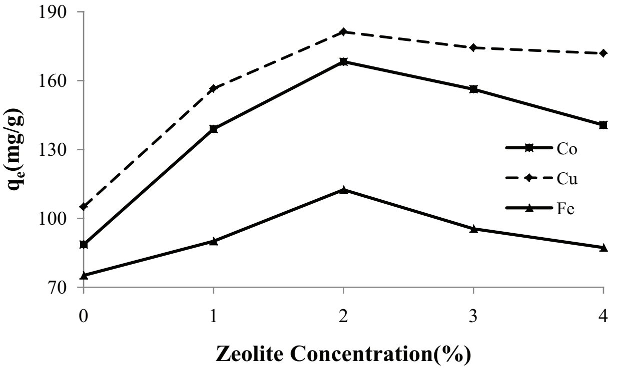

Fig. 2. Effect of zeolite concentration on adsorption.

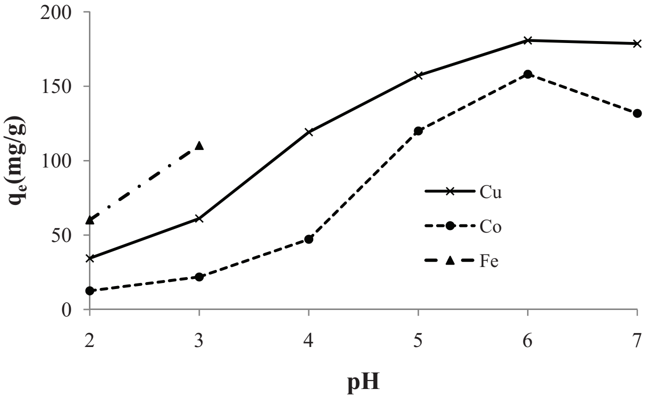

Fig. 3. Effect of pH on adsorption of heavy metal.

of copper and cobalt ions at pH values higher than 7 and for iron ions at a pH value higher than 3. Similar trends were reported by other researchers [25–29]. Accordingly, the pH value of 6 was selected for copper and cobalt, and 3 for iron ions as optimum pH values for further experiments.

3.4. Effect of contact time and adsorption kinetics

The effect of contact time on the adsorption of Cu^{2+}, Co^{2+} and Fe^{2+} ions onto the PES/NaX nanocomposite nanofibrous adsorbent for initial metal concentrations of 100 mg/L, and adsorbent dosage of 0.5 g/L at room temperatures is shown in Fig. 4. This figure shows that the sorption capacities for metal ions using nanofibrous adsorbent were increased remarkably within 10 min and the specimen reached the equilibrium condition after 60 min. Therefore, the equilibrium time of 60 min was selected for further experiments. Also, it can see that the adsorption capacity of nanocomposite nanofibrous adsorbent for Cu^{2+} ions was higher than Co^{2+} and Fe^{2+} ions. It is clear that electronegativity is a dominant factor for sorption [30]. It has been reported that ions with a smaller radius had a greater sorption affinity [31]. Electronegativities and the ionic radius of the elements were given in Table 2. This could be attributed to a smaller ionic radius of copper compared with cobalt and iron ions ($Cu^{2+} > Co^{2+} > Fe^{2+}$) and higher electronegativity of Cu^{2+} ions into the PES/NaX nanocomposite nanofibers in comparison to Co^{2+} and Fe^{2+} ions ($Cu^{2+} > Co^{2+} > Fe^{2+}$). Many mechanisms can be the root cause of a fast transfer and consequently an external surface adsorption of metal ions to the PES/NaX nanocomposite nanofibrous adsorbent. The diffusion of metal ions through the pores of nanofibers and the chemical adsorption between the functional groups of NaX nanozeolite such as silanol groups and sulfone groups of PES nanofiber with metal ions affected the adsorption of metal ions (Fig. 5). To investigate the kinetic parameters of metal ions by the nanocomposite nanofibrous adsorbent, the experimental data were analyzed using pseudo-first-order (Eq. (3)) [32], pseudo-second-order (Eq. (4)) [33] and double-exponential (Eq. (5)) kinetic models. These models were described as follows [34]:

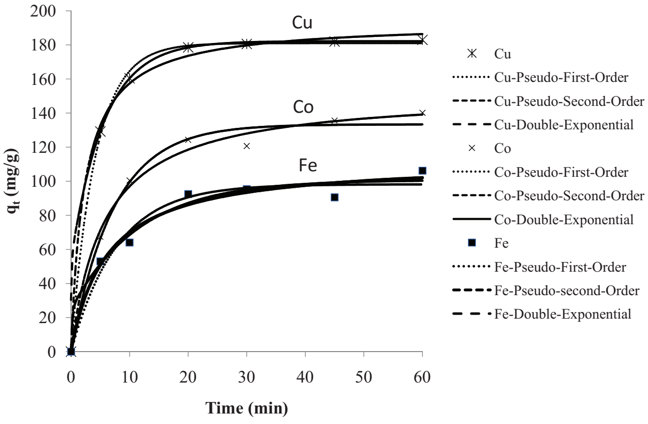

Fig. 4. Adsorption kinetics of copper, cobalt and iron ions onto nanocomposite nanofiber adsorbent.

Table 2
Electronegativities and ionic radius of Cu^{2+}, Co^{2+} and Fe^{2+} ions

Ion	Ionic radius (pm)	Electronegativity (Pauling)
Copper	72	1.9
Cobalt	74	1.88
Iron	76	1.83

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (3)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

$$q_t = q_e - (\frac{D_1}{x_{\text{ads}}})\exp(-K_{D1}t) - (\frac{D_2}{x_{\text{ads}}})\exp(-K_{D2}t) \quad (5)$$

where q_t and q_e (mg/g) are the amounts of metal adsorbed at time t and equilibrium time, respectively. k_1 and k_2 (1/min) are the constants of pseudo-first-order and pseudo-second-order kinetic models, respectively. D_1 and D_2 (mg/L) are rate constants of the rapid and slow steps and K_{D1} and K_{D2} (1/min) are constant controlling the mechanism and x_{ads} (mg/L) is the adsorbent concentration. Fig. 4 shows the plot of q_t vs. time. The parameters of different kinetic models for copper, cobalt and iron ions adsorption are presented in Table 3.

The average correlation coefficients (R^2) of three metal ions were successfully greater than 0.9804, 0.9810 and 0.9894 for pseudo-first-order, pseudo-second-order and double-exponential, respectively. It was found that the best model for fitting the kinetic data of metal ions is the double-exponential model. The results of fitting the kinetic data with two exponential models show that both molecular diffusion and adsorption phenomena are also effective in the metal adsorption process.

3.5. Modeling of equilibrium data

In the present study, in order to analyze the equilibrium data of Cu^{2+}, Co^{2+} and Fe^{2+} ions, and adsorption onto the PES/zeolite nanofibers, four well-known adsorption isotherms were used, namely Langmuir (Eq. (6)), Freundlich (Eq. (7)), Redlich–Peterson (Eq. (8)) and Temkin (Eq. (9)) were used as presented by the following equations [35]:

$$q_e = q_m \frac{bC_e}{1 + bC_e} \quad (6)$$

$$q_e = k_F C_e^{\frac{1}{n}} \quad (7)$$

$$q_e = \frac{PC_e}{1 + \alpha C_e^{\beta}} \quad (8)$$

$$q_e = \frac{RT}{h} Ln(AC_e) \quad (9)$$

where q_e and C_e are the adsorption capacity (mg/g) and metal equilibrium concentration in the solution (mg/L), respectively. In the Langmuir model, b (L/mg) is a sorption equilibrium constant which is related to the number of surface sites per unit mass of adsorbent and q_m is the maximum value of metal ion adsorption per unit mass of adsorbent that is related to the monolayer adsorption capacity. Freundlich parameters including k_F (mg/g) and n are related to the sorption capacity and the sorption intensity. P is the Redlich–Peterson isotherm constant (1/mg), α is the Redlich–Peterson isotherm constant (1/mg) and β is the exponent term which lies between 0 and 1. A and h are the Temkin isotherm equilibrium binding constant (L/mg) and Temkin isotherm constant, respectively.

The results are presented in Table 4. As presented, the equilibrium data of three metal ions were well described by the Redlich–Peterson ($R^2 > 0.9873$) isotherm model compared with the Freundlich isotherm model ($R^2 > 0.9244$), Langmuir ($R^2 > 0.9832$) and Temkin ($R^2 > 0.9717$). The β constant of the Redlich–Peterson isotherm equation is about 1 which indicates that the monolayer reaction of metal ions using PES/NaX nanocomposite nanofibrous adsorbent was the predominant reaction, but it was not the sole monolayer adsorption.

Fig. 6 shows the nonlinear relationship between the amounts of metal ions adsorbed per unit mass of nanocomposite nanofiber adsorbent and the concentration of residual metal ions in the solution, for copper, cobalt and iron at different temperatures. A comparison between the performance of PES/zeolite nanofibrous adsorbent with adsorbents for copper, cobalt and iron ions sorption is shown in Table 5. A careful search in the literature reveals that the adsorption capacity of PES/nanozeolite nanofibers for copper, cobalt and iron ions is higher than other corresponding adsorbents in the previous literature [36–42].

Moreover, the dimensionless separation factor (R_L) has been calculated using the Langmuir parameters shown in Table 6. This factor is a criterion of the tendency between sorbent and adsorbent [43]:

$$R_L = \frac{1}{1 + K_a C_0} \tag{10}$$

The R_L value is classified into categories including $R_L > 1$, $0 < R_L < 1$ and $R_L = 0$, suggesting that adsorption is unfavorable, favorable and irreversible, respectively [44]. As shown in Table 6 and Fig. 7, the R_L values decreased by increasing initial concentrations of metal ions. As the temperature is increasing, the K_α constant of the Langmuir model also increased. Consequently, the R_L decreased. This indicated

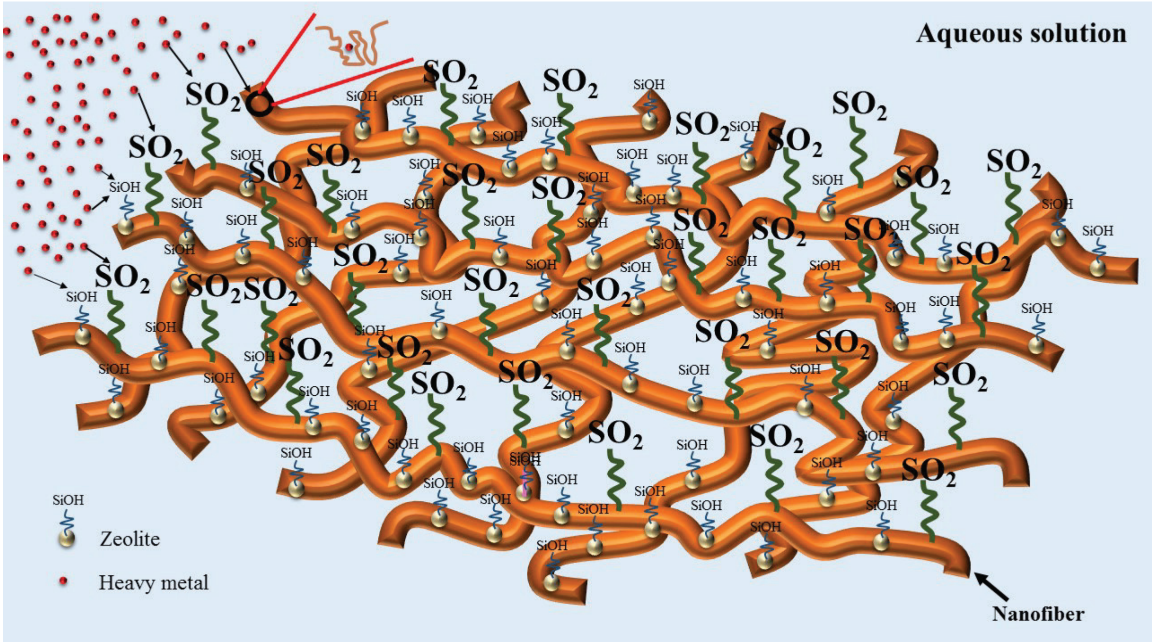

Fig. 5. Mechanism of heavy meal adsorption on PES/NaX nanocomposite nanofiber adsorbent.

Table 3
Kinetic parameters of metal sorptions onto nanocomposite nanofiber adsorbent

Metal	Pseudo-first-order			Pseudo-second-order			Double exponential					
	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e	k_2 (g/mg min)	R^2	q_e	D_1 (mg/g)	K_{D1} (min^{-1})	D_2 (mg/g)	K_{D2} (min^{-1})	R^2
Copper	181	0.2404	0.9863	193	0.002254	0.9722	182	64.23	0.1773	11.71	7.419	0.9993
Cobalt	133	0.1373	0.9867	152	0.001148	0.9924	133	66.43	0.1365	0.0001275	0.1624	0.9889
Iron	98	0.1279	0.9683	112	0.001147	0.9786	100	38.02	0.08587	12.38	4.632	0.98

that copper adsorption was more favorable at a higher temperature [43].

3.6. Determination of thermodynamic parameters

In the adsorption process, the temperature has an important role which determines the nature of the adsorption process by calculating the thermodynamic parameters.

The Gibbs free energy change of the adsorption process ($\Delta G°$) is calculated by the following equations:

$$\Delta G^o = -RTLn(K_c) \tag{11}$$

$$Kc = \lim_{C_{el} \to 0} \frac{C_{es}}{C_{el}} \tag{12}$$

where R is the gas constant (8.314 J/mol K), T is an absolute temperature (K) and K_c is the adsorption equilibrium constant. C_{es} and C_{el} are the values of solid phase concentration and liquid phase concentration in equilibrium at mg/L, respectively.

The enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were calculated by the following equations:

$$LnK_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{13}$$

where $\Delta H°$ and $\Delta S°$ were obtained from the slope and intercept of $\ln K_c$ vs. $1/T$ plot (the figure is not presented). The calculated thermodynamic parameters of metal ions onto the composite nanofiber are shown in Table 7. As it is shown, all the Gibbs free energy change values were negative and the increase in

Table 4
Isotherm parameters for metal adsorption onto the nanocomposite nanofiber adsorbent at different temperatures

Metal	Temperature (K)	Langmuir			Freundlich			Redlich–Peterson				Temkin		
		q_m (mg/g)	K_a (L/mg)	R^2	k_F (mg/g)	n	R^2	P (L/mg)	α (L/mg)	β	R^2	A	h	R^2
Copper	298	747	0.0312	0.9897	114.6	3.375	0.9555	32.61	0.08179	0.8996	0.9913	0.6988	20.85	0.9835
	308	779	0.03344	0.9786	124	3.416	0.9679	53.58	0.1851	0.8417	0.994	0.928	21.26	0.9819
	318	783	0.08672	0.988	171.7	3.994	0.9299	82.07	0.1508	0.9338	0.9925	1.755	22.33	0.9827
Cobalt	298	596	0.02435	0.9945	89.4	3.443	0.892	12.66	0.0142	1.063	0.9966	0.3754	23.52	0.9668
	308	640	0.02601	0.9928	97.21	3.436	0.9187	16.64	0.02595	1	0.9928	0.4706	23.53	0.9744
	318	654	0.03013	0.9815	107.1	3.534	0.9445	29.9	0.08855	0.8961	0.9882	0.6951	25.19	0.9814
Iron	298	482	0.009508	0.977	36.09	2.643	0.9069	3.998	0.00411	1.106	0.9798	0.102	24.38	0.9539

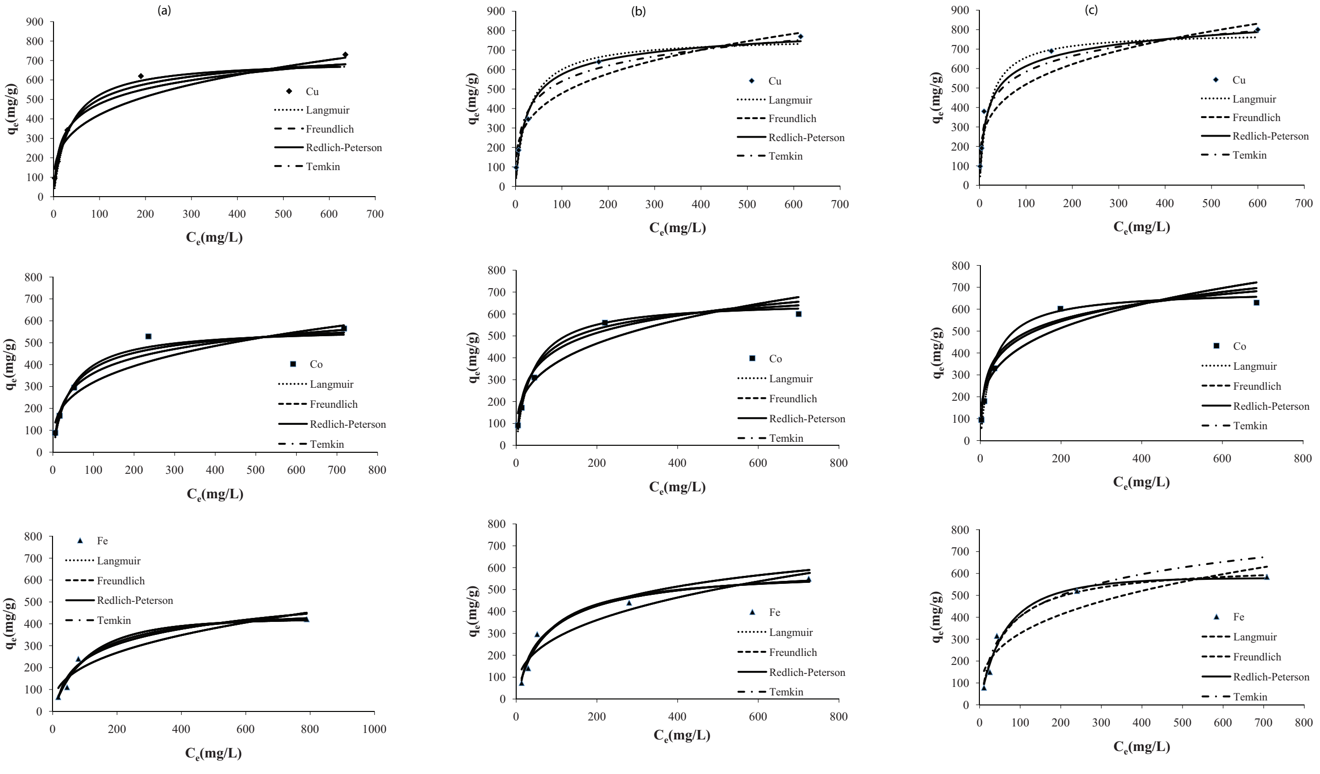

Fig. 6. Different isotherm plots for copper, cobalt and iron at (a) 25°C, (b) 35°C and (c) 45°C.

temperature leads to a decrement in the Δ*G*°. The positive value of Δ*H*° implies that the adsorption process was endothermic. The positive value of Δ*S*° confirms the increment randomness at the solid–solution interface during the adsorption process.

3.7. Reclamation of nanocomposite nanofibrous adsorbent

Reclamation of an adsorbent is considered as a key factor for financially improving a process. As a matter of fact, the reusability and metal recovery efficiency of the adsorbent were analyzed by implementing the adsorption/desorption cycles frequently. The results of four cycles of adsorption/desorption of copper, cobalt and iron onto the nanocomposite nanofibrous adsorbent are depicted in Fig. 8. As can be seen, the adsorption capacity of nanocomposite nanofibrous adsorbent for metal ions was gradually reduced after four adsorption–desorption cycles. The most significant reason supporting this result would be the indisputable fact that the

Table 5
Comparison of adsorption capacity (mg/g) of PES/zeolite nanofibrous adsorbent for copper, cobalt and iron sorption with other adsorbents reported in the literature

Adsorbent	Cu	Co	Fe	Reference
Aminated polyacrylonitrile nanofiber	30.4	–	5.42	[39]
Aminated electrospun polyacrylonitrile nanofiber	–	–	155.5	[38]
Poly(ethylene terephthalate)-thiosemicarbazide fibers	96.81	78.08	–	[40]
Modified wool chelating fibers	110.5	72.9	–	[41]
Chitosan-coated perlite	156.2	39.8	–	[42]
Microwaved olive stone activated carbon	–	–	62.5	[36]
Nano-NaX zeolite	144.9	125.3	–	[37]
PES/zeolite	783.3	654.4	642	In this study

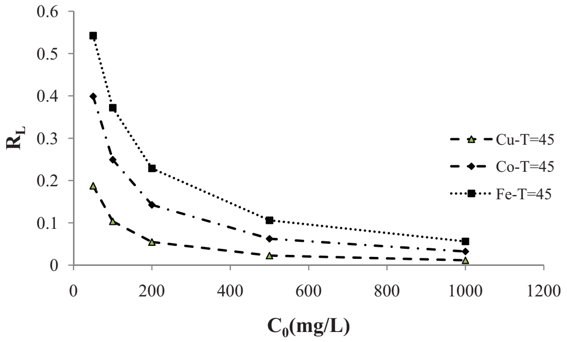

Fig. 7. Dimensionless separation factor for copper, cobalt and iron in *T* = 45°C.

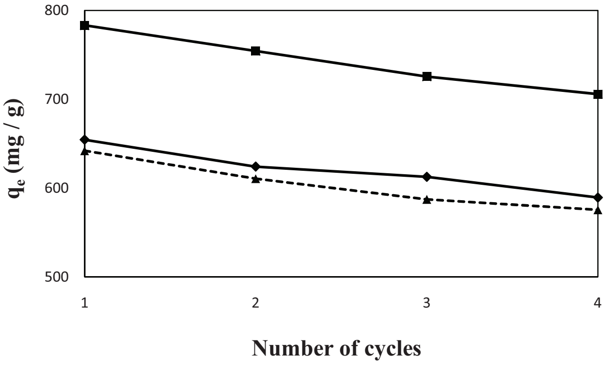

Fig. 8. Four cycles of copper, cobalt and iron adsorption–desorption with 0.5 M HNO_3/0.1 M HCl in equal ratio solution.

Table 6
Dimensionless separation factor for copper, cobalt and iron at different temperature

Initial concentration (mg/L)	Copper			Cobalt			Iron		
	T = 25°C	*T* = 35°C	*T* = 45°C	*T* = 25°C	*T* = 35°C	*T* = 45°C	*T* = 25°C	*T* = 35°C	*T* = 45°C
50	0.39	0.37	0.18	0.45	0.43	0.39	0.67	0.59	0.54
100	0.24	0.23	0.10	0.29	0.27	0.24	0.51	0.42	0.37
200	0.13	0.13	0.05	0.17	0.16	0.14	0.34	0.26	0.22
500	0.06	0.05	0.02	0.07	0.07	0.06	0.17	0.12	0.10
1,000	0.03	0.02	0.01	0.03	0.037	0.03	0.09	0.06	0.05

Table 7
Thermodynamic parameters of metal ions onto the nanocomposite nanofiber adsorbent

Metals	K_c			Δ*H*° (kJ/mol)	Δ*S*° (kJ/mol K)	Δ*G*° (kJ/mol K)		
	25°C	35°C	45°C			25°C	35°C	45°C
Copper	11.04	14.96	23.55	29	0.119	–5.95	–6.93	–8.35
Cobalt	4.94	6.504	9.186	24	0.095	–3.95	–4.79	–5.86
Iron	1.593	2.576	3.287	12	0.0471	–1.687	–2.4242	–3.1476

nanocomposite nanofibrous adsorbent loses some of its functional groups as a result of the acid cleavage. In other words, as the current nanocomposite nanofibrous adsorbent can be reused expeditiously in a process without a noteworthy reduction in an adsorption performance, it can be an appropriate option for industry as well.

4. Conclusion

In the present study, the potential of PES/nanozeolite nanocomposite nanofibrous adsorbent was investigated for the removal of Cu^{2+}, Co^{2+} and Fe^{2+} ions from aqueous solutions. The prepared nanofibers were developed by the electrospinning process and nanofiber morphologies were characterized by SEM analysis. The SEM images showed that an increase in the nanozeolite content led to an increment in the nanofibers diameter. The effect of parameters such as pH (2–7), contact times (10–360 min), initial metal ion concentrations (50–1,000 mg/L) and temperatures (25°C–45°C) were investigated for removing copper, cadmium and iron ions from the aqueous solutions by PES/zeolite adsorbent. Optimum parameters for copper, cadmium and iron sorption onto the nanofiber nanocomposite adsorbent were found at a pH of 6, 6 and 3, contact time of 60 min and temperature of 45°C. The best model for describing the kinetic data was the double-exponential model ($R^2 > 0.9894$) for all of the metal ions. It was found that 783, 654 and 642 are the maximum amounts of adsorption capacity of copper, cobalt and iron ions onto the PES/zeolite adsorbent, respectively. To put it differently, the results indicated that the sorption efficiency of PES/zeolite nanofibers for metal ions was in the order of Cu^{2+} > Co^{2+} > Fe^{2+} in the equilibrium time of 1 h. Thermodynamic parameters showed that the nature of the sorption process by the PES/zeolite nanofibers was endothermic. Regeneration of PES/NaX nanocomposite nanofiber and reuse of electrospun nanofiber in four adsorption–desorption cycles showed that the nanocomposite nanofiber could be used as an alternative adsorbent for the removal of copper, cobalt and iron ions from aqueous solution.

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