Copper and nickel removal from aqueous solutions using functionalized polyacrylonitrile fibers: equilibrium, kinetic, and thermodynamic studies

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ABSTRACT

Amidoximated polyacrylonitrile fibers (AO-PANF) were prepared from the pristine PANF by using hydroxylamine as chelating agent. Thereafter, the AO-PANF was used as adsorbent for removing toxic metals such as copper and nickel from aqueous solutions. Further, the effects of various adsorption parameters, affecting the metal removal from water, such as the aqueous phase pH, the contact time adsorbate–adsorbent, the adsorbent dose, and the temperature, were assessed. The overall data indicate that metal removal from water increases with increasing the magnitude of these adsorption parameters. Furthermore, to evaluate the theoretical trends of the metal adsorption from water onto the AO-PANF adsorbent, the experimental adsorption data were compared to the kinetic and equilibrium theoretical models. Thus, at the equilibrium, a good agreement was found between the data and the Langmuir model, whereas the kinetics results were found to follow the pseudo-second-order. The results have also showed that by using the Langmuir model equation, the obtained adsorption capacities for copper and nickel were 11.56 and 6.87 mg g^{-1}, respectively. Finally, the thermodynamic investigations indicate that the adsorption was spontaneous and endothermic. The overall data shown in the present work indicate that functionalized polyacrylonitrile fibers, AO-PANF, are efficient adsorbent for the copper and the nickel removal from water.

Keywords: Environmental chemistry; Water treatment; Amidoxime; Polyacrylonitrile; Heavy metal

1. Introduction

Wastewater containing heavy metals have attracted widespread interest due to their negative effect on human health and ecosystems [1]. Copper and nickel are widely used in various industries such as mining, oil refinery, batteries, textile, and electroplating industries [2]. These metals were classified by the United States Environmental Protection Agency (EPA) as priority pollutants [3,4] and tend to accumulate in the organisms through water, food chain, and blood due to their high solubility and non-biodegradability nature [5]. Copper and nickel, at levels traces, are considered

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an essential micro-nutrient to humans and other living species [6–8]. However, when human is exposed to high metal concentrations, it will result in irritation, diarrhea, mental and neurological diseases, memory loss, cancer, and liver damage [6,9]. According to the United States Environmental Protection Agency (EPA), the maximum copper and nickel concentrations permissible in industrial effluents are, respectively, 1.3 and 0.9 mg L^{-1} [10,11]. The human life toxicity of these two metals and the ecosystem alteration, underline the necessity to remove them from the polluted effluents. Up to now, various treatment methods including, chemical precipitation, electrocoagulation, adsorption, ion exchange, reverse osmosis, nano, and ultra-filtration have been used to remove heavy metals from aqueous solutions [12]. Adsorption technology is considered to be the most effective and economical method to remove copper and nickel from the polluted aqueous solutions [13,14]. The advantages of this method are summed up in its simplicity, speed, low-cost process, no sludge production, good stability, reusability, and the ability to remove trace metals ions [1,15]. The adsorption efficiency depends mainly on the nature of the adsorbents used to remove pollutants from aqueous solutions [16]. Commonly, activated carbon, powder or granular forms, were the most adsorbents used to remove heavy metals from aqueous solutions. However, the main drawbacks of these adsorbents are the high-cost production, the complicated pre-treatment [9,17]. Therefore, it is necessary to look for an adsorbent able to remove effectively heavy metals from aqueous while being simple chemically and low cost economically. The use of polymeric materials as an adsorbent has demonstrated its effectiveness to remove heavy metals from aqueous solutions. Among them, polyacrylonitrile are the most polymeric materials used. It is a commercial and low-cost polymers materials having good mechanical, chemical, thermal stability and good resistance to corrosion and solvent [18]. Polyacrylonitrile contain hydroxyl (OH) and amino (NH$_2$) groups in their backbone, making it a good adsorbent for water purification, heavy metals and dyes removal from aqueous solutions [19]. Chemical modification of polyacrylonitrile surface with various chemical reactants such as hydroxylamine, diethylenediamine [20], ethylenediamine, triethylenetetramine [21], carboxyl, imidazole [18], will improve its adsorptive property and then will enhance the removal efficiency of the pollutants from water. It should be noted that hydroxylamine is a promoting chelating agent, containing nitrogen and oxygen atoms, which have a strong affinity toward heavy metals ions. Further, the nitrile groups present on the polyacrylonitrile surface can be easily transformed onto a variety of functional groups such as carboxyl, amine, amidoxime, phosphoric, etc. Amidoxime group contains a combination of =NOH and NH$_2$ functional groups which can separate and recover heavy metals from solutions through the chelation process [22]. Regarding the use of polyacrylonitrile in different physical forms, many studies have concerned its capacity to remove copper and nickel from aqueous solutions. Zeng et al. [23], prepared an amidoxime adsorbent by grafting acrylonitrile onto natural loofah sponge, and reacted with hydroxylamine hydrochloride subsequently. In that reported work, the amidoxime-modified poly (AN-g-loofah) showed that the Cu^{2+} adsorption capacity reached

51.40 mg g^{-1}. Further, Abdouss et al. [20] have prepared polyacrylonitrile fibers (PANF) by electro spinning technique to be used in copper removal from aqueous solutions. The modification of the electro spun PANF was made by using 3.2 M of diethylenetriamine (DETA) chelating agents for 8 h at 92°C. According to Abdouss et al. [20] reported work, the achieved adsorption capacity of copper from water onto the modified PANF was 7 mg g^{-1}. Another investigation was carried out by using electro spun poly-acrylonitrile nanofiber modified with imidazole ligand at a concentration range of 0.15–1 M, for nickel removal from aqueous solutions. In this reported work, the conversion of nitrile groups has attained 36% for a reaction time of 1 h, and the adsorption capacity reached 0.8 mol Kg^{-1} at pH 5 [18]. Several methods were used to prepare amidoximated polyacrylonitrile fibers using a considerable amount of chemical products including the chelating agents. However, in developing countries, the process cost is an important decision factor. In addition, a low-cost process with a simple feasible method, saving energy, time, products, and at the same time being effective, is attractive for industrial utilization. At the same time, using polyacrylonitrile as fiber is effective for metal removal from aqueous solutions owing to their large surface area and a short diffusion rate [20]. Moreover, the removal of Cu^{2+} and Ni^{2+} was mainly carried out for high initial concentrations up to 2,000 mg L^{-1}, whereas the removal with lower concentrations was weakly discussed. Based on that, in a previous study, we synthesized AO-PANF using a straightforward and cheap method with a minimum condition of the modification, which is also realizable in industry. The removal capacity of Cr(VI) was evaluated. The achieved conversion of nitrile groups was 33.7% by using 0.15 M of NH$_2$OH for a reaction time of 1 h at reaction temperature T = 70°C. The synthesized adsorbent has demonstrated good performance for Cr(VI) removal from aqueous solutions with an adsorption capacity of 32.57 mg g^{-1}. The Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) analyzes were performed and have confirmed the conversion of nitrile groups.

Others researches have confirmed the ability of AO-PANF to remove Cr(VI) from aqueous solutions. Hence, Avila et al. [24] have prepared AO-PAN nanofibers to confirm the ability of amine and oxime groups of amidoximes to remove Cr(VI) from aqueous solutions. According to these authors, the maximum adsorption capacity was 156 mg g^{-1}, with a desorption percentage of 90%. However, in the work of Avila et al. [24], the preparation of the adsorbent was made by using DMF chemical product, and an electro spinning technique, which increases both the production cost and the environmental damage.

In the present work, the amidoximated polyacrylonitrile fibers (AO-PANF) were prepared and used in order to investigate their capacity to remove other heavy metals such Cu(II) and Ni(II) from aqueous solutions. The effects of adsorption parameters on the AO-PANF adsorption capacity were assessed. Furthermore, kinetics and isotherm studies were evaluated by comparing the experimental data to some equation's models. After adsorption process, the AO-PANF was tested for desorption and regeneration. The effects of co-existing ions in the aqueous solution, on the adsorption capacities of Cu(II) and Ni(II), were also evaluated.

2. Experimental section

2.1. Material and methods

Commercial polyacrylonitrile fibers (PANF) was cut, washed with distilled water, and then dried in an oven. Hydroxylamine hydrochloride, with a purity >99%, was purchased from Scharlab, whereas chemical salts, such as $CuSO_4 \cdot 5H_2O$ and $NiCl_2 \cdot 6H_2O$, with purities of 97% and 99%, respectively, were obtained from Sigma-Aldrich (Saint-Louis, Missouri, United States). Sodium hydroxide (NaOH, 0.1 mol L^{-1}) and hydrochloric acid, (HCl, 0.1 mol L^{-1}) aqueous solutions, were used to adjust the aqueous phase pH, which was measured, by using a pH meter Thermo Scientific (Waltham, Massachusetts, United States) Orion 4 STAR. The metal solutions were prepared by diluting 1 g L^{-1} of $CuSO_4 \cdot 5H_2O$, and $NiCl_2 \cdot 6H_2O$, with distilled water desired amounts. The residual concentrations of Cu(II) and Ni(II) were assessed by using complexometric titration and murexide as indicator. Chemical salts such as potassium dichromate ($K_2Cr_2O_7$), sodium sulfate (Na_2SO_4), and sodium phosphate (Na_3PO_4) were used to prepare Cr, SO_4, and PO_4 aqueous solutions. The residual concentrations of these elements were determined using Thermo-Fisher (Waltham, Massachusetts, United States) Evolution™ 300 UV-vis spectrophotometer, at room temperature.

2.2. PANF surface modification

The surface modification of PANF by one-step reaction was done according to the procedure described in our previous work as illustrated in Fig. 1 [25].

In the previous work, we synthesized an adsorbent, called "AO-PANF" for heavy metal removal, by converting the nitrile groups containing on the polyacrylonitrile fibers onto amidoximes groups. Such synthesis was carried out taking into account the production cost and the used

chemical additive natures. Hydroxylamine hydrochloride was added to a flask containing both PANF and NaOH solutions (methanol/water 5:1). The methanol was added to NaOH solution to dissolve hydroxylamine hydrochloride and to obtain a homogenous solution for the amidoximation reaction. After the treatment, the adsorbent was separated from the solution by filtration, washed several times with a mixed methanol/water solution, and finally dried in oven for 1 d at 60°C. The modified PANF obtained by using 0.15 M of hydroxylamine for 60 min, at reaction temperature $T = 70$°C, was found to produce high conversion rate of nitrile groups of 33.7% and to have acceptable mechanical properties. Note that the PANF color was changed from white to yellow after modification. As in our previous work, methods such as FTIR spectroscopy and SEM were used to characterize the PANF and AO-PANF samples. These techniques, of the AO-PANF characterization, were used by others researchers to confirm the modification process [24,26].

2.3. Copper and nickel removals from water onto AO-PANF

Cu(II) and Ni(II) solutions were prepared by dissolving defined quantities of $CuSO_4 \cdot 5H_2O$ and $NiCl_2 \cdot 6H_2O$ in distilled water. The adsorption experiments were investigated by making contacts of the AO-PANF samples with 50 mL of the aqueous metal solutions at given concentrations (30 mg L^{-1}) and by shaking the resulted mixtures at room temperature for contact time intervals of 60 min. Thereafter, for each mixture, the adsorbent was separated from the supernatant by filtration, washed with distilled water to remove the non-adsorbed metal and finally dried in an oven. The residual concentrations of Cu(II) and Ni(II) in the supernatant were determined by complexometric titration using ethylenediaminetetraacetic (EDTA) with murexide as indicator [27,28]. The titration method, compared with quantitative instrumental measurements such inductively
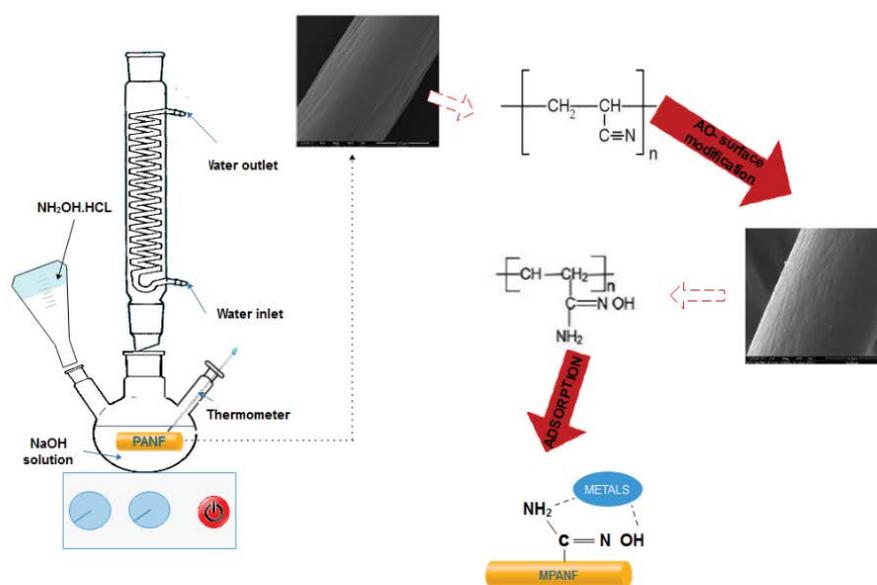
Fig. 1. Schematic illustration of the experimental surface modification of PANF with hydroxylamine, and metal adsorption process from water onto AO-PANF.

coupled plasma mass spectrometry or atomic absorption spectroscopy, is more accurate, sensitive and simple for the rapid and quantitative chemical analysis for metal ions [29]. The complexometric titration using EDTA as a chelator is a well-known analytical technique. In this study, the effect of adsorption parameters such as pH solution, contact time, temperature, initial concentration, and adsorbent dose on the adsorption capacity, were investigated. The method and the conditions will be mentioned in each part of the adsorption parameter study. The effect, of coexisting ions on the adsorption study, was investigated in this paper. The method and technique used will be described in the subsequent sections.

Triplicate experiments were carried out for all adsorption parameters. The adsorption capacity (mg g⁻¹) was calculated using Eq. (1):

$$q_e = V \times \left[\frac{(C_0 - C_1)}{W}\right] \tag{1}$$

where q_e is the equilibrium adsorption capacity (mg g⁻¹), C_0 and C_1 are, respectively, the initial and the final concentrations of Cu(II) and Ni(II) (mg L⁻¹), V is the volume of solution (L), and W is the adsorbent weight (g).

The reuse of AO-PANF was firstly investigated using 20 mL of 0.1 M of HCl, at 25°C, for 1 h in order to test the desorption efficiency. After the desorption process, the AO-PANF was washed with distilled water and prepared for the next adsorption–desorption cycle.

2.3.1. Kinetic adsorption models

In the present work, the adsorption kinetic models include the pseudo-first-order [Eq. (2)], the pseudo-second-order [Eq. (3)], the intra-particle diffusion [Eq. (4)]), and the Elovich model [Eq. (5)].

$$\log(q_e - q_t) = \log q_e - k_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

$$q_t = k_{id} t^{1/2} + C \tag{4}$$

$$q_t = \frac{1}{2}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{5}$$

where q_e and q_t are the adsorption capacities at equilibrium and at time (t), respectively, expressed in mg g⁻¹. The term k_1 is the pseudo-first-order rate constant (min⁻¹). k_2 is the pseudo-second-order rate constant (g mg⁻¹ min⁻¹). Where k_{id} is the intra-particle diffusion model constant (mg g⁻¹ min⁻¹/²), and C is the boundary thickness α and β are, respectively, the initial adsorption rate expressed in (mg g⁻¹ min⁻¹), and the desorption constant expressed in (g mg⁻¹), and related to the surface coverage and the activation energy.

2.3.2. Equilibrium adsorption models

Langmuir [Eq. (6)], Freundlich [Eq. (7)], and Dubinin–Radushkevich [Eq. (8)] models were used to discuss the adsorption capacity of the adsorbent and describe the interaction between the pollutant and the adsorbent.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{6}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{7}$$

$$\ln q_e = \ln q_m - B\varepsilon^2 \tag{8}$$

where ε, is the Polanyi potential (J² mol⁻²)

$$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right] \tag{9}$$

where C_e is the equilibrium concentration of the metal in the solution (mg L⁻¹), q_e is the amount of metal adsorbed onto AO-PANF at equilibrium (mg g⁻¹), q_m is the maximum adsorption capability (mg g⁻¹) and K_L is the Langmuir constant (L mg⁻¹). K_F [(mg g⁻¹) (L mg⁻¹)¹/ⁿ] and the exponent ($1/n$) are the Freundlich constants representing the adsorption capacity and the intensity of adsorption, respectively. B, in the Dubinin–Radushkevich equations, is a constant associated with the adsorption energy.

3. Results and discussions

3.1. Effect of aqueous solution initial pH

The initial pH of the aqueous solution is an important parameter affecting the surface charge of the adsorbent and the metal speciation. The pH effect on the AO-PANF adsorption capacity was investigated by varying the aqueous solution initial pH, from 2.0 to 6.0 for Cu(II) and from 2.0 to 8.0 for Ni(II) (Fig. 2).

The pH effect was investigated at room temperature, by mixing an amount of a metallic solution having initial concentration of 25 mg L⁻¹, with 0.1 g of the adsorbent, for a period time of 60 min. We choose to work at this pH interval to prevent any precipitations of metal hydroxides.

As can be seen in Fig. 2, for Cu(II) and Ni(II), the removal efficiency (R) increases with increasing aqueous solution initial pH to reach an adsorption capacities of 9.39 mg g⁻¹ ($R = 75.79\%$) at pH = 5.0 and 2.66 mg g⁻¹ ($R = 56.79\%$) at pH = 7, respectively, which are consistent with previous reported works [9,30,31].

In fact, with an pH$_{pzc}$ of AO-PANF = 3.9, when the aqueous solution initial pH is <pH$_{pzc}$, the adsorbent charge is positively charged due to the high concentration of hydronium ions (H$_3$O⁺, H⁺), leading to an electrostatic repulsion occurring between the positively charged metal ions present in solution, and the positively charged AO-PANF, and resulting in low adsorption capacity. However, an increase in solution pH at pH > pH$_{pzc}$ leads to negatively
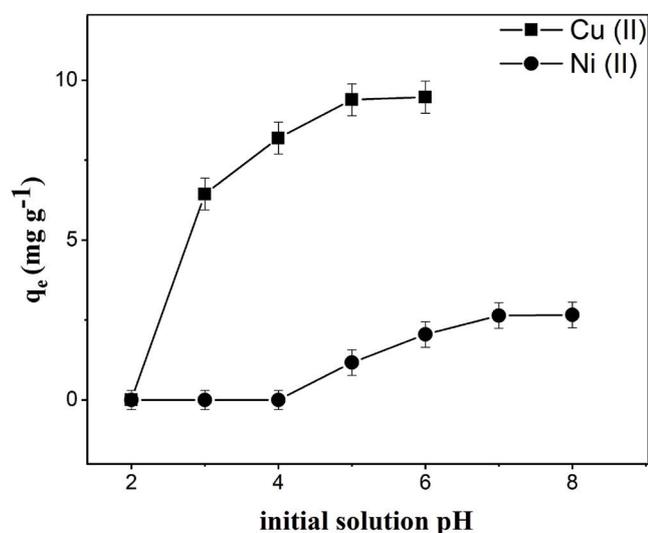
Fig. 2. Effect of initial solution pH on adsorption capacity of Cu(II) and Ni(II) from aqueous solutions.

Fig. 3. Effect of contact time on Cu(II) and Ni(II) adsorption capacity from aqueous solutions.

charged adsorbent surface due the deprotonation of the solid functional groups, and generate an increase in the adsorption capacity, as resulting from an electrostatic attraction between the negatively charged AO-PANF and the positively charged metals ions (Cu^{2+}, $Cu(OH)^+$, and Ni^{2+}) [32,33]. Therefore, the following experiments will be performed at pH = 5 and at pH = 7 for Cu(II) and Ni(II), respectively.

3.2. Effect of the contact time adsorbent–adsorbate

The effect of the contact time of the AO-PANF and the divalent cations, on the adsorption capacity was studied using a constant initial metal concentration of 30 mg L^{-1} for Cu(II) and Ni(II), at pH = 5 and 7, respectively. Thus, the obtained adsorption data for a various contact times varying in the range 10–120 min, are represented in Fig. 3.

As can be seen in this figure, the adsorption capacity increases with increasing contact time and leveled out, at 90 and 30 min, for Cu(II) and Ni(II), respectively. In case of Ni(II), the adsorption shows an abrupt jump in the 1st min and quickly reaches the equilibrium plateau. These results demonstrated that the adsorption onto AO-PANF takes place on the external surface on which there is no need to reach the equilibrium for a longer contact time [1]. Therefore, the optimal contact time of 90 and 30 min for Cu(II) and Ni(II), respectively, were selected for further experiments.

3.3. Adsorbent dosage effect

The removal efficiency of AO-PANF toward Cu(II) (10 mg L^{-1}) and Ni(II) (25 mg L^{-1}), were studied separately by varying the adsorbent weight from 0.02 to 0.4 g, and the data are presented in Fig. 4.

Note that the optimization of adsorbent dose allows the utilization of the full adsorbent surface. As shown in Fig. 4, increases of the adsorption capacities from 3.46 to 4.16 mg g^{-1} for Cu(II) and from 0.84 to 2.07 mg g^{-1} for
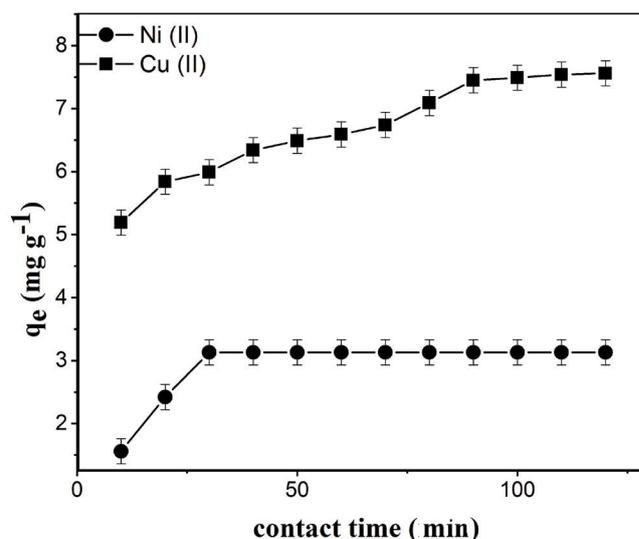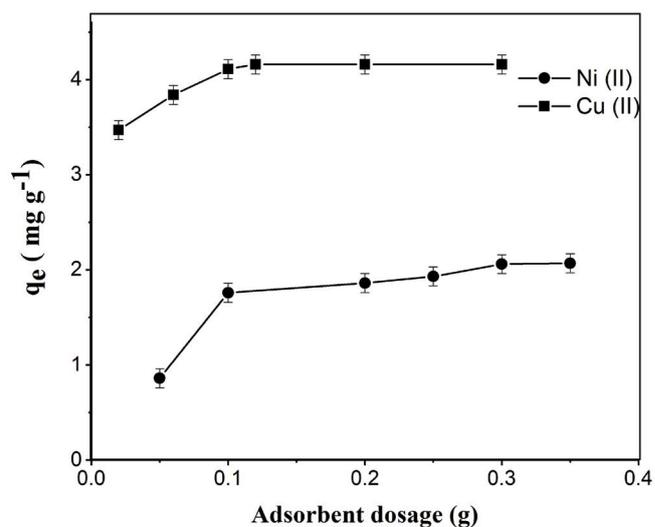
Fig. 4. Effect of adsorbent dose on the Cu(II) and Ni(II) adsorption capacity from aqueous solutions onto the AO-PANF.

Ni(II) are observed, with increasing the adsorbent dosage. In the case of Cu(II), no removal increase was obtained after reaching 0.1 g of the adsorbent dose, while for Ni(II) adsorption needs more adsorbent amount (0.3 g) to reach the equilibrium. It is noteworthy that an increase in adsorbent weight provides more AO-PANF surface sites which enhance the heavy metals removal efficiency [30]. A rapid adsorption of Cu(II) compared to Ni(II) from water onto the AO-PANF surface demonstrated that the adsorbent has more affinity towards Cu(II) as compared to Ni(II) ions. The results analyses have shown that the optimal adsorbent dose for Cu(II) and Ni(II), are, 0.1 and 0.3 g, respectively. Therefore, in the following experiments only the optimal adsorbent doses will be used.

3.4. Temperature effect and thermodynamic studies

The effect of temperature on the adsorption was investigated by varying the temperature, from T = 10°C to 65°C while keeping the others parameters constants. Fig. 5 shows that for Cu(II), the adsorption capacity increases from 2.20 to 9.02 mg g^{-1} with increasing temperature up to T = 30°C, and thereafter the adsorption is slowed.

In case of Ni(II), the adsorption increases from 1.51 to 2.7 mg g^{-1} with increasing temperature up to 30°C and it levels out thereafter. The increase in adsorption capacity with increasing the temperature indicates an endothermic adsorption process. A similar temperature effect was also observed in previous reported work dealing with the adsorption of Cr(VI) from water onto AO-PANF surface, which was also endothermic. From Fig. 5, we can see that the adsorption capacity of Cu(II) increases sharply with temperature while the adsorption capacity of Ni(II) is experiencing a slight increase before becoming constant. This is due to the full occupation of actives sites of AO-PANF with the temperature increase [34]. Our results are in agreement with previous works carried out by other authors [34]. Here, we find that the optimal temperature for maximum adsorption capacity is T = 30°C. Thereafter, after 30°C, no significant change was observed in the adsorption capacity of metals. This is why we choose to perform adsorption experiments at room temperature in order to avoid energy consumption. The thermodynamic parameters including Gibbs free energy $\Delta G°$ (KJ mol^{-1}), entropy change $\Delta S°$ (J K^{-1} mol^{-1}), and enthalpy change $\Delta H°$ (KJ mol^{-1}), were calculated using Van't Hoff equation and are gathered in Table 1.

$$\Delta G = -RT \ln K_d \tag{10}$$

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{11}$$

where K_d is the equilibrium constant, R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the Kelvin temperature.

Note that the values of $\Delta H°$ and $\Delta S°$ were determined from the plot of $\ln K_d$ vs. $1/T$.

According to Table 1, the negative values of $\Delta G°$ indicate the spontaneity of the process for the removal of Cu(II) and Ni(II) ions from aqueous solutions. As well, the increase of temperature decreases the $\Delta G°$ values, which

demonstrated that the adsorption is effective and spontaneous at higher temperature values. The calculated $\Delta G°$ values are more negative for Cu(II) as compared to Ni(II) ions, suggesting hence that the adsorption of Cu(II) is more feasible on the adsorbent surface. The $\Delta H°$ values of both Cu(II) and Ni(II) are found between –20 and –40 KJ mol^{-1}, indicating a physical adsorption process [30]. Also, the positive values of $\Delta S°$ and $\Delta H°$ confirms the randomness and endothermic process for Cu(II) and Ni(II) adsorption onto AO-PANF [1]. However, from kinetics study, we found that the adsorption of Cu(II) and Ni(II) was chemical in nature. From these results, we can said that the adsorption of metals onto AO-PANF followed a physico-chemical process [35].

3.5. Kinetics adsorption modeling

The modeling of the kinetic adsorption of Cu(II) and Ni(II) onto AO-PANF were performed by using pseudo-first-order, pseudo-second-order, intra-particle, and Elovich models. For all kinetics adsorption models, the equations were applied for the adsorption period ranging from 10 to 120 min. The modeling results are presented in Fig. 6 and summarized in Table 2.
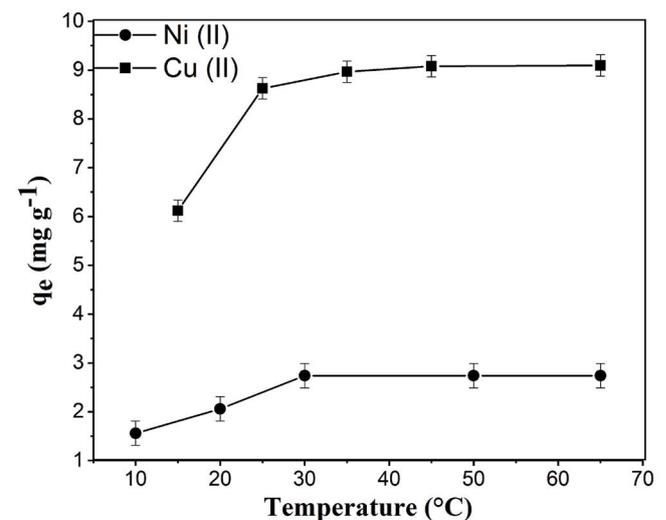
Fig. 5. Effect of temperature on Cu(II) and Ni(II) adsorption capacity from aqueous solutions.

Table 1
Thermodynamic parameters of Cu(II) and Ni(II) adsorption

	Cu(II)			Ni(II)		
T (°K)	$\Delta G°$ (KJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})	$\Delta H°$ (KJ mol^{-1})	$\Delta G°$ (KJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})	$\Delta H°$ (KJ mol^{-1})
283	−16.20			−12.04		
293	−20.68			−14.08		
303	−22.51	185.88	35.81	−17.80	144.58	27.95
323	−23.75			−18.98		
338	−25.91			−19.86		
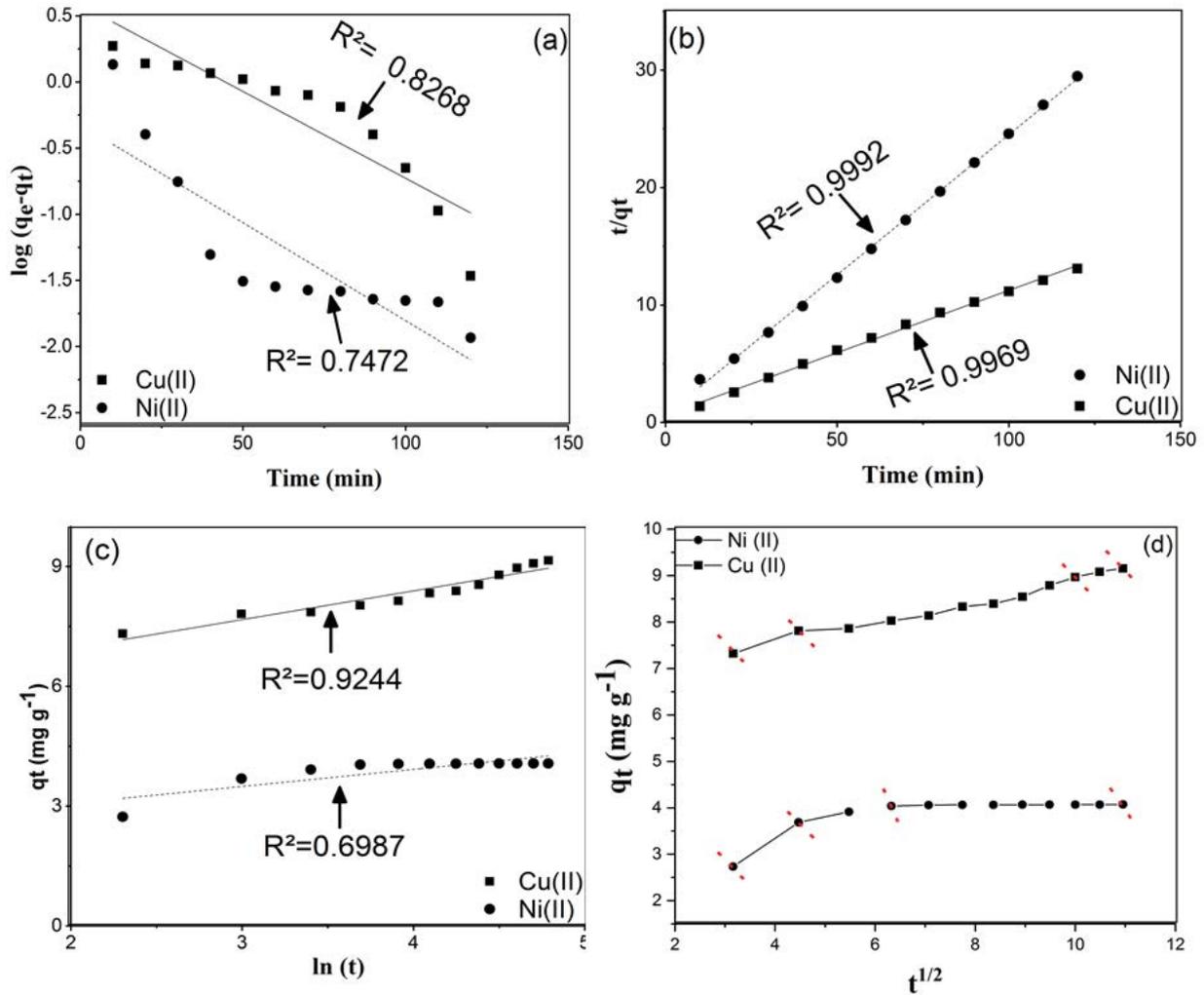
Fig. 6. Kinetics models representation of pseudo-order (a), second-order (b), Elovich (c), and intra-particle (d) for Cu(II) and Ni(II) adsorption from aqueous solutions onto AO-PANF.

Table 2
Kinetics models constants for Cu(II) and Ni(II) removal from aqueous solutions onto AO-PANF

	Pseudo-first-order				Pseudo-second-order				
	k_1	$q_{e,calc}$	R^2	SD	k_2	h	$q_{e,calc}$	R^2	SD
Cu(II)	0.013	3.83	0.82	0.06	0.02	1.57	9.42	0.99	0.03
Ni(II)	0.014	0.47	0.74	1.06	0.75	0.37	4.18	0.99	0.03

	Elovich model			Intraparticle diffusion								
	β	α	R^2	k_{id1}	C_1	R_1^2	k_{id2}	C_2	R_2^2	k_{id3}	C_3	R_3^2
Cu(II)	1.3	1,510	0.92	0.80	1.93	1	0.22	6.67	0.95	0.018	8.89	0.86
Ni(II)	2.3	75.5	0.69	0.72	0.43	1	0.19	2.84	0.98	0.004	4.02	0.70

The adsorption kinetics of both, Cu(II) and Ni(II), are best represented by the pseudo-second-order model, with the highest correlation coefficient values R^2 (0.99). Therefore, the adsorption of Cu(II) and Ni(II) on AO-PANF follow the pseudo-second-order at all times intervals. These data indicate

that the chemical sorption took place through chelation interaction involving ion exchange where adsorption capacity is proportional to the number of active sites occupied [36]. The values of $q_{e,exp}$ (9.19 and 4.09 mg g^{-1}) and $q_{e,calc}$ (9.42 and 4.18 mg g^{-1}) for Cu(II) and Ni(II), respectively, are in

agreement which confirms the validity of pseudo-second-order model, unlike the pseudo-first-order model where the values are so far and the errors is large. The AO-PANF showed an initial adsorption rate (1.57 and 0.37 mg g^{-1} min^{-1}, respectively) for Cu(II) and Ni(II). The comparison of initial adsorption rate values (h) (1.57 and 0.37) for Cu(II) and Ni(II), respectively, suggested that the adsorption of copper onto AO-PANF is faster than the nickel ions. Additionally, copper present a higher adsorption capacity than nickel.

Concerning the intra-particle diffusion model, the plot of q_t vs. $t^{1/2}$ illustrated the multi-linearity correlations [37]. For Cu(II) and Ni(II) adsorption, three sections were produced for adsorption of Cu(II) and Ni(II) onto AO-PANF. The first section represented the instantaneous adsorption, which the heavy metals are attached instantaneously and rapidly from the solution to the AO-PANF surface. The subsequent phase describe the gradual adsorption with a slow rate which can be attributed to the intra-particle diffusion of the metals inside the adsorbent [10]. This decrease can be to the unavailability of active sites in surface of adsorbents [38]. The last section is assigned to the attainment of equilibrium adsorption. The results are in concordance with previous researches [37,39]. The intra-particle diffusion constant in every section of the plots follows the order $k_{id1} > k_{id2} > k_{id3}$ demonstrating that adsorption was maximal in the first cycle due to the availability of active sites on the adsorbent surface.

3.6. Equilibrium adsorption studies

Adsorption isotherms models were used to correlate the experimental data in order to understand the nature of adsorption of metals toward AO-PANF. In this study, Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) models have been evaluated. The equilibrium adsorption capacity is determined using different concentrations (5–80 mg g^{-1}) at a constant temperature. The linearized isotherm models are illustrated in Fig. 7 and the calculated parameters are tabulated in Table 3.

The adsorption of Cu(II) and Ni(II) onto AO-PANF fit well with the Langmuir equation (Fig. 7a) with a higher regression coefficient ($R^2 = 0.9988$ and 0.9852, respectively)
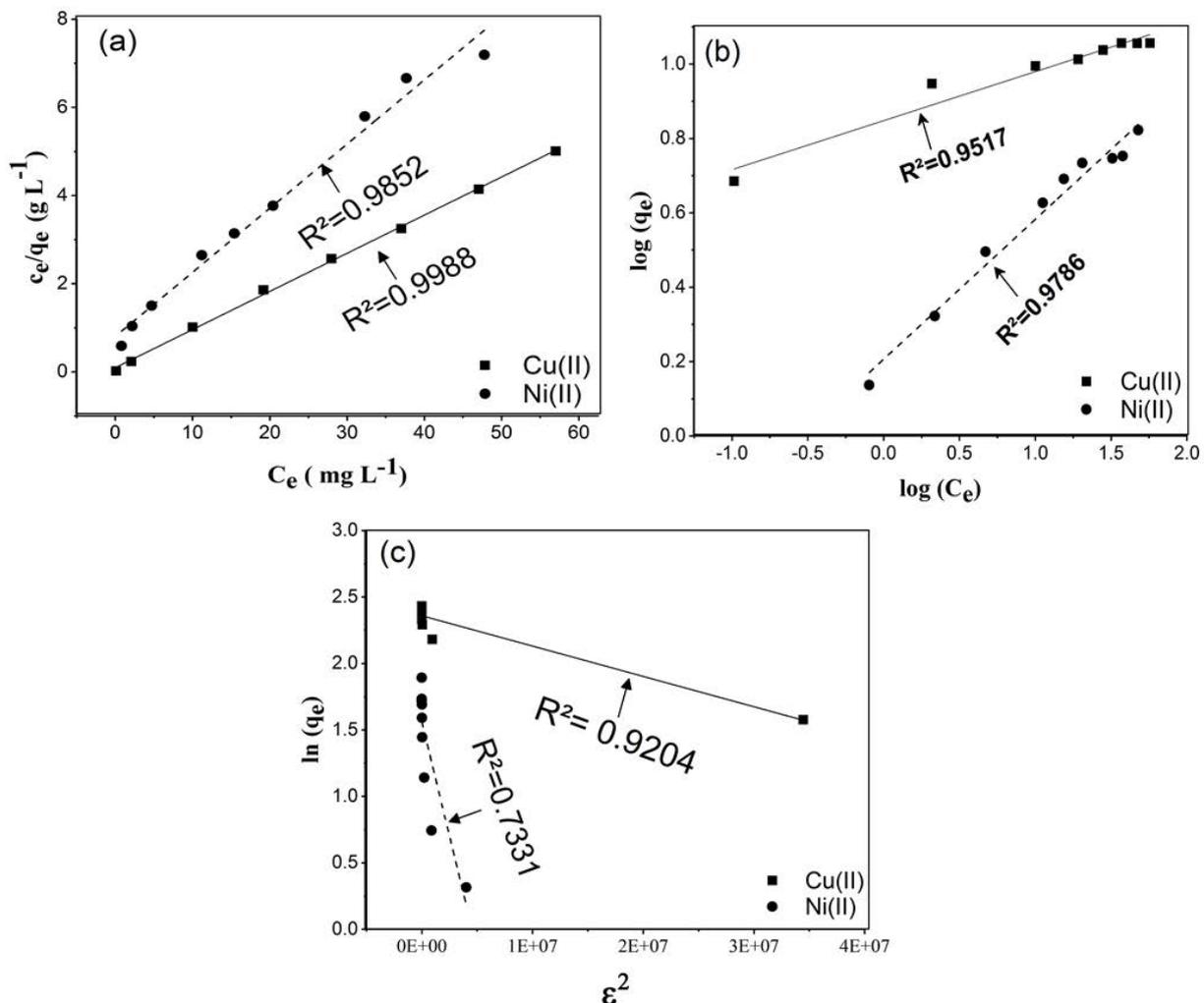
Fig. 7. Isotherm adsorption models representations of Langmuir (a), Freundlich (b), and Dubinin–Radushkevich (c) from aqueous solutions onto AO-PANF.

Table 3
Isotherms models constants for Cu(II) and Ni(II) removal from water by adsorption onto AO-PANF

	Langmuir					Freundlich				Dubinin–Radushkevich			
	K_L	R_L	q_m	R^2	RMSD[a]	K_F	$1/n$	R^2	RMSD	q_s	E	R^2	RMSD
Cu(II)	0.9	0.1	11.56	0.99	0.04	7	0.1	0.95	0.6	10.58	5	0.92	0.8
Ni(II)	0.2	0.3	6.87	0.98	0.1	1	0.3	0.97	0.4	4.77	1.2	0.73	1.8

[a]root mean standard deviation.

and lower RMSD (0.041 and 0.125, respectively) as shown in Table 3. Therefore, it can be concluded that the distribution of metals onto adsorbent surface is homogeneous and a monolayer is formed [40]. In this study, D–R isotherm model may not be applied for Ni(II) adsorption onto AO-PANF with a low correlation coefficient (R^2 = 0.7332) and RMSD (1.88) suggesting that the isotherm models cannot fit with the experimental data. Previous studies have reported that the adsorption of Cu(II) and Ni (II) was best described by Langmuir isotherm model [9]. The values of $1/n$ are less than one indicating a favorable process, also the dimensionless separator factor values R_L for Cu(II) and Ni(II) adsorption were 0.1 and 0.37, respectively, confirming that the adsorption is favorable. The values of K_L indicate a stronger affinity of adsorbent to Cu(II) than Ni(II). The free energy E is <8 KJ mol^{-1} demonstrating that the adsorption nature is physique. The maximum adsorption capacity of AO-PANF calculating using Langmuir equation was 11.38 mg g^{-1} for Cu(II) and 6.24 mg g^{-1} for Ni(II), closer to the experimental values and higher compared to other studies [41]. Finally, the study demonstrates that a quantity of 0.1 and 0.3 g can effectively remove Cu(II) and Ni(II) from aqueous solutions. Moreover, the ability of AO-PANF to remove Cr(VI) from aqueous solutions was also studied (q_m = 32.57 mg g^{-1}).

3.7. Effect of co-existing ions

Generally, in an industrial wastewater, Cu(II) and Ni(II) co-exists with others ions. The effect of co-existing ions present in solutions is an important parameter, which can interfere with the removal of heavy metals. Anions and cations were selected to study the effect of co-existing ions on adsorption capacity of Cu(II) and Ni(II). The co-existing ions including chromium ($Cr_2O_7^{2-}$), phosphate(PO_4^{2-}), copper (Cu^{2+}), and nickel (Ni^{2+}) were separately added to a solution (50 mL) containing initial concentrations of 30 mg L^{-1} of either Cu(II) or Ni(II) at pH 5 and 7, respectively, at room temperature (Fig. 8). Different concentrations of co-existing ions were chosen to study the effect.

In a solution containing $Cr_2O_7^{2-}$ no change was observed in the removal of Cu(II) and Ni(II) using AO-PANF. For Ni(II) removal, in the presence of co-existing ions (PO_4^{2-}, Cu^{2+}, and SO_4^{2-}), at low concentrations (20 mg L^{-1}), no obvious change was discovered. Maximal variation was 10%, compared to the adsorption efficiency without co-existing ions, attributed to PO_4^{2-}, indicating that they have inconspicuous effect on the adsorption efficiency. Nevertheless, increasing concentration levels of Cu(II) leads to a significant decrease of the adsorption efficiency of Ni(II). This is due to the competitiveness between Cu(II) and Ni(II) and the affinity of AO-PANF toward Cu(II) [42]. However, the decrease of adsorption efficiency in the presence of PO_4^{2-} and SO_4^{2-} at higher levels can be attributed to the interaction of AO-PANF with anions [43]. For Cu(II) removal, Co-existing ions (Ni) had no significant change in the adsorption efficiency, which confirms the more affinity of the AO-PANF towards the Cu(II) than Ni(II). The removal efficiency decreases from 100% to 85% at higher levels of Ni(II). The
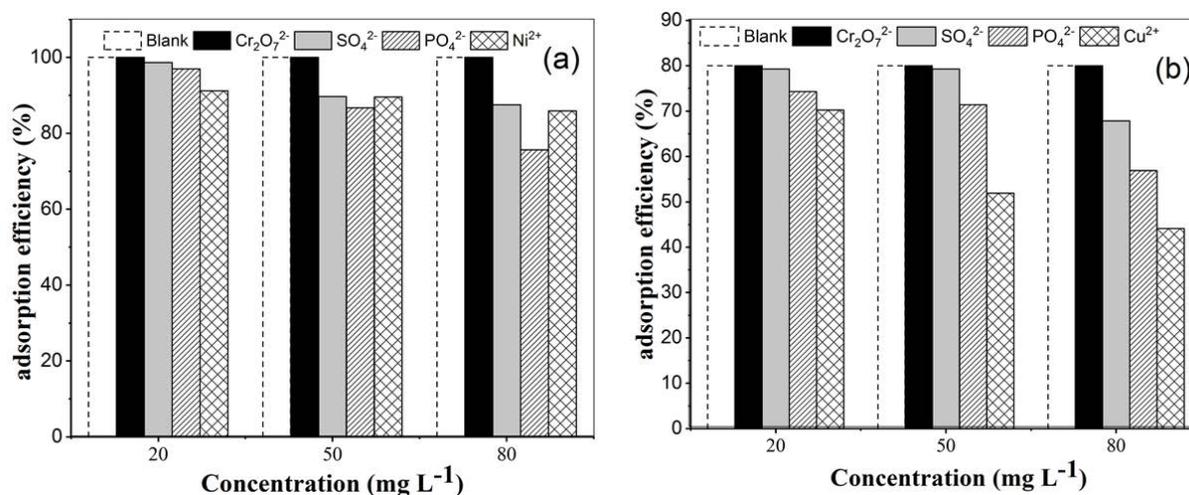
Fig. 8. Effect of co-existing ions on Cu(II) (a) and Ni(II) (b) on the adsorption capacity from aqueous solutions.

same effect of PO_4^{2-} and SO_4^{2-} was noticed with about the same rate decrease. We can conclude that the existence of PO_4^{2-} and SO_4^{2-} has an effect on the adsorption of Cu(II) and Ni(II). In addition, the adsorption of Ni(II) is strongly influenced by the presence of Cu(II) on solution.

3.8. Reusability of AO-PANF

Desorption and regeneration study were carried out using 20 mL of 0.1 M of HCl for 1 h after adsorption of 30 mg L^{-1} of Cu(II) and Ni(II) solutions using 0.2 g of AO-PANF. The desorption efficiency of Cu(II) and Ni(II) using HCl reached 92% and 100%, respectively. The desorption efficiency demonstrates that AO-PANF is an effective support for recycling heavy metals from different sources. In fact, according to Table 4, the regenerated AO-PANF could still adsorb Cu(II) and Ni(II) from aqueous solutions after three adsorption–desorption cycles.

Thus, the adsorption efficiency of AO-PANF gradually decreases to 70% and 51% of the original adsorption efficiency, respectively but still applicable in heavy metal removal. This decrease is may be due to the destruction of functional groups during the adsorption–desorption experiments in acidic solutions. This results has also been observed by others researchers [44,45].

4. Conclusion

Amidoximated polyacrylonitrile fibers (AO-PANF) were synthesized by using hydroxylamine hydrochloride. The resulting AO-PANF adsorbent has demonstrated its capacity for removing copper and nickel ions from aqueous solutions. Moreover, the copper and nickel ions removals from water were found to depend on various adsorption parameters such as the aqueous phase pH, the contact time, the adsorbent dose the temperature, and the presence of co-existing ions in solution. The optimal pH values of copper and nickel removal from water were evaluated and were, respectively, pH = 5 and 7.

A good agreement was found between the experimental adsorption data and the Langmuir theoretical predictions, whereas the kinetics results were found to follow the pseudo-second-order. The maximum adsorption capacity for Cu(II) and Ni(II) using AO-PANF were, respectively, 11.38 and 6.24 mg g^{-1}. At the equilibrium, the adsorbed amounts were obtained at 90 and 30 min, for Cu(II) and Ni(II), respectively. In addition, the endothermic and the spontaneous nature of the adsorption reaction were evidenced from the thermodynamics studies. The adsorption experiments were found to be efficient at room temperature. Finally, the presence of the co-existing ions in the aqueous solution was found

to decrease the adsorption efficiency of these metals. The reuse of AO-PANF was found to be possible for three cycles of adsorption–desorption. The Overall data indicate that the AO-PANF can be used as adsorbent to remove, efficiently, the Cu(II) and Ni(II) from aqueous solutions.

Symbols

q_e — Equilibrium adsorption capacity, mg g^{-1}
C_0 — Initial concentration of metals, mg L^{-1}
C_1 — Final concentration of metals, mg L^{-1}
V — Volume of the solution, L
W — Adsorbent weight, g
q_t — Equilibrium adsorption capacity at time (t), mg g^{-1}
k_1 — Pseudo-first-order rate constant, min^{-1}
k_2 — Pseudo-second-order rate constant, g mg^{-1} min^{-1}
k_{id} — Intraparticle diffusion model constant, mg g^{-1} min$^{-1/2}$
C — Boundary thickness
α — The initial adsorption rate, mg g^{-1} min^{-1}
β — Desorption constant, g mg^{-1}
C_e — Equilibrium concentration of the metal in the solution, mg L^{-1}
q_m — Maximum adsorption capability, mg g^{-1}
K_L — Langmuir constant, L mg^{-1}

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Table 4
Regeneration efficiency of AO-PANF

Metals	Adsorption efficiency (%)			
	Cycle 1	Cycle 2	Cycle 3	Cycle 4
Cu(II)	100	100	86	70
Ni(II)	92	90	78	51

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