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Synthesis of Amidoximated Polyacrylonitrile Fibers and its Use as Adsorbent for Cr (VI) Ions Removal from Aqueous Solutions

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Functionalized fibers, especially polyacrylonitrile fibers (PANF), have attracted wide interest as an effective and economical material for environment and water protection. In this study, polyacrylonitrile fibers modified with hydroxylamine hydrochloride were used as an adsorbent to remove hexavalent chromium ions from aqueous solutions. The novelty of the present study compared to the literature is the functionalization of polyacrylonitrile fibers surface by optimizing cost and energy while achieving a yield fast removal rate and high adsorption capacity of hexavalent chromium from aqueous solutions. The amidoximated polyacrylonitrile fibers were characterized using Fourier Transform InfraRed spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The results confirmed the success of polyacrylonitrile fibers modification. The adsorption capacity was evaluated by investigating the effect of initial pH solution ranging from 2.0 to 7.0, the adsorbent dose varied from 0.05 to 0.25 g, the initial Cr (VI) concentration range was (5–70 mg g⁻¹), the temperature varied from 5 to 60°C, and the contact time ranged from 0 to 180 min. We have used the Langmuir and Freundlich adsorption models to describe the equilibrium sorption data. The maximum adsorption capacity estimated using the Langmuir model reached 32.57 mg g⁻¹ under optimal conditions. The thermodynamic parameters (ΔG , ΔH , and ΔS) were also determined. In addition, the adsorbent showed a desorption rate of Cr (VI) up to 92% with 0.5 mol of NaOH, which can be reused for three adsorption–desorption cycles. The overall data showed the efficiency of amidoximated polyacrylonitrile fibers in removing Cr (VI) from aqueous solutions. © 2019 American Institute of Chemical Engineers Environ Prog, 38: e13196, 2019

Keywords: wastewater treatment, adsorption, recycling, chromium (VI)

INTRODUCTION

The various uses of metals in industry, domestic, agricultural, medical, and technological applications, have caused their excessive release into various ecosystems. Their discharge into the

environment without appropriate treatment is hazardous for both, the human health and the environmental ecosystems. Heavy metals are not biodegradable, they are highly soluble in water and tend to accumulate in living tissues [1]. Chromium pollution is one of the most important environmental concerns; it is released by various industrial processes such as electroplating, leather tanning, dyes and pigments synthesis, dyeing, cement, wood preservation, etc. [2]. In the environment, chromium ions generally take two stable oxidation states Cr (III) and Cr (VI). The Cr (III) ion is a micronutrient which is essential for human health, whereas Cr (VI) ion is a primary contaminant which is very irritating and it is 500 times more toxic than trivalent chromium ion [3]. Furthermore, Cr(VI) is listed in group A of toxic pollutants in wastewater by the Environmental Protection Agency (EPA) [4]. Cr (VI) species may exist in wastewater as chromates (CrO₄²⁻), dichromate Cr (VI) (Cr₂O₇²⁻) and bichromate (HCrO₄²⁻), depending on the pH and the Cr (VI) concentration [5]. Exceeding the limit, he cause skin and stomach irritation for a short-time exposure and damage to liver, and death in large doses for a long-time exposition [6]. Hence, according to the world health organization (WHO), the maximum level of chromium in drinking water, in land surface water and industrial wastewater is 0.05, 0.1 and 0.25 mg L⁻¹, respectively [7]. The Environmental Protection Agency recommended the maximum permissible concentration of chromium in drinking water into 0.1 mg L⁻¹ [8]. Accordingly, the wastewater contaminated by Cr (VI) should be treated and reduced to permissible levels before their release into the environment.

According to the literature, methods such as chemical precipitation, electrochemical process, ion exchange, reverse osmosis, membrane separation, and cementation [9] are used to remove hexavalent chromium species from wastewater. However, all these techniques include high operating cost, high energy consumption, low throughput, low selectivity, toxic sludge generation, and maintenance problems [10]. Adsorption process, on the other hand, has the advantage of the effective and low-cost process, easy operational conditions, flexibility, low secondary pollution, and reusability [11]. The adsorption efficiency of an adsorbent is mainly depending on its surface functional groups. Nevertheless, the material uptake capacity (chemisorption) is not the important point, but also its ability to desorb subsequently

metals (physisorption) [12]. Various adsorbents such as activated carbon, waste biomass, industrial waste, bio-sorbents, chitosan, and chelating materials, have been used to remove Cr (VI) from aqueous solutions [13–18]. Activated carbons, having powder or granular forms, are mostly used for heavy metal ions removal from wastewater. However, this adsorbent is expensive for a developing country and its selectivity is limited [19]. The adsorption capacity of Cr (VI) from aqueous solutions using biomass was evaluated by investigating various parameters. Jain *et al.* [14], have treated *sun flower* waste with sulfuric acid which was used as an adsorbent for Cr(VI) removal from water. According to this reported work, the maximum Cr (VI) adsorption was found to be 53 mg g⁻¹ at pH 2.0. Rao *et al.* [16] found that the fruits of *Ficus glomerata* achieved a Cr (VI) adsorption capacity of 23.1 mg g⁻¹ from wastewater. Natural cactus has also been used as an adsorbent for Cr (VI) removal (21.19 mg g⁻¹) at optimal conditions [20]. Removal toxic metals from water by using an industrial waste have been also investigated. The olive oil factory waste pomace was studied to remove Cr (VI) from aqueous solutions [15], the adsorption amount was 19.58 mg g⁻¹. Activated sludge biomass has been used and proved its ability to remove Cr (VI) from aqueous solutions with a total removal of 77% [21]. The use of bacteria for Cr (VI) removal has already been studied [22–24]. Recently, researchers evaluated the potential of nanoscale zero valence iron to remove Cr (VI). Fu *et al.* [25] synthesized a resin supported nanoscale zero-valence iron by the borohydride reduction method and reached a removal efficiency of 84.4%. Table 1 shows various low-cost adsorbents used in literature to remove Cr (VI) ions from aqueous solutions.

Among these adsorbents, polymer fibers are considered to be one of the efficient adsorbents used for wastewater treatment, removal and recovery of toxic metals [27]. Polyacrylonitrile fiber (PANF) is a commercial and cheap synthetic, semi-crystalline organic polymer [28], applied to develop a wide range of products such as carbon fibers [29], catalysts [30], protective and biomedical materials [31], composite materials [32], filtration and ultrafiltration membrane [33], heavy metals sensors and adsorbents [34], and conductive materials [35]. Due to their strong chemical resistance, excellent mechanical properties, good thermal stability, resistance to corrosion and solvent, low flammability and commercial viability, PANF is one of the most favorable polymer fibers for heavy metals removal from aqueous solutions [33]. Compared to the traditional adsorbents, PANF reaches a high adsorption capacity with a low-cost process and fast adsorption equilibrium due to the large surface area which is five times larger than porous beads [27] and the shorter diffusional distance, it is also easily recovered and easy to separate [28]. The production technology of chelating fibers is simple, easier and can produce various shapes which can be used in several applications. Moreover, the nitrile group, which has lone pair of electrons, strong polarity and triple bonds of carbon-nitrogen (C $\equiv$ N), is found profusely in PANF surface and can be easily transformed into a number of functionalities (Carboxyl, amide, amine, amidoxime, tetrazine, phosphoric, etc.) [36]. The amidoxime group has been found to be effective for heavy metals removal from aqueous solutions [37]. However, in developing countries, the process needs to be based on lower cost technologies and should simultaneously offer attractive, efficient and eco-friendly options for Cr (VI) removal.

In the present study, amidoximated polyacrylonitrile fibers (AO-PANF) were prepared through a one-step reaction of polyacrylonitrile fibers with hydroxylamine hydrochloride in aqueous solutions. The AO-PANF was used as an adsorbent to remove Cr (VI) from aqueous solutions. The effects of various parameters on Cr (VI) adsorption such as the initial pH solution, the adsorbent dose, the initial Cr (VI) concentration, the temperature and the contact time, are discussed. In addition, the desorption of the adsorbed Cr (VI) ions from the (AO-PANF) was also investigated.

Table 1. Comparison of Cr (VI) adsorption capacity by different adsorbents.

Adsorbents	$q(\text{mg. g}^{-1})$	References
Carbonaceous	53.76	[14]
Apple peels	36.01	[26]
Ficusglomerata	23.1	[16]
Cactus	21.9	[20]
Pomace	18.69	[15]
Dried biomass	17.61	[21]
Polyacrylonitrile fibers	32.57	Present study

MATERIALS AND METHODS

Material and Instrumentation

Commercial polyacrylonitrile fibers (PANF) was cut, washed with distilled water and dried in an oven. The chelating agent, Hydroxylamine hydrochloride, with purity $\geq 99\%$ was purchased from Scharlab. Potassium dichromate, purity: 99%, was provided from Riedel-de Haen and used as received. NaOH and HCl, were used to adjust solutions pH.

Fourier Transform InfraRed (FTIR) spectroscopy analysis of PANF samples was obtained using the Thermo Scientific™ Nicolet™ iSTM10 FT-IR spectrometer at room temperature. The samples morphologies were evaluated using Scanning Electron Microscopy (SEM) analysis, using an FEI Quanta 400 ESEM equipped with the Everhart Thornley Detector (ETD) as a Secondary Electron (SE) detector, and Energy Dispersive X-ray detector, Oxford, INCA Instruments. The SEM was operating at electrical potentials ranging between 12.5 and 30 kV, and at working distance (WD) ranging between 9.1 and 11 mm. The quantification of Cr (VI) concentration was determined using diphenyl carbazide by colorimetric method (3500-Cr.B, AWWA-APHA standard code), at 540 nm according to AFNOR standard T91/F under ThermoFisher Evolution™ 300 Uv-Vis spectrophotometer, at room temperature. The pH measurements were performed using a pH meter Thermo Scientific Orion 4 STAR.

Adsorbent Preparation

The PANF were treated with hydroxylamine hydrochloride under different reaction conditions. The chelating agent and PANF (0.2 g) were added to a flask which contains 50 mL of NaOH solution (methanol/water 5:1), and stirred. The reaction was carried out at 70°C [38] using different concentrations of hydroxylamine hydrochloride (0.05–0.15 M) for various durations times (30–120 min). The final products were separated from solutions by filtration, and washed several times with distilled water/methanol mixture. Thereafter, the AO-PANF was dried in an oven at 60°C for 1 day (Figure 1).

The conversion of nitrile groups in PANF into amidoxime groups was evaluated according to Equation (1):

$$C_n = \frac{W_1 - W_0}{W_0} \frac{M_0}{M_1} \times 100 \quad (1)$$

Where C_n is % percentage conversion of nitrile groups in PANF into amidoxime groups, W_0 is the weight of the PANF before reaction (g), W_1 is the weight of PANF after reaction (g), M_0 is the molecular weight of acrylonitrile monomer (53 g mol⁻¹) and M_1 is the molecular weight of hydroxylamine (33 g mol⁻¹).

Chromium Adsorption Process

Aqueous Cr (VI) solutions with initial concentrations range from 5 to 70 mg L⁻¹ were prepared by dissolving appropriate amounts of potassium dichromate in distilled water. Aqueous Cr (VI) solution (50 mL) was shaken with AO-PANF at 150 rpm under different conditions. After a while, the non adsorbed chromium ions present in the supernatant were separated from the aqueous solutions by filtration.

Figure 1. (a) Schematic illustration of AO-PANF synthesis and (b) the amidoximation reaction. [Color figure can be viewed at wileyonlinelibrary.com]

The effect of the initial pH solution on the Cr (VI) adsorption using AO-PANF was first studied by varying the pH from 2.0 to 7.0 using 0.1 M NaOH or HCl solutions. In addition, the optimum adsorbent dose was evaluated by varying the adsorbent dose in the range of 0.05–0.25 g, at contact time of 1 h, initial Cr (VI) concentration of 10 mg L⁻¹ and pH 3.0. The adsorption kinetics were conducted in 0–180 min interval time at initial Cr (VI) concentrations of 10 mg L⁻¹, pH = 3.0, using the optimum adsorbent dose. The effect of initial concentrations (5–70 mg L⁻¹) on Cr (VI) sorption was then evaluated by immersing the adsorbent with 50 mL of Cr (VI), at 25°C, for 1 h, in a constant rotating shaker, at pH 3.0. In addition, the influence of temperature (5–60°C) was also studied.

The remaining concentration of Cr (VI) was measured by spectroscopy Uv–Visible at $\lambda_{\text{max}} = 540$ nm, using 1.5 diphenylcarbazide as a complexing agent which react with Cr (VI) and oxidizes into 1.5 diphenylcarbazone in acidic medium, resulting in formation of red-violet complex.

The removal efficiency of chromium ions R (%) and equilibrium adsorption capacity q (mg g⁻¹) was calculated as follows:

$$\%R = \frac{C_0 - C_1}{C_0} \times 100 \quad (2)$$

$$q = V \frac{(C_0 - C_1)}{W} \quad (3)$$

Where % R is the removal efficiency, q is the equilibrium adsorption capacity of the adsorbent (mg g⁻¹), C_0 and C_1 are, respectively, the initial and the final concentrations of Cr (VI) (mg L⁻¹), V is the volume of solution (L) and W is the adsorbent weight (g).

Desorption Experiments

After the adsorption, to study the ability to reuse the adsorbent, various desorbing solutions (NaOH, NaCl, and HCl) with a concentration of 0.5 M were used to desorb Cr (VI) from the adsorbent. First, a given amount of the adsorbent (100 mg) was mixed and shaken with 50 mL of Cr (VI) at optimum conditions. Cr (VI) was then desorbed using one of the desorbed solutions (NaOH, NaCl, and HCl) for a period time of 16 h at 25°C. After the desorption experiment, the adsorbent was recovered by filtration, washed with distilled water, dried, and reuse for the next adsorption–desorption cycle.

RESULTS AND DISCUSSION

InfraRed Characterization

FTIR spectra of raw and AO-PANF prepared with various NH₂OH.HCl concentrations are shown in Figure 2a. As can be

seen in this figure, the raw PANF shows absorption peaks of nitrile group at 2242 cm⁻¹, carboxylic group at 1737 cm⁻¹ and hydrocarbons compounds at 1449 and 1234 cm⁻¹ [37]. Further, the comparison of both raw and AO-PANF spectra under optimum conditions, as depicted in Figure 2a,b, indicates the effect of increase NH₂OH.HCl concentrations leads to the decrease of the nitrile group absorption peak. This result is in accordance with previous studies [39,40]. This decrease results from the conversion of nitrile groups to amidoxime groups, leading to the apparition of new absorption peaks occurring at 943 and 1650 cm⁻¹ [41]. In addition, the amidoximation reaction which results in the formation of amide groups and carboxylic acid is characterized by absorption bands occurring at 1650 and 1562 cm⁻¹, respectively [37]. Consequently, the FTIR spectra comparison of the raw and the AO-PANF brings forth evidence that the PANF functionalization reaction took place.

The effect of the adsorption process on the AO-PANF is shown in Figure 2c. The comparison between the AO-PANF before and after adsorption shows that the chromium adsorption on the adsorbent surface, in the main, does not alter the initial structure of the modified adsorbents, with a small change in the intensity of carboxylic acid spectrum.

Influence of Reaction Time and NH₂OH.HCl Concentrations on the PANF Functionalization

The influence of reaction conditions such as the reaction time and the NH₂OH.HCl concentrations on the PANF modification were investigated. Figure 3 indicates the effects of NH₂OH.HCl concentrations and the reaction time on the PANF amidoxime group contents. As can be seen in Figure 3a, the conversion of PANF nitrile groups into amidoxime group increased as the concentration of NH₂OH.HCl and the reaction time increased (Figure 3b). The conversion of nitrile groups can be explained by the high diffusion of NH₂OH from solution into the fibers, as resulting from the increase of NH₂OH.HCl concentration and/or the reaction time. To save energy and to keep good fibers properties, 0.15 M of NH₂OH.HCl at 70°C for 1 h can be selected as the optimum experimental conditions for the modification of PANF.

SEM Photographs

The morphologies of the raw PANF, AO-PANF, and AO-PANF after Cr (VI) adsorption are shown in Figure 4. The raw PANF has smooth and uniform surface (Figure 4a). The comparison between raw and AO-PANF shows that the fibers surface after modification becomes rougher and corroded (Figure 4b). The adsorption of chromium ions are obvious, as can be seen in the Figure 4c. The SEM photographs show that the fibers diameter after modification remains unchanged.

Figure 2. (a) FTIR spectra of raw and AO-PANF at different concentrations of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.05–0.15 M) for a reaction time of 1 h, (b) under optimum conditions, and (c) after adsorption. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 3. (a) Influence of $\text{NH}_2\text{OH}\cdot\text{HCl}$ concentrations, (b) duration time on the content of amidoxime groups in AO-PANF. Experimental conditions: $T = 70^\circ\text{C}$, contact time = 1 h, $C(\text{NH}_2\text{OH}\cdot\text{HCl}) = 0.1 \text{ M}$.

Adsorption Mechanism

Effect of pH

The effect of initial pH solutions on Cr(VI) adsorption (Figure 5) from aqueous solutions onto AO-PANF was investigated by ranging pH from 2.0 to 7.0, at room temperature, with an initial Cr(VI) concentration 10 mg L^{-1} , using 0.1 g of adsorbent dose. The initial solution pH affects mainly not only the chromium

speciation in solution but also the surface charge of the adsorbent. In this study, the point zero charge of adsorbent pH_{PZC} was determined through the pH-drift method to evaluate the surface charge of adsorbent [42]. The pH_{PZC} of AO-PANF is 3.9. When $1 < \text{pH} < 3$, Cr(VI) exists as HCrO_4^- form. At pH range of 3.0–6.0, chromium coexist as $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- , which is considered the predominant ions (80%). For $\text{pH} > 6.0$, CrO_4^{2-} dominates [43].

Figure 4. (a) SEM micrographs of the raw PANF, (b) AO-PANF before Cr (VI) adsorption, and (c) AO-PANF after Cr (VI) adsorption. Experimental conditions: C (NH₂OH.HCl) = 0.15 M, C (Cr (VI)) = 10 ppm, $T = 70^{\circ}\text{C}$, contact time = 1 h).

Figure 5. (a) Cr (VI) adsorption capacity from aqueous solutions onto AO-PANF as a function of the initial pH values and (b) schematic interpretation of electrostatic attraction between the adsorbent and adsorbate. Experimental conditions: C (NH₂OH.HCl) = 0.15 M, C (Cr(VI)) = 10 ppm, adsorbent dose = 0.1 g, contact time = 1 h, and room temperature). [Color figure can be viewed at wileyonlinelibrary.com]

According to Figure 5a, the highest adsorption capacity for chromium ions was reached 4.6 mg g^{-1} at pH 3.0, which is consistent with previous researches [44]. While, with increasing initial pH values from 3.0 to 7.0 the adsorption capacities of Cr (VI) decreased from 4.6 to 0.5 mg g^{-1} . These results can be explained as follows. Below pH <3.9, the adsorbent surface containing amine and hydroxyl groups became protonated with increasing H^+ to (NH_3^+ , OH_2^+) and form a positively surface charge [45]. These positive charges exert a strong electrostatic attraction with the anionic species of Cr (VI) present in the solution resulting on an efficient adsorption capacity of HCrO_4^- ions which is the dominant form at pH 3.0. The schematic diagram of electrostatic attraction between the adsorbent and adsorbate is shown in Figure 5b. However, while pH >3.9, a decrease in adsorption capacity was noticed due to the deprotonation of functional groups resulting in a surface negatively charged. This leads on an electrostatic repulsions and competition between the OH^- groups and Cr_4O_2^- , which was hard to adsorb on adsorbent surface. Therefore, pH 3.0 was selected as optimum pH for the following experiments.

Effect of Adsorbent Dose

The effect of the adsorbent dose on the Cr (VI) adsorption was evaluated by varying the initial amount of adsorbent 0.05–0.25 g, using 50 mL of Cr (VI) solutions at initial concentration of 10 mg L^{-1} , at pH = 3.0, $T = 25^{\circ}\text{C}$, a contact time of 1 h, and a stirring speed of 150 rpm (Figure 6). The data shown in Figure 6 indicate that with increasing the adsorbent

dose, the Cr (VI) adsorption capacity increased until reaching an equilibrium value. The increase of Cr (VI) adsorption with increasing the adsorbent dose is probably due to the availability of more adsorbent active sites [26].

Effect of Contact Time

The maximum adsorption capacity of Cr (VI) as function of contact time was studied in the time interval of 0–180 min, using 50 mL of Cr (VI) solutions, 0.1 g of adsorbent dose, at room temperature, pH = 3.0, and a stirring speed of 150 rpm (Figure 7). As can be seen, the Cr (VI) adsorption increased rapidly during the first 15 min, and reached the equilibrium after 60 min of contact time. Therefore, the time interval of 60 min was selected as the optimum contact time for the Cr (VI) adsorption.

Thermodynamic Study

The Cr (VI) adsorption onto AO-PANF under optimal conditions (C (NH₂OH.HCl) = 0.15 M, C (Cr (VI)) = 10 ppm and contact time = 1 h) at T ranging from 5°C to 60°C , is shown in Figure 8. The adsorption capacity increases from 4.1 to 4.7 mg g^{-1} with increasing the temperature from 5°C to 45°C . However, at higher temperature ($T = 60^{\circ}\text{C}$), a decrease in the adsorption capacity was found which may result from a possible desorption of Cr (VI) from the AO-PANF.

The thermodynamic activation parameters of AO-PANF towards Cr (VI), including the Gibbs free energy ΔG (KJ. mol^{-1}), the enthalpy change ΔH (KJ. mol^{-1}) and the entropy

Figure 6. Effect of adsorbent dose on Cr (VI) adsorption from aqueous solutions onto AO-PANF (C (NH₂OH.HCl) = 0.15 M, C (Cr(VI)) = 10 ppm, pH = 3.0, contact time = 1 h, at room temperature).

Figure 7. Effect of the contact time on the Cr (VI) adsorption from aqueous solutions onto AO-PANF. Experimental conditions: C (NH₂OH.HCl) = 0.15 M, C (Cr (VI)) = 10 ppm, pH = 3.0, adsorbent dose = 0.1 g, and room temperature.

change ΔS (J.K⁻¹.mol⁻¹) were calculated using van't Hoff Equations [46]:

$$\Delta G = -RT \ln K_d \quad (4)$$

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (5)$$

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. The values of ΔH and ΔS were determined from the plot of $\ln K_d$ versus $1/T$, and summarized in Table 2.

According to the Table 2, the negative values of ΔG indicate the spontaneity nature of the adsorption process. The augmentation of ΔG value after 318 K showed that, at higher temperatures, the adsorption process become unfavorable and required

Figure 8. Effect of temperature on the Cr (VI) adsorption from aqueous solutions onto AO-PANF. Experimental conditions: C (NH₂OH.HCl) = 0.15 M, C (Cr (VI)) = 10 ppm, pH = 3.0, adsorbent dose = 0.1 g, and contact time = 1 h.

Table 2. Thermodynamics parameters for Cr (VI) adsorption by AO-PANF.

T (K)	ΔG (KJ.mol ⁻¹)	ΔH (KJ.mol ⁻¹)	ΔS (K.J ⁻¹ .mol ⁻¹)
278	-13.14	30.25	163.92
288	-17.14		
303	-21.80		
318	-26.64		
333	-19.23

Figure 9. Effect of initial concentration on Cr (VI) adsorption from aqueous solutions onto AO-PANF. Experimental conditions: C (NH₂OH.HCl) = 0.15 M, pH = 3.0, adsorbent dose = 0.1 g, contact time = 1 h, and room temperature).

more energy [47]. The ΔH value for Cr (VI) 30.25 > 40 mention that the adsorption process is physical [48]. Furthermore, the positive value of ΔS (163.92 K.J⁻¹.mol⁻¹) indicate the feasibility of the adsorption and suggest an increase of the randomness at the solid liquid -interface during the fixation of Cr (VI) onto AO-PAN [49].

Figure 10. (a) Langmuir and (b) Freundlich plot of Cr (VI) adsorption onto AO-PANF. Experimental conditions: C (NH₂OH.HCl) = 0.5 M, pH = 3.0, adsorbent dose = 0.1 g, and room temperature.

Table 3. Langmuir and Freundlich constants for Cr (VI) adsorption on AO-PANF.

Langmuir				Freundlich		
q_m (mg.g ⁻¹)	K_L (L.mg ⁻¹)	R^2	R_L	K_F (mg.g ⁻¹)	$\frac{1}{n}$	R^2
32.57	0.54	0.997	0.20	9.729	0.193	0.755

Effect of Initial Concentration of Cr (VI)

The adsorption capacity of Cr (VI), at various initial concentrations, is shown in Figure 9. The experiments were conducted using Cr (VI) initial concentration varying from 5 to 70 mg L⁻¹, an adsorbent dose of 0.1 g, contact time of 1 h, at room temperature, and a stirring speed of 150 rpm. Figure 9 shows that with an increase of initial concentration, the adsorption capacity increased also. The increase of adsorption capacity with increasing of initial concentration is due to the increase of driving force of the concentration gradient [15].

Isotherm Study

The adsorption isotherms describe the interaction between the adsorbents and the concentrations of metal ions in solutions at a constant temperature. Langmuir and Freundlich isotherm models are the two important isotherm models employed to analyze the equilibrium sorption data and to evaluate the nature of adsorption of metal ions onto adsorbent [50]. Equilibrium adsorption experiments were carried out at pH 3.0, at a constant temperature with increasing initial concentration of Cr (VI) in the solutions from 5 to 70 mg g⁻¹, and the results are presented in Figure 10. The Langmuir model describes a monolayer adsorption on a uniform surface of adsorbent with homogenous distributions of the adsorption sites without interaction force between molecules. The linear equation is given as follows [51]:

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

Where C_e is the equilibrium concentrations of Cr (VI) ions in the solution (mg L⁻¹), q_e is the amount of Cr (VI) adsorbed onto AO-PANF (mg g⁻¹), q_m is the maximum adsorption capacity (mg g⁻¹), and K_L is the Langmuir constant related to the energy of adsorption (L mg⁻¹). The values of q_m and K_L was determined using the plot of C_e/q_e versus C_e (Figure 10a).

Another Langmuir parameters, the dimensionless separation factor R_L , was calculated using the following Equation [52]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

Where C_0 is the initial concentration of Cr (VI) in solution. The R_L value is classified into different categories. In case $R_L = 0$ the monolayer adsorption is irreversible, $0 < R_L < 1$ the adsorption is favorable, $R_L = 1$ the adsorption is linear and $R_L > 1$ the adsorption is unfavorable [53].

Freundlich model isotherm describes the multilayers adsorption of metal ions on a heterogeneous surface of the adsorbent. The linear equation is as follows [51]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

Where K_F [(mg g⁻¹) (L mg⁻¹)^{1/n}] and n are the Freundlich constant representing the adsorption capacity and the adsorption intensity, respectively [54]. The values of these parameters are determined by plotting $\log q_e$ as a function of $\log C_e$ (Figure 10b).

Table 3 displayed the constant parameters and the correlation coefficient of R^2 of Langmuir and Freundlich isotherm models. The values of correlation coefficients in Table 3 show that the Cr (VI) in the AO-PANF were fitted better with the Langmuir model ($R^2 = 0.997$) compared to the Freundlich model ($R^2 = 0.755$), confirming that Cr (VI) sorption mechanism onto AO-PANF surface is monolayer adsorption. The values of maximum adsorption capacity q_m of Cr (VI), calculating using Langmuir equation was found to be 32.57 mg g⁻¹, relatively greater than others adsorbents used [54]. In addition, the calculated R_L values was 0.20 indicating that the Cr (VI) adsorption onto AO-PANF is favorable.

Desorption Study

The capacities of AO-PANF to be regenerated after the Cr (VI) adsorption using various desorbing agents (NaOH, NaCl,

Figure 11. (a) Desorption efficiency of Cr (VI) from AO-PANF using different desorbing agents, (b) adsorption–desorption cycles of AO-PANF. Experimental conditions: C (desorbing agents) = 0.5 M, C (Cr (VI)) = 10 ppm, contact time = 16 h and room temperature.

Table 4. Summary of different results obtained during the present study.

NH ₂ OH.HCl (M)	PANF modification time (min)	C _n (%) Equation (1)	Adsorption time (hour)	% R Equation (2)	q (mg g ⁻¹) Equation (3)
0.05	30	4.01	1	5.17	2.57
	60	6.42		39.42	9.62
	90	19.27		43.47	11.64
	120	22.48		60.07	19.90
0.1	30	5.62		16.41	8.16
	60	16.06		59.10	19.42
	90	20.8		64.55	22.13
	120	32.12		73.37	26.52
0.15	30	6.42		18.08	9.00
	60	33.7		92.19	23.89

and HCl) with concentration of 0.5 M, are depicted in Figure 11a. The best results were obtained by using 0.5 M of NaOH for a contact time of 16 h, and allowed the recovery in water of >90% of adsorbed Cr (VI). After the desorption experiment with 0.5 M of NaOH, the adsorbent was filtrated from solution, washed with distilled water, dried at 60°C and reuse for Cr (VI) adsorption. Figure 11b showed the adsorption–desorption cycles of AO-PANF. It can be seen that the Cr (VI) removal efficiency was kept nearby of 90% after three cycles. Then, the removal percentage decreased significantly with subsequent adsorption–desorption cycles. It can be due to the accumulation of incomplete desorption of Cr (VI) from the AO-PANF surfaces. The results concluded that the AO-PANF is reusable and effective for three adsorption–desorption cycles.

Summary of the Results

Table 4 shows different results and values obtained in this study. Note that the adsorption values mentioned in this table relate to the values obtained under optimal conditions.

CONCLUSIONS

The surface modification of PANF, consisting in the conversion of the fibers nitrile groups into amidoxime groups, produced a new efficient adsorbent for Cr (VI) removal from aqueous solutions. The PANF functionalization process was

achieved by using various NH₂OH.HCl concentrations. Optimum conditions for the PANF modification process lead to the highest nitrile groups conversion. The resulting AO-PANF provides a great ability to remove Cr (VI) ions from aqueous solutions. Optimal conditions leading to highest Cr (VI) removal from aqueous solutions were found. The Cr (VI) adsorption capacity was found to increase with increasing the temperature. At temperatures higher than 45°C, a decrease in the adsorbed amount was observed. The maximum sorption capacity was 32.52 mg g⁻¹ under optimal conditions. Finally, the adsorbed Cr (VI) ion on the AO-PANF was found to be easily recovered using NaOH desorbing agents and the adsorbent was reused for three adsorption–desorption cycles.

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