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Fast extraction of vanadyl ion using grafted cotton fiber inserted with amidoxime moiety

Magda A Akl*, Wael Ali & Mohamed Moneir

Department of Chemistry, Faculty of Science, Mansoura University, Mansoura 35516, Egypt

*E-mail: magdaakl@yahoo.com

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Egyptian cotton cellulose fibers have been adapted by graft copolymerization of polyacrylonitril (PAN) and then by ingestion of amidoxime moiety to finally generate C-AXO chelating fibers, which have been characterized by various instrumental techniques such as SEM, FTIR, EDX and XRD spectra. Using batch tests, the obtained C-AXO is used for removal and extraction of VO^{2+} from its aqueous solution. The kinetic studies have shown that the pseudo second-order model is the best fit for the experimental data.

Keywords: Cotton fiber, Grafting, Acrylonitrile, Amidoxime

Vanadium is a trace element which is widely distributed in the crust of the Earth. Naturally high vanadium levels are often found in simple rocks and minerals and vanadium industrial origins include combustion of fossil fuel and wastes comprising slags from the steel industry. The researchers have performed studies and evaluations over the last few years on the geochemistry of the ecosystem and the ecological danger of vanadium in the mining and smelting area[1]. Vanadium (V) has a number of properties that make it suitable for use in ceramic production and decoration, pigment production for a wide range of products, an accelerator for drying paint, aniline black dye production, and as a reagent in textile colouring making use of its hardness, strength, ability to shape alloys and its corrosion resistance. It is being used in the manufacture of instruments, steel, equipment and surgical implants. It is also used in the production of photographic designers, batteries, and semi-conductors, and in the recycling processes based on catalysts[2]. That is why many eco-friendly methods for the efficient extraction and recovery of vanadium from its limited sources and industrial effluents have been created. Effective methods are considered traditional and efficient for the separation and isolation of the metal ions by using solvent extraction techniques[3,4] and chromatographic separating methods[5]. Chelating materials from cheap natural and synthetic sources considered particularly economically important, between all methods listed above[6-11]. In this case, chelating materials are important. Chelating materials are commonly used as beads, resins, or membranes[12,15]. Recently moreover, a wide range of studies have focused on the production and application of fibrous chelating materials from both natural fibers like wool fibers[16] or synthetic fibers like PET and polypropylene fibers[13,14,17]. The chelating fibers actually have numerous advantages over traditional chelating materials in the form of pearls or membrane, above all ease of preparation, extraction and adjustment as well as the ability to be applied as felt or as a fabric that provides a high degree of efficiency and high surface during contact with the media.

Oversight of modified cellulosic materials as effective and cost-effective biosorbents has been the subject of numerous research over the past few years. Besides the advantages of cellulose as a highly abundant, cheap and biodegradable material, cellulose also can be easily modified because of the high number of random of the active hydroxyl groups that are an important part of various types of reactions, such as oxidation, ether formation, estrification and free co-polymerisation of cellulose derivatives[18-20].

Brand-new chelating fibers from cellulosic cotton materials modified with amidoxime moieties (C-AXO) were prepared in this article for the quick removal of vanadyl ion from aqueous solution. Different instrumentation techniques such as elementary analysis, SEM electron microscope, FTIR

and broad radiation spectroscope were used to fully characterize the prepared C-AXO chelating fibers. In order to determine optimum adsorption conditions and overall adsorption efficiency, different parameters such as pH, temperature, kinetic and adsorption isotherm were also studied.

Experimental Details

Materials

The used cotton fibers were gathered and washed and dried in the oven for 24 h with distilled water and ethanol. Acrylonitrile (AN) (Sigma-Aldrich) has been purified by 3% (w / w) NaOH and then washed off alkali with distilled water. The following were purchased from Sigma Aldrich: potassium persulphate (KPS), Thiourea(TU)(BDH-England); hydrazine (Adwic); hydroxyl amine and supplied pure vanadyl pentahydrate $VOSO_4.5\ H_2O$. Acrylonitril was treated with an aqueous NaOH solution of 3% for the removal of the stabilizer, then washed out with distilled water until alkaline-free. As obtained, that's all chemicals were used.

Synthesis of C-AXO chelating fibers

In the first synthetic phase cotton fibers have been modified with the use of the KPS / TU combined redox initiator, through free radical graft copolymerization. Dry cotton fiber (0.1 g) was applied to 100 mL tapering flask, applied to which 50 mL tapers, containing 2 mmol KPS and 2 mmol TU were combined, then added H_2SO_4 solution of 0.5 mL 1 percent (V / V), and then shaken for approximately 10 min. The reaction mixture was then sprayed with Acrylonitrile monomer (2 mL) and stirred for 2 additional hours at 80°C. With 10 mL of 3% (w / v) of the hydroquinone solution, the reaction was stopped after this period. In order to extract the PAN homopolymer and finally to drain the grafted fibers at 50°C for 24 h the fiber was removed from the reaction mixture.

Grafting percentage (*GP*) was evaluated according to the following mathematical expression:

$$\text{Grafting Percentage } (GP) = (A\text{-}B / B) \times 100 \quad ...(1)$$

Where *A* and *B* are the weight of grafted product and native PET fibers, respectively.

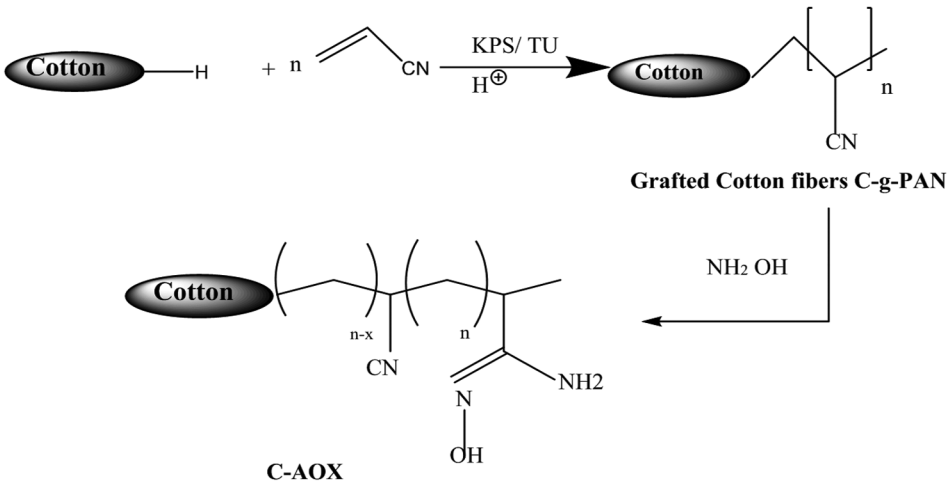
From the previous step the resultant C-g-PAN was then treated with NH_2OH. In a mixture of 25 mL aqueous 20 percent (w/v) hydroxylamine hydrochloride solution and 25 mL aqueous 20 percent (w/v) NaOH solution a 1 g of the grafted C-g-PAN copolymer was immersed. *Via* treatment, the prepared C-g-PAN undergoes modification by transforming the – CN group into amidoxime (H_2N – C N – OH) groups. The reaction flask was then equipped with a reflux condenser and magnetic stirring continued the reaction for 5 h at 80°C. The chelating grafted polymer obtained has been named as C-AOX as shown in Scheme 1.

Schematic presentation for the synthetic steps of the C-AXO is shown in Scheme 1.

Characterization of the polymer samples

The native cotton fibers, C-g-PAN, C-g-PAH and C-AXO elementary analysis (E.A.) was collected from a Perkin – Elmer 240 C Elemental Analytical Instrument (USA).

A Perkin – Elmer instrument was used to test the FTIR spectra. Under reduced pressure the fiber samples were dried overnight at 60°C and pressurized



Scheme 1 — Synthesis of C-AXO chelating fibers

with a glass slide on top of the ATR instrument's quartz panel.

The native and modified surface morphologies of the fibers were observed using a 20 kV FEI Quanta-200 scanning electron microscope (FEI Group, The Netherlands) equipped with an Oxford energy dispersive X-ray system (EDX). ASAP 2010 Micrometrics instrument was used by N_2 adsorption isotherm and Brunauer – Emmett – Teller (BET) method to predict the precise surface area of the studied samples.

Polymer sample crystallinity was measured using X-ray powder diffractometer (Japanese Dmax-rA, wavelength = 1.54 Å, CuKα radiation). Speed of generator was 40 kV, current of generator was 50 mA. The sample was then screened in phase 0.020 from 2 premises = 5–700. The resulting graphics were printed on origin programe.

Metal ion uptake experiments using batch method

Instrumentation

An inductively coupled plasma optical emission spectrometer (ICP-OES) (Thermo iCAP6500, England) was used for spectrometric vanadium measurements.

Adsorption and desorption experiments

The experiments were conducted with a batch method in all adsorption studies. 0.03 g of the fiber samples tested were put in small glass-stoppered bottles containing a 30 mL metal ion solution with a key concentration of 100 mgL^{-1} (except for adsorption isothermic studies in which the concentration ranged from 10 to 400 mgL^{-1}), at 30°C (except for thermodynamic studies in which the temperature ranged from 20 to 40°C), at *p*H 5 (except for *p*H studies in which the *p*H ranged between 1-5). The bottles were equilibrated on a thermostated shaker at 150 rpm. The percent removal and the amount adsorbed can be estimated according to the following mathematical expressions:

$$\text{Percent removal (\%)} = (C_i - C_e) \times 100 / C_i \quad ...(2)$$

$$q_e = (C_i - C_e)V/W \quad ...(3)$$

where: C_i (mgL^{-1}) and C_e (mgL^{-1}) initial and equilibrated metal ion concentrations, respectively; q_e (mg/g) adsorption capacity; V (L) volume of added solution and W(g) the mass of the adsorbent (dry).

The desorption experiments were performed as in the following: C-AXO chelating fibers initially loaded with vanadyl ions have been made with the 0.1 g of the fibers soaking at *p*H 5.0 and 30°C in 100 mL (100 mgL^{-1}) metal ion solution. The load was balanced on an adjustable 150 rpm thermostatic shaker. The filled ion fibers were then stripped and washed to obtain red from the unadsorbed ions with distilled water, which would then be agitated by 100 mL of HNO_3 solution for 60 min. The desorped metal ion concentrations were measured using atomic absorption techniques. Reusability of the chelating fiber was tested five times, and the percentage of desorption (D, %) was determined as in Eq (4) by repeating the above adsorption-desorption process.

$$D\% = (C_{HNO3}/C_{ad}) \times 100 \quad ...(4)$$

where C_{HNO3} is the metal ion desorbed to the HNO_3 solutions (mgL^{-1}) and C_{ad} is the metal ion adsorbed onto the resin (mgL^{-1}).

Results and Discussion

Characterization

The results obtained from the primary elemental analyses, C-g-PAN, C-g-PAH, and C-AOX are shown in Table 1. As can be shown, after grafting and hydrazine shifts, the nitrogen content is considerably higher, indicating that PAN chains are merged into H_2N-C = NH-NH_2 and that the vast majority of CN-groups have been transformed. In addition there is an increase in the content of nitrogen and oxygen suggesting further improvements in PAH chains and the production of amidoxime units on the surface of the greased polymers. Scanning electron microscope (SEM) was used to analyze surface morphologies of indigenous and modified fibers, and images of native cotton, C-g-PAN and C-AXO were shown in Fig. 1. The observed increase in the C-g-PAN size can be attributed, as can be noted, to the addition of the grafted PAN chain on the main backbone of the cells. Furthermore, the relatively raw surface observed by both native and grafted fibers in C-AOX may result from additional therapies when the active chelating amidoxime moieties are inserted. All native cotton and C-AOX fibers had surface dimensions of 2432 m^2/g and 5934 m^2/g, respectively, based on the BET surface

Table 1 — Elemental analysis of native cotton, C-g-PAN, C-g-PAH and C-AXO

Fibers	C (%)	H (%)	N (%)
Native cotton	42.2	6.01	0
C-g-PAN	57.2	5.8	15.41
C-g-PAH	42.9	6.1	34.7
C-AXO	52.7	5.5	21.7

area measurements. Such comparatively small surface area is shown primarily by coordination with the active functional group on the fibers that the heavy metal ion absorption is induced.

The morphologies of the native and modified fibers, as well as the SEM images from unmodified cotton fibers and the loaded fibers, have been studied using scanning electron microscope (SEM, Fig. 1).

The modified and unmodified cotton fibers FTIR spectra were presented in Fig. 2. For native cotton fibers,

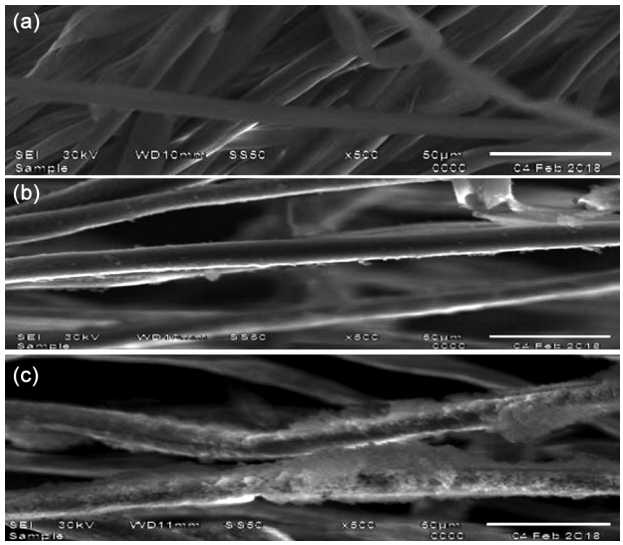


Fig. 1 — SEM photos of unmodified, modified cotton fibers and loaded fibers:(a) Native unmodified cotton fibers, (b) C-AXO, (c) C-AXO-VO^{2+}

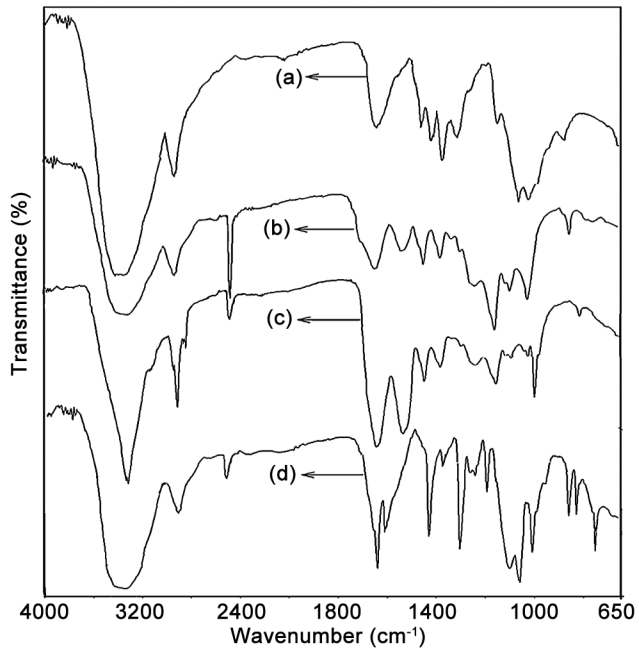


Fig. 2 — FTIR spectra of (a) native cotton fibers, (b) C-g-PAN, (c) C-g-PAH and (d) C-AXO

IR spectrum (Fig. 2a) showed the key characteristic cellulose peaks at around 1070–1150 cm^{-1} due to C-O stretching, 1260–1410 cm^{-1} due to O-H bending, and 3600–3100 cm^{-1} due to O-H stretching[18]. On the other hand, the distribution of grafted cotton fibers C-g-PAN (Fig. 2b) supports the insertion of the PAN onto the polysaccharide cellulose backbone by the CN unique peak presence at 2350 cm^{-1}. However, the further modification by transforming the majority of CN groups into $H_2N - N = C - NH_2$ groups (Fig. 2c) was obviously clarified by the observed reduction of the C-N characteristic peak at 2350 cm^{-1} and peak appearance at approximately 1660 cm^{-1} and 3200 cm^{-1} corresponding to azomethine (C= N) and $–NH_2$ groups respectively, in addition to the simple N – N characteristic peak at approximately 1030 cm^{-1}, respectively. Eventually, there was no significant change in the spectrum of C-AOX (Fig. 2d), merely an improvement in the amplitude of the CN- and O-H peaks at 1665 cm^{-1} and 1260-1410 cm^{-1}, respectively, as a result of the interaction between the cross-linker and the inserted $–NH_2$ groups[15].

The variations of the crystalline structure were analyzed using wide angle X-ray (XRD) diffraction as a result of the chemical modifications. As we can notice from Fig. 3a, The XRD pattern of native cotton fibers displayed crystalline peaks at approximately 15°, 16° in addition to a sharp extreme peak at approximately 23°, which is consistent with the previous report[21]. On the other hand, the crystalline pattern of the modified C-g-PAN and C-AXO (Fig. 3b and c) shows a sharp intensive peak at approximately

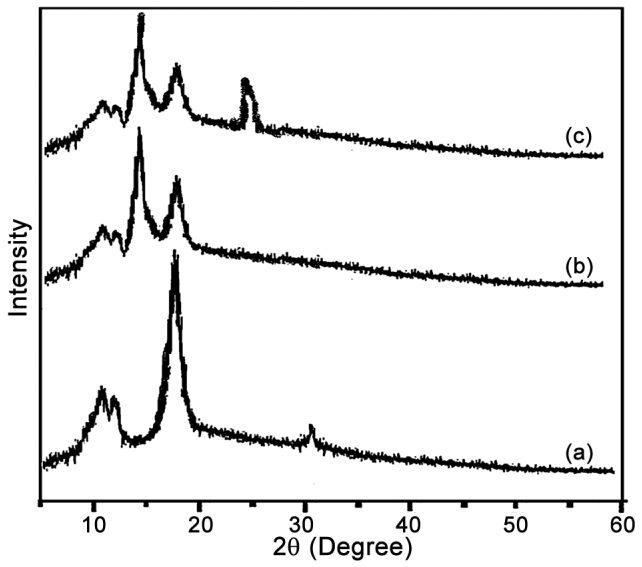


Fig. 3 — X-ray diffraction pattern of (a) native unmodified cotton fibers, (b) C-g-PAN, and (c) C-AXO

17° as a result of the crystalline pattern of the grafted PAN chains[22]. This can be proof of PAN's growing to relative long chains and forming a well organized crystalline pattern during graft copolymerization. In addition, after grafting and alteration, characteristic cotton fiber intensities peak 15°, 16°, and 23°, which indicate decrease in crystallinity.

Fig. 4a-c shows the EDX spectra of unmodified native cotton fibers, C-g-PAN and C-AXO chelating fibers, respectively. It is apparent that, in addition to the original carbon and oxygen peaks found in the native cotton fibers spectrum, the spectrum of C-g-PAN (Fig. 4b) showed an additional nitrogen peak (Fig. 4a), which confirms the positive grafting reaction. In addition, the C-AXO spectrum (Fig. 4c) showed the increase in nitrogen peak strength, which may provide evidence of further modification of the grafted chains *via* the introduction of amidoxime chelating groups.

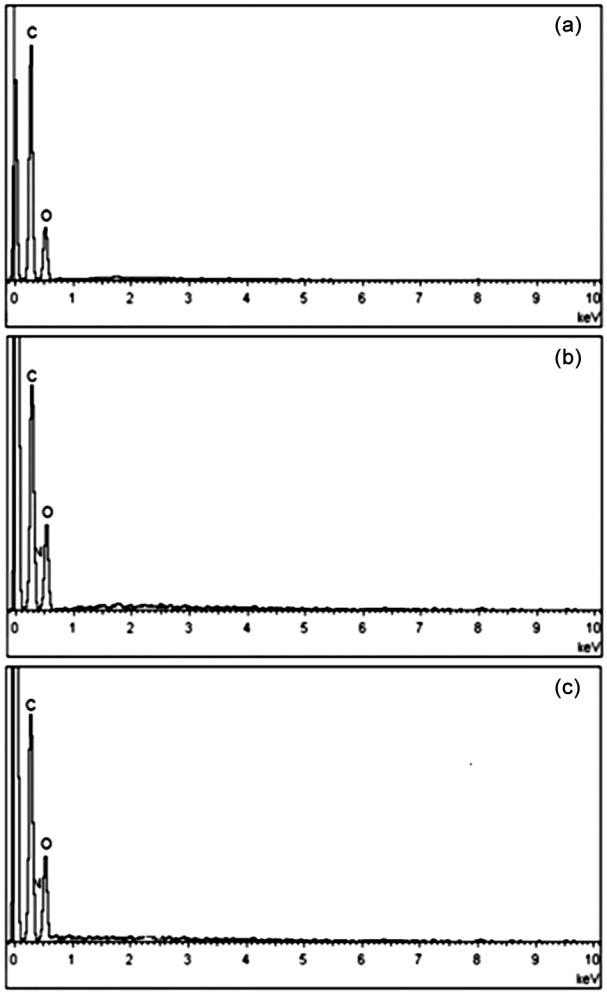


Fig. 4 — EDX analysis of (a) native cotton fibers, (b) C-g-PAN, and (c) C-AXO

Metal ions uptake studies

Effect of functionalization

Cotton functionalization's effect on the ability to extract vanadyl ions was investigated at 30°C while all other circumstances remained unchanged. The results of this are shown in Table 2. As can be observed, the original unmodified cotton fibers as well as C-g-PAN fibers showed no characteristic potential for the extraction of the studied vanadyl ions, which was caused by the lack of functional groups that could possibly bind to these metal ions. Additionally, C-g-PAH showed a remarkably high potential for extracting ion. For amidoxime-functionalized C-AXO fibers, there was a notable increase in the percentage of removal of the metal ions VO^{2+}, which may result from a wider surface area with sufficient exposure to considerably more active sites where heavy metal ions might be able to bind.

Influence of pH

Fig. 5 indicates the pH effect on the removal of VO^{2+} ions by percentage. As can be observed, before the precipitation limits of the studied ions, the adsorption experiments were conducted within a *p*H range 1–5. As predicted, the percentage removal of metal ions showed a substantial increase at high *p*H

Table 2 — Effect of the functionalization on the percent removal of VO^{2+} ions

Fibers	Percent Removal of VO^{2+} (%)
Native cotton	2.3
C-g-PAN	6.2
C-g-PAH	69.5
C-PTS	85.7

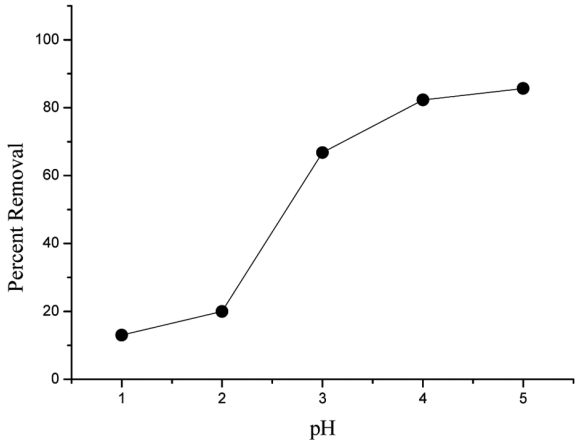


Fig. 5 — Effect of pH on the uptake of VO^{2+} ions by C-AXO (initial concentration 100 mgL^{1}; C-AXO. 1 gL^{-1}; contact time 3 h; shaking rate 150 rpm, 30°C)

value that could be due to the low H^+ concentration that could compete with the metal ion to align with active amidoxime moieties and consequently decrease the percentage removal by changed C-AXO chelating fibers at low *p*H values.

Effect of temperature

The thermodynamic parameters for the adsorption of VO^{2+} ions were studied by adding 0.03 g C-AXO chelating fibers with 30 mL of the metal ion solutions tested at *p*H 5, with concentration 30 mgL^{-1} at 293, 303 and 313 K. In all the cases examined, increasing temperature reduces adsorption, which can provide evidence for the adsorption's exothermic existence. Furthermore, according to the following mathematical equations, we can estimate the thermodynamic parameters (free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°)):

$$K_C = C_{ad} / C_e$$

Where C_{ad} is the concentration of solute adsorbed on the fibers at equilibrium (mg/g) and C_e is the equilibrium concentration of metal ion in the solution (mgL^{-1}).

Free energy of the adsorption $(\Delta G°_{ads})$ can be calculated using the following equation:

$$\Delta G°_{ads} = -RT \ln K_C$$

The adsorption standard enthalpy ($\Delta H°_{ads}$) and entropy ($\Delta S°_{ads}$) can be evaluated using the following equation:

$$\ln K_C = (\Delta S°_{ads}/R) - (\Delta H°_{ads}/RT)$$

Where: R (8.314 J/mol K) is the gas constant.

By plotting $\ln K_C$ *vs* $1/T$ (Fig. 6), the values of the slope $-\Delta H°_{ads}/R$ and the intercept $\Delta S°_{ads}/R$ were employed in calculating both $\Delta H°_{ads}$ and $\Delta S°_{ads}$ for VO^{2+} ions adsorption onto the modified C-AXO chelating fibers.

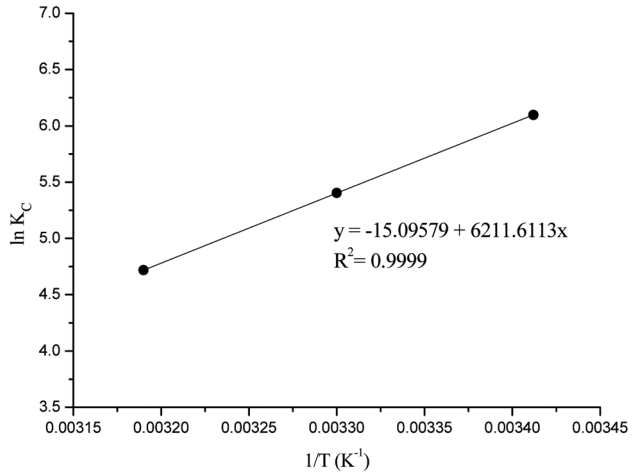


Fig. 6 — Plot of ln K_C as a function of reciprocal of temperature (1/T) for the adsorption of VO^{2+} ions by C-AXO fibers

In Table 3, the measured thermodynamic parameters were collected and, as can be noted in all cases, negative values were shown by G°ads, which means adsorption is a spontaneous operation. However, both $\Delta H°_{ads}$ and $\Delta S°_{ad}$ are also negative suggesting that the process is an exothermic process with a decrease in entropy that could be due to the accumulation of the metal ion on the chelating fibers surface. This is a typical observation during the process of extracting ion from metal[15].

Kinetic studies

The effect of the adsorption time by modified C-AXO chelating fibers on the removal of VO^{2+} ions is shown in Fig. 7 and Table 4. As can be seen, for the first 20 min, the removal exhibited a rapid rate where the percentage removal reached about 75% with an initial rate of about 3.8 mg g^{-1} min^{-1}.

The resulting experimental data were fitted with the well-known kinetic pseudo-first - order and pseudo-second - order models according to the following equations for better evaluation of the kinetic mechanism which governs the entire removal process:

$$1/q_t = k_1/q_e t + 1/q_e$$

Where k_1 is the pseudo-first-order rate constant (min^{-1}) of adsorption and q_e and q_t (mg/g) are the amounts of metal ion adsorbed at equilibrium and time t (min), respectively. The value of $1/q_t$ was calculated from the experimental results and plotted against $1/t$ (min^{-1}). The linear form of pseudo-second-order equation can be written as:

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t$$

Where: k_2 is the pseudo-second-order rate constant of adsorption (g/(mg min)).

The resulting experimental data were fitted with the well-known kinetic pseudo-first - order and pseudo-second - order models according to the following equations for better evaluation of the kinetic mechanism which governs the entire removal process.

The pseudo-second - order kinetic model also demonstrated the best fit with the experimental data in the studies conducted by Monier and Abdel-Latif[14] on the adsorption of Hg^{2+}, Cu^{2+} and Co^{2+} on PET-based

Table 3 — Thermodynamic parameters for the adsorption of VO^{2+} ions on C-AXO fibers

Metal ion	K_c			$-\Delta G°_{ads}$ (kJ/mol)			$\Delta H°_{ads}$ (kJ/mol)	$\Delta S°_{ads}$ (J/mol K)
	293 K	303 K	313 K	293 K	303 K	313 K		
VO^{2+}	442.13	222.58	111.97	14.839	13.617	12.278	–51.643	–125.506

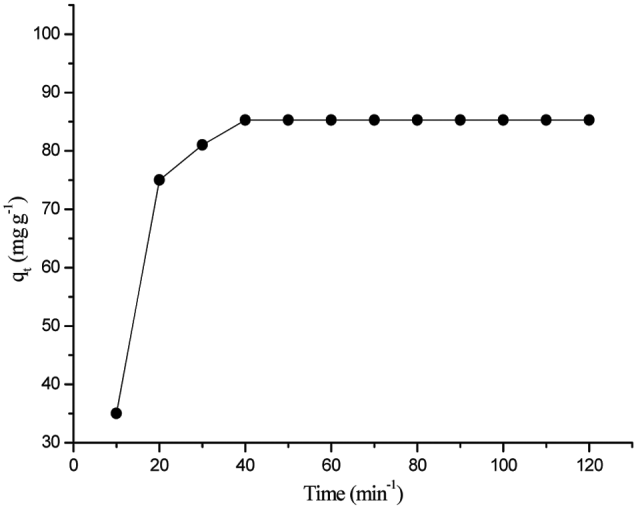


Fig. 7 — Effect of contact time on the uptake of VO^{2+} ions by C-AXO(initial concentration 100 mgL^{-1}, C-AXO 1 gL^{-1}, pH 5.0, shaking rate 150 rpm, 30°C)

chelating fibers; by Hajeeth *et al.*[19] on the removal of Cu^{2+} and Ni^{2+}.

Adsorption isotherms

Adsorption isothermic studies are necessary to predict the characteristic relationship between the adsorbent and the adsorbent[23] and thereby provide useful information about the adsorption process, which is very important for the adsorption device design. The VO^{2+} ion adsorption isotherms were performed under the optimal conditions of *p*H, temperature, contact time and concentration range between 10-400 mgL^{-1}.

As shown in Fig. 8, the adsorption of the studied ions was slowly increased by increasing the initial concentration until the high concentration of C-AXO exceeded the full saturation capability. The adsorption parameters are calculated using both the Langmuir and Freundlich models. The isothermic model of Langmuir adsorption assumes that the adsorbed form is monolayer on the adsorbent surface, the surface is homogeneous with energetically similar adsorption sites and there are no intermolecular forces between the adsorbed species[23].

The mathematical expression of Langmuir adsorption model is represented according to the following equation:

Table 4 — Kinetic parameters for VO^{2+} ions adsorption by C-AXO fibers

Metals	First-order model		
VO^{2+}	k_1 (min^{-1})	q_{e1}(mg/g)	R^2
	6.642	82 ± 3	0.9362
Metals	Second-order model		
	k_2 (g/(mg min))	q_{e2} (mg/g)	R^2
VO^{2+}	5.7×10^{-3}	86 ± 1	0.9999

$$C_e/q_e = (1/K_L q_m) + (C_e/q_m)$$

where q_e is the amount of metal ion adsorbed on one gram of the adsorbent (mg g^{-1}) at equilibrium, C_e the equilibrium concentration in the solution (mg L^{-1}), q_m the maximum adsorption in monolayered adsorption systems (mg g^{-1}) and K_L is the adsorption equilibrium constant related to adsorption energy (L mg^{-1}). The adsorption parameters (q_m and K_L) were evaluated from the slop and intercept of C_e/q_m *vs* C_e plot.

For Freundlich isotherm model, the adsorbate assumed to form a multilayer on energetically nonequivalent heterogeneous adsorbent surface. The model can be mathematically expressed as in the following equation:

$$\ln q_e = \ln K_F + 1/n \ (\ln C_e)$$

Where K_F is a constant related to the adsorption capacity and 1/n is an empirical parameter related to the adsorption intensity, which depend on the material heterogeneity. Both K_F and n can be estimated by plotting $\ln q_e$ *vs* $\ln C_e$.

Table 5 assembled both the parameters Langmuir and Freundlich. The experimental results showed the best match with Langmuir model, indicating a monolayer homogeneous adsorption of the studied metal ions to the modified C-AXO chelating fibers, according to the correlation coefficients. As can be seen in Table 5, the maximum adsorption power of VO^{2+} ions was 156.50 mg g^{-1}, suggesting a very strong potential for removal of these metal ions from aqueous solution by the prepared fibers.

Desorption and regeneration of C-PTS chelating fibers

Desorption experiments are essential for evaluating the recovery of metal ions and the regeneration of adsorbents for the requirements of reusability. Used

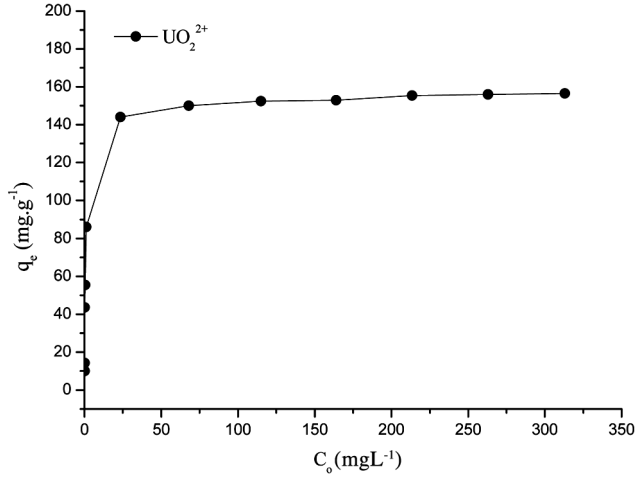


Fig. 8 — Adsorption isotherms of VO^{2+} ions by C-AXO (initial concentration 10-400 mgL^{-1}, C-AXO 1 gL^{-1}, pH 5.0, shaking rate 150 rpm, 30°C)

Table 5 — Parameters for VO^{2+} ions adsorption by C-AXO fibers according to different equilibrium models

Metal ion VO^{2+}	Langmuir isotherm constants		
	K_L(L/g)	q_m(mg/g)	R^2
	23.2×10^{-2}	156.5	0.9997
Metal ion VO^{2+}	Freundlich isotherm constants		
	K_F	n	R^2
	24.882	3.198	0.9127

Table 6 — Repeated adsorption of VO^{2+} ions by C-AXO (initial concentration 100 mgL^{-1}, C-AXO 1 gL^{-1}, *p*H 5.0, contact time 3 h, shaking rate 150 rpm, 30°C)

Cycle Number	Adsorption Capacity (%) VO^{2+}
1	100
2	99.7
3	98.6
4	97.5
5	94.5

as an eluent for desorption experiments in the current study 0.1N HNO_3 solution, the process was repeated for five cycles of adsorption-desorption and the results were presented in Table 6. As can be seen, there was no significant drop in desorption quality, after the fifth cycle, the fibers still maintain over 95% of their original power. The findings obtained indicated that there is no substantial reduction of operation over a period of five cycles.

Conclusion

Removal of VO^{2+} ions was conducted using an adsorbent amidoxime modified cotton fibers (C-AXO). The kinetic studies of adsorption showed that the adsorption mechanism fits in with the pseudo-second - order model. On the other hand, the isothermic adsorption studies have verified that the Langmuir model fits the experimental findings. Different techniques such as SEM, FTIR, and EDX were used to classify the modified chelating C-PTS fibers. In addition, FTIR spectra were performed to understand the mechanism of the studied ions coordination with the active amidoxime moiety deposited on modified cotton chelating fibers.

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