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Nanofibrous Membranes for Low-Concentration Cr^{VI} Adsorption: Kinetic, Thermodynamic and the Influence on ZFL Cells Viability

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There is a great demand to develop different techniques for the continuous removal, immobilization, and remediation of metallic ions from contaminated water. Human contamination by metallic ions could even occur by ingestion of seafood causing carcinogenic and mutagenic activities. In this study, a nanofibrous membrane of poly (vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) produced by electrospinning technique and coated with polyaniline (PAni) was tested for the removal of chromium in low-concentration solutions. The viability of ZFL cells (zebrafish liver cells) was performed to evaluate the water quality enhancement after chromium adsorption. The results indicated that the nanofibrous membrane successfully adsorbed the chromium species in low-concentration (Q_e = 2.44 mg/g, at pH 4.5, room temperature (RT) and 24h) by Freundlich model and followed a pseudo-second-order kinetics model indicating a possible chemisorption in multilayers, at pH 4.5, RT and [Cr^{VI}] = 5.0 mg/L. At pH 2.0 (24h, RT and [Cr^{VI}] = 5.0 mg/L), the membrane adsorbed around 91.64% of Cr^{VI} contaminants. The thermodynamic studies revealed that the process was spontaneous and exothermic. The cells viability demonstrated the efficiency of the membrane tested in the aquatic ecosystem protection; the viability increased 19.2% in 5.0 mg/L Cr^{VI} solution. Thus, the results of this study shows that the nanofibrous membrane can be an alternative to remove low concentration of Cr^{VI} from aqueous solutions.

Keywords: Membrane Technology, Nanofibers, Adsorption, Chromium, Water Decontamination.

1. Introduction

The world progress has brought comfort for people, making the life easy, developing new materials and process, which can be used day by day. With this progress, some disadvantages come together, such as improper waste disposal of solid and liquid materials containing many contaminants[1,2]. Among the contaminants, metallic ions, such as cadmium[3], lead[4], mercury[5] and chromium[6], have been highlighted in several industries like electroplating, batteries, leather tanning, fertilizer and painting industries[7]. In nature, chromium exists in two forms, trivalent and hexavalent chromium. The hexavalent form [Cr^{VI}] is highly toxic and mobile in aqueous solutions, being responsible for environmental contaminations[8].

Contamination by metallic ions can happen through direct ingestion of contaminated food, consumption of contaminated water, inhalation or even contact with the skin[9]. When in contact with the organism, heavy metals tend to alter the activity or damage proteins, enzymes and DNA molecules, promoting changes which generate diseases as well as carcinogenic and mutagenic activities[10,11]. When released into effluents these metals tend to contaminate the aquatic com-munities, not biologically so they may be bioaccumulated in the food chain since they are found at high concentrations in fish living in contaminated water[12].

Several pathways have been seeking to the removal of chrome pollutants from water by chemical precipitation[13], electrochemistry reduction[14], reduction by fungi[15], phytoremediation[16], adsorption by cellulose-based materials[17,18], adsorption by mesoporous materials[19,20] and, adsorptive membrane[7,21,22].

We have recently introduced the design concept of electrospinning PVDF-HFP/PAni membranes for high concentration of chromium removal from aqueous medium[21] as well as the good desorption efficiency of these membranes.

Herein, we optimize the use of nanofibrous membrane of PAni-coated electrospun PVDF-HFP nanofibers in low-concentration hexavalent chromium removal from aqueous solutions simulating an industrial effluent released into the environment. In addition, we evaluated the influence of chromium concentration on ZFL cells viability and, the

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efficiency of electrospun membranes in the purification of water from chromium.

2. Experimental

2.1. Chemical and materials

Potassium dichromate ($K_2Cr_2O_7$, 99,5%) was acquired from Synth Chemicals, 1,5-Dyphenilcarbazide (ACS-grade) was purchased from Fisher Scientific. Zebrafish (*Danio rerio*) liver cell line (ZFL- BCRJ 0256) was obtained from UFRJ-Brazil, it was supplemented with Leibovitz L-15 medium (Gibco®) and RPMI 1640 medium (Gibco®). All chemicals were used without further purification.

The electrospun membranes used to adsorb the pollutant were produced as described in previous work[21]. Briefly, Poly(vinylidinefluoride-co-hexafluoropropylene) (PVDF-HFP) (Kynar Flex 2821-00®, provided by Arkema Brazil Inc.) was dissolved sequentially in a binary mixture of DMF/acetone at a concentration of 20 wt%. In order to produce membranes, the PVDF-HFP homogeneous solution was electrospun at voltage of 26 kV using the flow rate of 1.0 mL/h and with the tip-collector distance of 15 cm.

2.2. Membrane characterization

The morphology of the electrospun nanofibers was analyzed by Scanning Electron Microscopy (SEM), Carl Zeiss model EVO LS15 using the software ImageJ® as auxiliary. A Mitutoyo 547-526S micrometer was used to study the thickness of the membranes. The contact angle of the membranes was measured using the sessile drop method by a contact angle measuring device OCA15EC using deionized water (DataPhysics, Germany). The porosity of the membrane was defined by gravimetric method, using isopropyl alcohol as a wetting fluid to penetrate the pores of the membrane. The point of zero charge (PZC) of membranes was performed by pH measurement (digital pHmeter AKSD®). The membrane was suspended in 15-mL of water in adjusted pH for 24 h at 25 ºC. The pH of each suspension was adjusted to different values ranging from 2 to 11 by adding NaOH and HCl (0.5 and 0.1 M), and the initial and final pH values were recorded[23,24]. To verify the thermal stability of membrane was carried out Thermogravimetric Analysis (TGA), Netzsch model 209 (10 ºC min^{-1} and N_2 atm).

2.3. Adsorption tests

Potassium dichromate solutions with various Cr^{VI} concentrations ranging from 0.05 to 5.0 mg/L were prepared to study the adsorption capacity of the membranes. In this test, a 10 mg rectangular piece of membrane was immersed into 15 mL of chromium solution at a chosen concentration during 24 h. To analyze the pH effect, solutions with concentrations of 5.0 mg/L and pH values ranging from 2 to 6 were prepared. The contact time test was also carried out with a 5.0 mg/L Cr^{VI} solution at a pH value of 4.2, and time interval from 10 min to 48 h. The Cr^{VI} concentration was determined by a UV-Visible spectrophotometer (Shimadzu, model 1800) using 1,5-diphenylcarbazide (DPC) solution as an indicator at 540 nm[25]. Briefly, the 10.0 mL of sample was acidified with 0.2 M H_2SO_4 solution (pH ~ 1.0). Then 0.5 mL of freshly prepared 0.25% (w/v) DPC in acetone was added, mixed and let to stand 5 min for full red-violet color development. A calibration curve was created by plotting the absorbance versus known Cr^{VI} concentrations for this test. The amount of Cr^{VI} ions adsorbed on the membrane (mg/g) was calculated by the following equation:

$$Q = \frac{\left(C_O - C_f\right)V}{M} \tag{1}$$

where Q is the amount of Cr^{VI} adsorbed (mg/g), C_O and C_f are the initial and final Cr^{VI} concentrations (mg/L), respectively, V is the solution volume, and M is the weight of adsorbent membrane used. The adsorption removal rate (R) of Cr^{VI} was also calculated by the equation as follows:

$$R = \frac{\left(C_0 - C_f\right)}{C_0} x100\% \tag{2}$$

The Langmuir (3) and the Freundlich (4) isotherm models were applied for the mathematical description of the adsorption equilibrium of Cr^{VI} ions on the membrane. The non-linearized equations are as follows:

$$q_e = \frac{Q_{max}.k_l.C_e}{1 + k_l.C_e} \tag{3}$$

$$q_e = k_f.C_e^{1/n} \tag{4}$$

where q_e is the adsorption capacity of the membrane at the equilibrium concentration (mg/g), is the equilibrium concentration of metal ion (mg/L), q_m is the maximum adsorption capacity of the membrane (mg/g), b is the Langmuir constant, and k_f is the Freundlich constant[26].

To analyze the nature of the kinetics and the rate of Cr^{VI} adsorption, pseudo first-order and pseudo second-order models were used. The non-linear forms of these two models are given in Equations 5 and 6, respectively.

$$q_t = q_e\left(1 - e^{-k_1.t}\right) \tag{5}$$

$$q_t = \frac{k_2.q_e^2.t}{1 + q_e k_2.t} \tag{6}$$

where q_e and q_t denote the amount of Cr^{VI} adsorbed per mass of gram on the membrane surface at equilibrium and at time t, respectively, k_1 and k_2 are the first and second-order rate constants, respectively[27].

To conclude if the adsorption is spontaneous or not, the thermodynamic aspects are important. The experimental data obtained at different temperatures (288.15, 298.15, 308.15 and 318.15 K) were used to calculate the thermodynamic parameters such as Gibbs free energy change (ΔGº), enthalpy change (ΔHº) and entropy change (ΔSº). The Gibbs free energy change of the sorption reaction is given by the equations:

$$\Delta G^\circ = -RT\,lnk_0 \tag{7}$$

$$K_0 = \frac{C_{Ae}}{C_e} \tag{8}$$

where k_0 is the constant of thermodynamic equilibrium, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is absolute temperature (K), C_{Ae} and C_e are the concentration (mg/L) of chromium on the adsorbent and in solution, respectively[28].

2.4. MTT assay

The cytotoxic potential of the decontaminated water was evaluated through the *in vitro* MTT assay (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyl tetrazolium bromide) in different initial concentrations of chromium. ZFL cells were seeded on 10.0 mL of culture medium (50% of Leibovitz L-15, 40% of RPMI, and 10% of fetal bovine serum, with density of 1.2 x 10^5 cells well plate). The cells were incubated for 24 h with culture (CTR). A positive control using Triton X 1% was also prepared. It was kept in a free-CO_2 incubator at 28 ºC.

Then, the culture medium was removed and dimethyl sulfoxide (DMSO) was added and the absorbance corresponding to each sample was determined at 540 nm. The absorbance obtained for the CTR cells was considered as 100% of cell viability, which was determined by Equation 9[29]:

$$CVK = \frac{AK - AB}{ACTR - AB} x100\% \quad (9)$$

where CVK is the cell viability of the cells exposed to the decontaminated solution, AK is the absorbance found for cells exposed to decontaminated solutions, AB is the absorbance of the culture medium, and $ACTR$ is the absorbance of the control cells.

3. Results and Discussion

3.1. Membrane characterization

Electrospun membranes have a great advantage when compared to other type of membranes due their large surface area and the presence of pores[30]. Figure 1 shows the produced membrane 25 mm diameter and the SEM image of the adsorbent membrane used in the decontamination of the tested solution. The image presents a fibrous membrane. This morphology favors the adsorption process due to the pores among the fibers, which allows the infiltration of the contaminated solution and, consequently, increases the contact area of metal-membrane[31,32]. The complementary characterization is presented in Table 1, where the low contact angle provides a high interaction between the adsorbent and the contaminant solution, which is also enhanced by the high porosity obtained (76.8%).

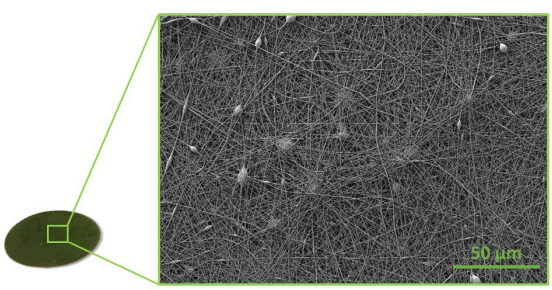

Figure 1. Photograph of the produced nanofibrous membrane 25mm diameter (*left*) and SEM image of adsorbent membranes morphology (*right*).

The pH_{PZC} value of the electrospun nanofibrous membrane was 4.18 (Figure 2). Below the pH_{PZC}, the surface charges on the adsorbent membrane become positively charged favoring the adsorption of chromate and dichromate ions present in the solution due to the amino group on the membrane surface[33,34]. The polyaniline amino groups can be protonated at lower pHs and create adsorption sites that allow chromium species to be captured[21].

The membrane showed a thermal stability property (Figure 3). Both the bulk polymers presented a totally different behavior, the PVDF-HFP has a high thermal stability, with degradation onset at 413 ºC and one main degradation peak at 448 ºC, similar with the previous literature[35,36], which refers to the backbone degradation of PVDF-HFP. Meanwhile, the polyaniline structure has been shown to be less stable with increasing temperature. This polymer presents four thermal events which refers to degradation of doped structure of polyaniline (quinoids and benzenoids units). The adsorbent membrane was also analyzed, showing a similar behavior of PVDF-HFP with only one main peak shifted to 371 ºC and, with the degradation onset at 293 ºC. Thus, the adsorbent membrane has thermal stability to works from room temperature by 100 ºC easily.

3.2. Adsorption results

To investigate the capacity of Cr^{VI} adsorption at low concentrations by the electrospun membrane, batch tests were performed at initial Cr^{VI} concentrations and the percentages of contaminant removed are shown in Figure 4. The removal rate of Cr^{VI} by the membrane decreased as the initial concentration of contaminant increase, this rate decreased from 82.4 to 48.4% when the initial chromium concentration reaches from 0.05 to 5.0 mg/L, respectively.

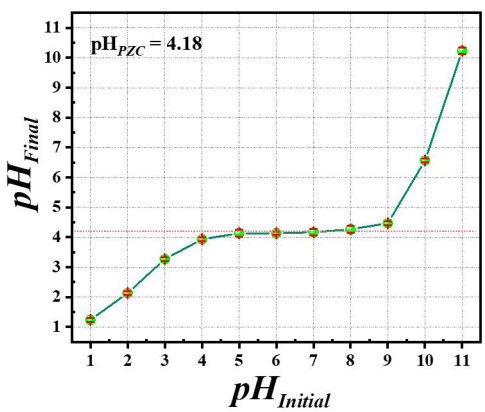

Figure 2. Point of zero charge (pH_{PZC}) of the adsorbent membrane.

Table 1. Characteristics of the adsorbent membrane.

Thickness (µm)	Contact Angle (θ)	Average Fiber Diameter (nm)	Porosity (%)
234.9 ± 3.7	44.2 ± 2.2	140.7 ± 6.3	76.8 ± 0.1

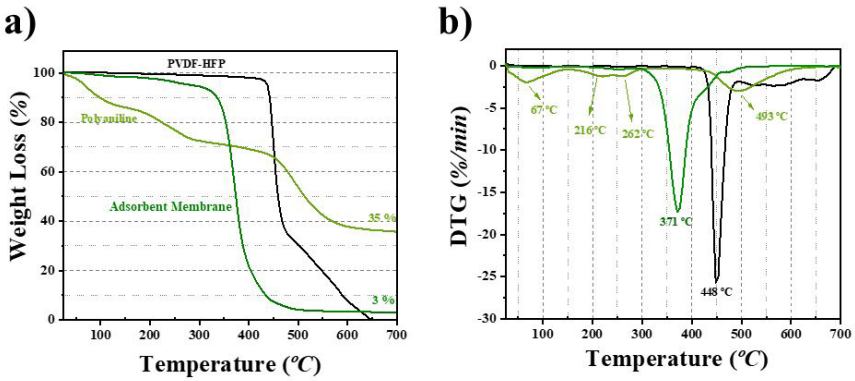

Figure 3. Thermal analysis of bulk PVDF-HFP, Polyaniline and, adsorbent membrane (a) TGA curves and, (b) DTG curves.

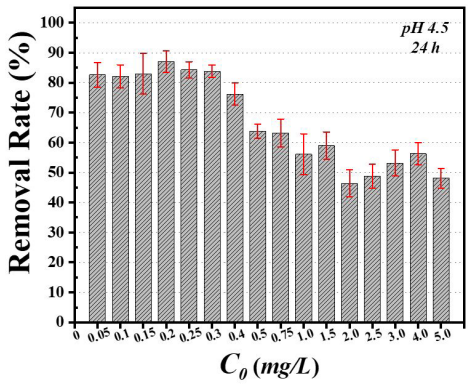

Figure 4. Effect of initial concentration on the percentage of chromium removal (%) at pH 4.5 for 24 h.

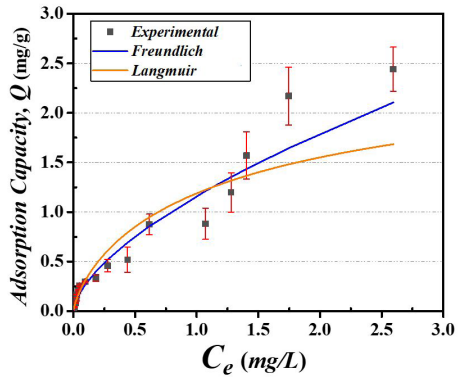

Figure 5. Plot of non-linear Freundlich and Langmuir Isotherm Models for Cr^{VI} adsorption on the nanofibrous membrane at pH 4.5 for 24 h.

According to Wang et al.[37], this phenomenon is assigned to the constant amount of surface-active adsorption sites on the membrane. The contact between the metal and the membrane is feasible when the initial chromium concentration is lower due to the small content of chromium.

In order to estimate the adsorption capacity (Q) of the adsorbent, two isotherm models were applied to the mathematical description for the adsorption equilibrium of Cr^{VI} ions on the membrane (Langmuir and Freundlich Models). The results obtained by non-linearized isotherm models are shown in Table 2. The non-linear Langmuir and Freundlich Models are plotted in Figure 5.

The results demonstrated that Freundlich Isotherm Model can better describe the adsorption process with a higher R^2, which suggests a multilayer adsorption of chromium ions on the membrane, with non-uniform distribution on a heterogeneous surface[38]. It indicates that polyaniline has different charged regions on the surface or does not fill all the pores onto the membrane causing a heterogeneous coverage. These results were similar to some adsorbent materials used for chromium removal, such as nanochitosan/polyvinyl alcohol/carboxymethyl starch ternary blend[39], ionic liquid functionalized cellulose[40] and, chitosan/nylon 6[41].

Cr^{VI} is highly soluble and mobile in aqueous solutions and generates a significant environmental concernment, but it can be reduced to Cr^{III} under some conditions[42]. The use of

Table 2. Constant correlation values for Langmuir and Freundlich adsorption isotherms.

Langmuir Model		*Freundlich Model*	
R^2	0.89402	R^2	0.95499

polyaniline on the membrane surface allows the adsorption of hexavalent chromium, as described on literature, by two possible steps: (*i*) reduction of Cr^{VI} to Cr^{III} species by electron donors into the PAni structure and also the possible chemical bond between nitrogen species and Cr^{VI}, with simultaneous oxidation of -NH- to =N-, and (*ii*) then the interaction between reduced Cr^{III} and polyaniline[21,43,44]. This mechanism can corroborate for a possible chemisorption mechanism that is proven by kinetic tests.

The kinetic results, Figure 6, are in accordance with the non-linear form of the kinetic models. The adsorption followed a pseudo second-order reaction, manifested by the better curve fitting observed by the calculated R^2 using *OriginPro*®, as shown in Table 3. The Cr^{VI} adsorption process by this membrane, at low concentrations of chromium species, is considered as chemisorption process, implying that this process involves valence forces by the sharing or exchange of adsorbent-adsorbate electrons[37,45]. Nevertheless, this result should be interpreted with some caution once our previous paper[21] demonstrated that in higher concentrations, over

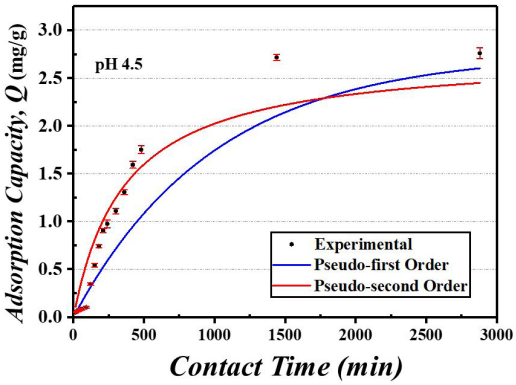

Figure 6. Kinetic curves of Cr^{VI} adsorption by the nanofibrous membrane at pH 4.5 ([Cr^{VI}]=5.0 mg/L).

Table 3. Correlation coefficient values, R^2, obtained by non-linear form of kinetic model.

Pseudo-first order		*Pseudo-second order*	
R^2	0.82371	R^2	0.91287

10 mg/L, the kinetic indicates a physisorption process, but for most of the cases there is a combination of chemisorption and physisorption.

Moreover, the initial concentration, the contact time and the pH effect are important factors to describe the adsorption process on the membrane[46]. As shown in Figure 7, a higher percentage of Cr^{VI} removal occurred at pH values between 2 and 6, where is possible to find hydrogen chromate ($HCrO_4^-$) and dichromate ions ($Cr_2O_7^{2-}$) as predominant species[47,48]. This behavior is related to the pH_{PZC} due to fact that at low pH, the protonation of polyaniline enhances Cr^{VI} adsorption.

The thermodynamic parameters, Gibbs free energy change (ΔGº), enthalpy change (ΔHº) and entropy change (ΔSº) were calculated using the experimental data obtained at different temperatures plotted as $\ln K_0$ *vs.* $1/T$ (Figure 8) and listed in Table 4. The negative values of Gibbs free energy change confirm the feasibility of this process. This result suggests a spontaneous nature of the adsorption at the studied temperatures, and also potentializes the use of this adsorbent in water decontamination[15,49,50]. The negative enthalpy change indicates that the adsorption reaction was exothermic, thus, the interaction of chromium species and the membrane surface has left energy for the system[15]. The decrease in the degree of freedom of the adsorbed chromium was determined by the negative entropy change[15,51], which promoted a more ordered interaction to the process.

3.3. MTT assay

Figures 9 and 10 show the effectiveness of the nanofibrous membrane tested in the viability of *D. rerio* fish cells (ZFL). The results of MTT assay (Figure 9) indicate that when ZFL cells were exposed to 2.0-5.0 mg/L of Cr^{VI} and compared to the negative control they showed a decrease in the cell viability. According to the literature, the exposure to chromium may result in cellular toxicity when *in vitro* and *in vivo* systems are employed. Goodale et al.[52] studied a fish cell line exposed to chromium, and found that the

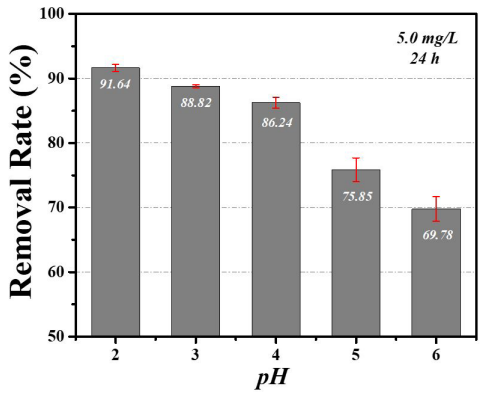

Figure 7. pH effect on the adsorption of Cr^{VI} by the nanofibrous membrane during 24 h ([Cr^{VI}]=5.0 mg/L).

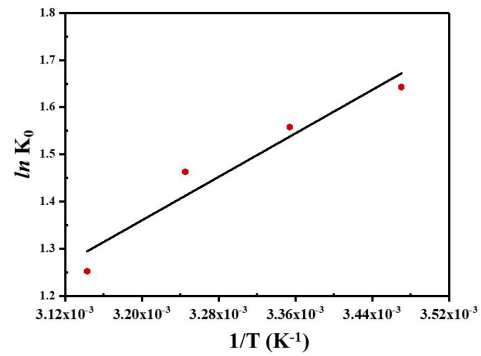

Figure 8. Van`t Hoff plot of Cr^{VI} adsorption on the nanofibrous membrane.

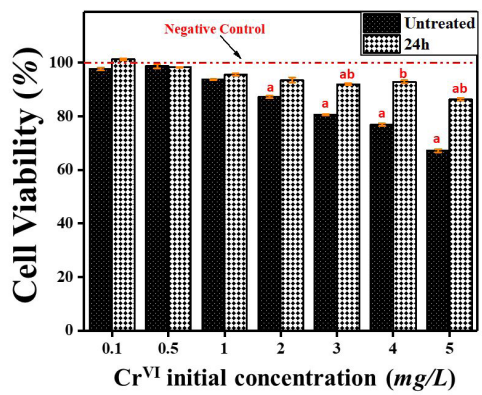

Figure 9. Cell viability (%) of ZFL cells exposed to different concentrations of Cr^{VI} solution, before (Untreated) and after the adsorption test (24h). (*a* and *b* indicate significant difference compared to the negative control and the Untreated solution in the same concentration, respectively).

metal presented a cytotoxicity and genotoxicity activity on these cells. Tan et al.[53] evaluated chromium and cadmium cytotoxicity to six different cell lines of fish by MTT assay. After 24 h of exposure, the viability decreased with the increase of the metal concentration. Also, the cell viability percentage of seven cell lines exposed to different chromium

Table 4. Thermodynamic parameters for adsorption of Cr^{VI} on the nanofibrous membrane.

Temperature (K)	K_0 (m^3 mol^{-1})	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
288.15	5.17	-3.94	-9.57	-19.32
298.15	4.75	-3.86		
308.15	4.32	-3.75		
318.15	3.50	-3.32		

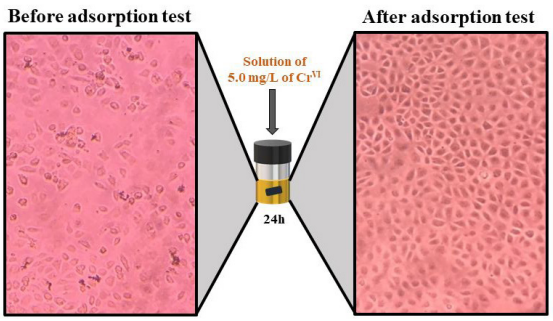

Figure 10. Photograph of ZFL cells exposed to 5.0 mg/L of Cr^{VI} solution before (*left*) and after (*right*) the adsorbent membrane contact.

concentrations and the toxicity of all the studied lines were reported by Taju et al.[54]. In this paper, the decrease in cells viability of ZFL cells exposed to Cr^{VI} proved to be dosage-dependent, and in the highest concentration (5.0 mg/L), a cell mortality around 32% was verified.

With the increase of the contaminant concentration, the cells viability tended to decrease due to the toxic medium in which the ZFL cells were exposed. However, after 24h in contact with the adsorbent membrane, the free chromium species in the solution were present in lower amount. The highest concentration of these species (5.0 mg/L) provided a higher cell viability of 19.2% for ZFL cells (from 67.1 to 86.3%), as observed in Figure 10.

For the cells exposed to Cr^{VI} 5.0 mg/L, rounded cells, slower cell growth, cell lysis and destroyed cell layer fragments were observed. For the cells exposed to the same concentration (5.0 mg/L) after the adsorption process, the identified morphological changes were milder, as it has caused less damage to the cells.

Therefore, the results of MTT assay indicate that the membrane decreased the chromium concentration in the solution and, consequently, increased the cell viability of the fish cell line tested. As a result, the membrane can be applied to decontamination systems and enable the aquatic life to survive in ecosystems after the adsorption treatment.

4. Conclusion

In the present study, the behavior of low concentration Cr^{VI} adsorption on nanofibrous membrane of coated-polyaniline electrospun PVDF-HFP was investigated. The membrane presented high adsorption capacity simulating an industrial effluent released into the environment. The percentage of removal was over 80% for Cr^{VI} at 0.3 mg/L. In addition, the kinetic and thermodynamic parameters for this process were studied. The time effect showed that the adsorption occurred in pseudo-second order indicating a chemisorption process. The thermodynamic studies demonstrated that the process was spontaneous and exothermic. Lastly, the cells viability was tested after the decontamination process using the membrane as adsorbent and, the results showed an increase of 19.2% of ZFL cells viability. Therefore, this material can be applied to decontamination systems in order to protect the aquatic ecosystems from Cr^{VI} contaminated effluents.

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