Polypyrrole doped with 4-amino-3-hydroxynaphthalene sulfonic acid for an efficient removal of hexavalent chromium

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Abstract

The presence of heavy metals in the aquatic environment is a major global health problem as heavy metals are toxic and lethal to humans and aquatic life. Chromium is one of the most toxic heavy metals because it is highly carcinogenic. The most common oxidation states are trivalent III and hexavalent VI. However Cr^{6+} is 1000 times more toxic than Cr^{3+}. Hence the need to find effective techniques for the removal of these pollutants harmful to human and his environment. In this work we chemically synthesized a polypyrrole doped with 4-amino-3-hydroxy-1-naphthalenesulphonic acid (PPy-AHNSA). This polymer powder was characterized by FTIR which confirms the insertion of AHNSA into the polypyrrole chain. Then this polymer served as an adsorbent for the removal hexavalent chromium. This elimination requires the optimization of parameters such as the mass of the adsorbent and the pH of the metallic solution. Thus a mass of polymer of 80 mg and a pH = 2 are the optimal condition. The maximum adsorption capacity of the PPy-AHNSA film for chromium was 242 mg g^{-1}. A 96% chromium removal from pure aqueous solution was reached after about 6 h of the immersion. The kinetic of this chromium removal were found to follow second-order curves. Removal of the metal in the solution by forming a complex with the polymer is confirmed by the changes in FTIR spectra

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1. Introduction

Industrial development has caused the release of large quantities of metals into the waters. These heavy metals such as lead, copper chromium and cadmium are a threat to the environment and health [1]. They are highly toxic and recalcitrant even at very low concentrations, and they can pollute drinking water resources [2, 3]. Many studies show that the presence of these metals in our natural waters [4-8]. Among these metals chromium is one of the most toxic because it is carcinogenic and can also cause skin and mucous membrane damage with respiratory [9,10]. In addition, water contaminated with chromium is also dangerous to animals [11]. The limit concentration of chromium not to be reached in drinking water of 0.05 mg/L and 0.1 mg/L in surface water and groundwater to be declared polluted [2, 3].

To comply with standards it is necessary for industries to treat their wastewater before dumping it. Several treatment techniques have been used such as adsorption, biosorption, laco-precipitation, electrodialysis, chemical precipitation, electrochemical precipitation, membrane filtration, solvent extraction, reverse osmosis, and reverse osmosis. ion exchange [12-16]. These different techniques have the disadvantage of being difficult to achieve, very expensive, inefficient and often generate toxic waste which makes it necessary to design a chemical sensor to remove these metals in waters.

In recent years the research is focused on the use of conductive organic polymers for the removal of heavy metals in wastewater. Among these polymers, polypyrroles and polyanilines are the most studied because of their stability, their high electrical conductivity and the ease of their preparation [17]. For better use of these polymers in the field of water treatment containing heavy metals are added other chemical compounds capable of trapping these metal ions.

. In this respect, Bhaumik et al [18] have successfully synthesized, for the first time using the simultaneous in situ chemical polymerization technique, nanoparticles based on

PPy-PANI which they have effectively applied as adsorbent in the elimination of Cr (VI) in aqueous solution.

Ballav et al used a glycine-doped polypyrrole film [19] to remove hexavalent chromium. With this device, these authors obtained a percentage of elimination close to 100%, at an optimal pH of the analytical solutions of the order of 2.

Recently Kera et al [20] have successfully incorporated 2,5-diaminobenzene sulfonic acid (ADABS) in the pattern of a polypyrrole for use in the removal of chromium. Incorporation of ADABS in PPy homopolymer was confirmed by ATR-FTIR, XPS, EDX and DRX analyzes The resulting PPy / ADABS composite has a high adsorption capacity of 303 mg / g (25 ° C) for Cr (VI) in aqueous solution at a pH of about 2.

Tian et al [21], who chemically synthesized a polypyrrole film doped with sodium para-toluenesulfonate (PTS), which they used for the electrochemical reduction of hexavalent chromium.

Thus in this work a polypyrrole film, doped with 4-amino-3-hydroxynaphthalene-1-sulfonic acid were chemically synthesized for the adsorption of chromium (VI). The kinetics adsorption is followed by Uv-visible spectroscopies We have previously optimized the polymer mass and studied the effect of the pH of the solution on the adsorption. We also monitored the influence of adsorption on the FTIR properties of the polymer.

2. Experimental

2.1. Chemicals

Pyrrole (Py - 99%), 4-amino-3-hydroxynaphthalene-1-sulfonic acid (AHNSA), sodium hydroxide (NaOH), sulphuric acid (H_2SO_4), Potassium peroxodisulfate (KPS) and potassium dichromate ($K_2Cr_2O_7$) were obtained from Sigma-Aldrich, and used as received.
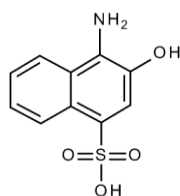
Scheme 1 - Chemical structure of 4-amino-3-hydroxynaphthalene-1-sulfonic acid (AHNSA)

2.2. Synthesis and IRTF characterization of PPy-AHNSA

3.2 g of 4-amino-3-hydroxynaphthalenesulfonic acid were dissolved in 90 ml of distilled water. Since the acid is not soluble in water, we added NaOH until it is completely soluble and the resulting pH is 5.1. To this solution we add pyrrole and let it stir for 30 minutes. Finally, we gradually add 10.8 g of potassium peroxodisulfate (KPS) dissolved in 60 ml of distilled water and stir the mixture for 12 hours without stirring. We put acetone to stop the reaction. We obtain a black powder which we wash with distilled water of acetone until the filtrate is colorless. The filtered and washed powder was dried for 6 h at 60 ° C in an oven.
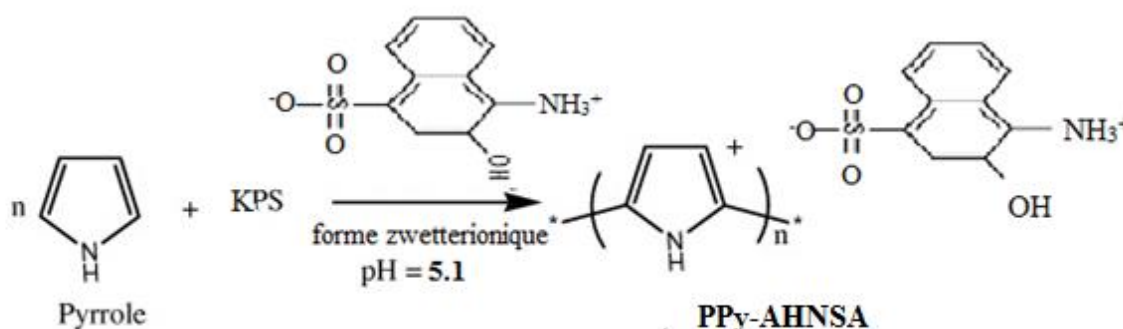
Scheme 2: la polymérisation du pyrrole en présence de AHNSA

To study the structure of our powder we performed Fourier Transformed Infrared Spectra (FT-IR).

The IR spectra of the powder show two bands towards 1520 cm^{-1}, 1420 cm^{-1}, 1080 cm^{-1} et 910 cm^{-1} characteristics of the C = C, C-N, C-H and C-H bonds of the pyrrole. These bands show that we do have polypyrrole [18, 19].

Other bands appearing around 930 cm^{-1} and 813 cm^{-1}, due to the CH bonds of the asymmetric trisubstituted aromatic ring (δCsp2-H) and two bands around 1600 cm^{-1},and 1535 cm^{-1}, that we attributed to the movements of link elongations C = Car of the naphthalene nucleus. Moreover this spectrum has localized bands towards 1035 and 1150 attributed to the vibrations of the links S-O and bands towards 1312 cm^{-1} and 1204 cm^{-1}corresponding to the vibrations of elongation of the group C-N. We also note the presence of bands at 3200 cm^{-1} and 3400 cm^{-1} respectively corresponding to O-H and N-H vibrations. All of these bands show that the amphoteric acid salt 4-amino-3-hydroxynaphthalene-1-sulfonic acid is well inserted into the polymer chain [22-25].
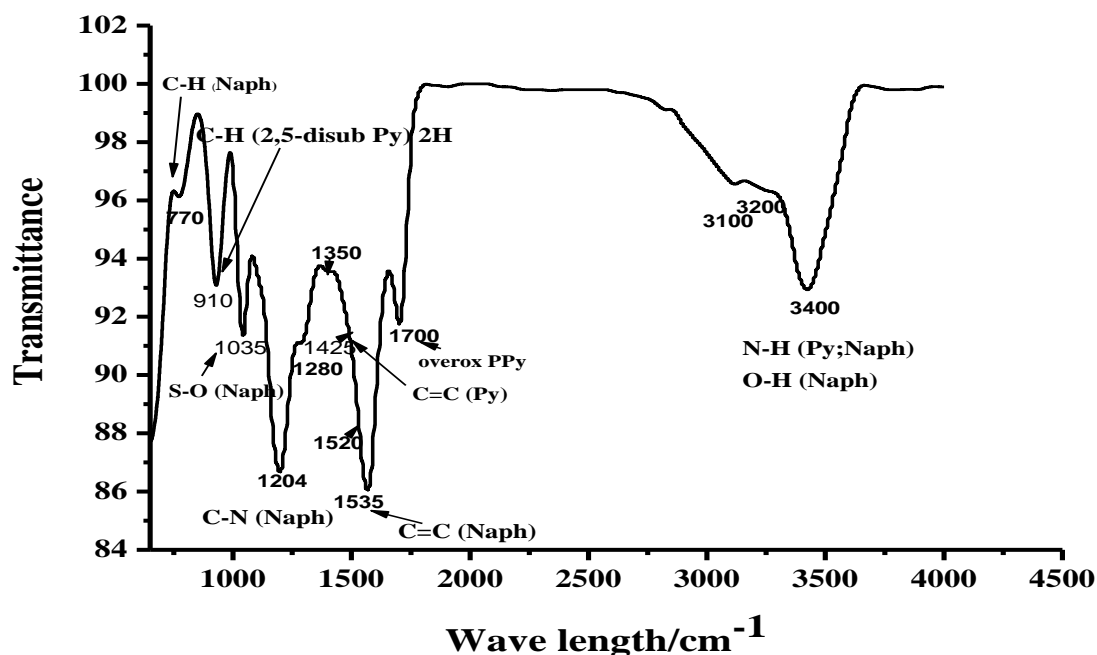
Fig. 1 : FTIR spectra of a powder of polypypyrrole doped with AHNSA

2.3. Spectral measurements

Fourier Transform-Infra Red (FT-IR) absorption spectra were obtained on a Magna-IR 860 FT-IR spectrometer (Nicolet Instrument Corp., Madison, WI), at a 2 cm^{-1} spectral resolution. FT-IR spectra of the polymer powder (PPy-AHNSA) befor and after chromium removal, were recorded in pressed KBr pellets, using a standard DTGS detector, by collecting 50 scans. All spectra were baseline corrected, using OMNIC internal software, and were unsmoothed.

The uv-visible spectra were carried with a spectrophotometer Perkin Elmer type UV-Vis Spectrometer Lambda 2.

2.4. Procedures for the determination of chromium removal

A few amount of PPy-AHNSA powder was immersed in an aqueous solution of 50 mg L^{-1} $K_2Cr_2O_7$, and the evolution of the chromium (VI) 350-nm UV-VIS absorption bands was followed in function of the polymer impregnation time, medium pH and polymer mass.

The effect of chromic solution pH changes on the polymer adsorption capacity was examined between pH values of 1.0 and 12.0 by measuring the Cr (VI) solution UV-VIS absorbance. The solution pH values were adjusted by adding small amounts of H_2SO_4 or HNO_3. The final metal concentrations were determined by applying the Beer-Lambert law.

The Cr (VI) removal efficiency (% R) of the polymer was estimated as a function of Cr (VI) concentration using equation (1):

$$\% R = [(C_0 - C_t) / C_0] \times 100 \qquad (1)$$

where C_0 and C_t are, respectively, the concentrations (mg/L) of Cr (VI) at times t=0 and t.

The adsorption capacity of the polymer at the time t (q_t), was calculated by means of equation (2):

$$q_t = [(C_0 - C_t)/m] \times V \qquad (2)$$

where C_0 and C_t are, respectively, the Cr (VI) concentrations (mg/L) at times t=0 and t; m = polymer mass (g) ; V = potassium dichromate solution volume (L).

3. Résultats et discussions

The polymer thus synthesized and characterized by FTIR will be used for the removal of hexavalent chromium in solution. The process of elimination requires the optimization of several parameters such as the mass of the absorbent and the pH of the chromic solution

3.1.Optimisation de la masse du polymère

We dissolved 50 mg of potassium dichromate in 1 liter of water then we added H_2SO_4 to have a pH = 2. In 400 mL volume samples of this solution, we dive different plates covered with polymer films of variable mass (m1 = 20 mg, m2 = 40 mg m3 = 80 mg, m4 = 120 mg) and we will follow the evolution of the absorbance of chromium in solution in depending on the impregnation time (Figure 2). The analysis of this Figure 2 shows a decrease in absorbance as a function of the contact time with the impregnated polymer. In all cases, it is found that the longer the impregnation time increases, the absorbance decreases, thus showing a capacity for progressive elimination of the chromium ions present in the solution by our impregnated polymer. This elimination by simple contact of the metal ion with the polymer could be explained by the existence of ion chelating sites within the polymeric unit. In

addition, it is also found that the greater the mass of impregnated polymer, the greater the decrease in the absorbance of chromium in the solution is accentuated. To better study this mass effect, we will follow the evolution of the percentage of chromium removed as a function of the mass of impregnated polymer (Figure 3).
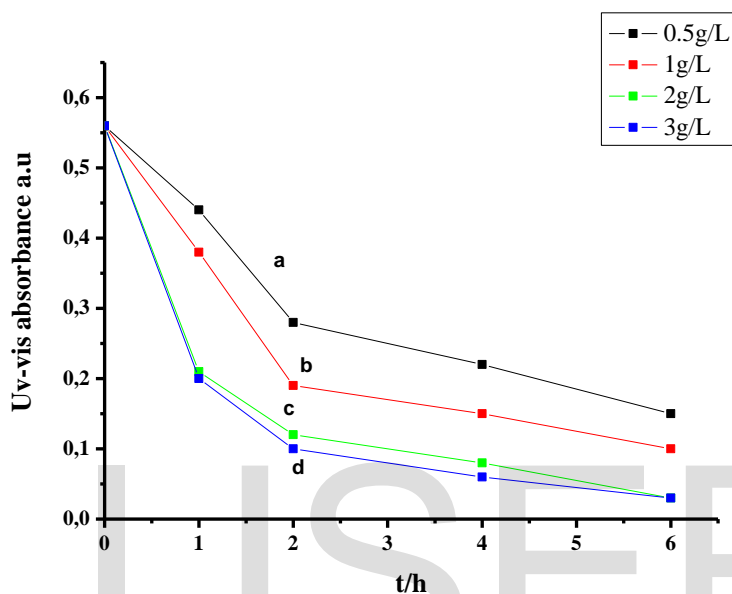

Fig. 2 : Evolution of the Cr(VI) UV-visible absorbance (at 350 nm) with time, according to the PPy-AHNSA polymer mass (m). Curves: a) m1 = 20 mg, b) m2 = 40 mg, c) m3 = 80 mg, and d) m4 = 120 mg
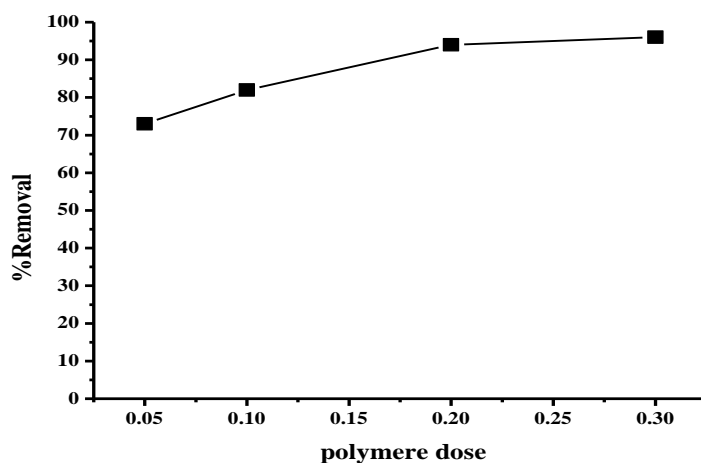

Fig. 3: Evolution of the percentage eliminated according to the different dose of polymer

This percentage of chromium absorbed, calculated from the following formula: % R = $[(C_0-C_t) / C_0]$ x100, shows that the greater the mass of impregnated polymer, the better the elimination is better. This is supported by a percentage change eliminated ranging from 55 to 96% by varying the mass from m1 to m4. Moreover, with a mass of m3 after 6 hours, a percentage of elimination of chromium of the order of 96% is obtained. This higher value obtained with masses m3 and m4 remains constant even beyond 6 hours, which is not the case for the other values obtained with masses m1 and m2. This result also allowed us to consider that the mass m3 of 80 mg of polymer corresponds to a dose of 0.2 g / L as the optimum mass for a more effective removal of chromium under these conditions. In what follows we will work with this already optimized mass.

3.2.Effet du pH

The pH of the solution is one of the most important parameters in metal adsorption processes because the dominant form of the metal is strongly dependent on the pH of the solution. We will therefore study the influence of pH on the ability of the polymer to absorb chromium. To do this, we used the same study as above, only with the optimized mass m4 by varying the pH of the solution between 0 and 12 after a 24-hour impregnation time. We followed the evolution of the percentage. chromium adsorbed as a function of the pH of the dichromate solution (Figure 4). The analysis of the results shows a decrease in the percentage of chromium adsorbed as a function of the increase in the pH value. Indeed, there is a gradual and very significant decrease in the percentage of chromium adsorbed, ranging from 96 to 20%, when the pH of the dichromate solution is increased from 1 to 12. In general, we find that the adsorption is better in acidic medium and weak in basic medium. This good adsorption in an acid medium is explained by the fact that chromium, in its $HCrO_4^-$ form, is better attracted to NH_3^+ than the AHNSA formed following a strong protonation in an acid medium. On the other hand, in the pH range of 1 to 9, very satisfactory values of percentage of chromium removed, greater than 70%, are recorded. These results make it possible to point out that the use of 4-amino-3-hydroxynaphthalene-1-sulphonic acid offers a greater pH range of 1 to 9 for the removal of hexavalent chromium compared to glycine which has a domain effective at pH ranging from 1 to 6 [19]. As the pH values of 1 and 2 have the same percentages of reductions, we opted to work for the optimized value of pH = 2.

Thus, after these optimization works, the optimum conditions of pH = 2 and a polymer mass of 80 mg for the treatment of water containing chromium (VI).
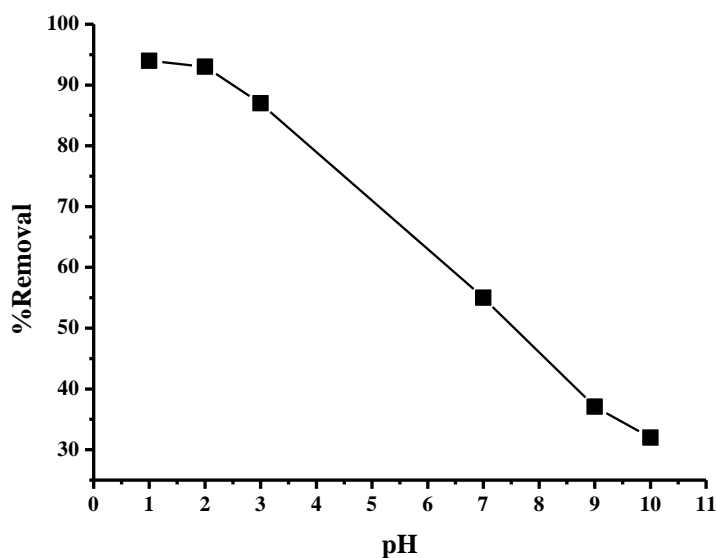
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Fig. 4 : Effect of pH on the percentage of adsorption of Cr(VI) by the PPy-AHNSA polymer, after 6 h

Thus, after these optimization works, the optimum conditions of pH = 2 and a polymer mass of 80 mg for the treatment of water containing chromium (VI).

3.3.Study of the elimination of chromium (VI) by the polymer

We introduce 80 mg of polymer in 400 ml of potassium dichromate at pH = 2 and then we follow the evolution of the Uv-visible absorbance as a function of time. There is a decrease in the absorbance that shows the polymer eliminates chromium.

Under these optimized experimental conditions, a gradual decrease of the chromium absorption bands at 350 nm is observed, accompanied by a progressive discoloration of the solution with the treatment time, thus indicating that the concentration of chromium in the solution decreases significantly. depending on the contact time with the polymer (Figure 5 and 6). This progressive decrease in the concentration of chromium in solution could be explained by the formation of a complex between the PPy-AHNSA and the chromic ion. To better understand the kinetics of chromium removal by PPy-AHNSA, we have shown in Figure 7, the variation of the absorbance of chromium in solution as a function of the contact time with the polymer. The decay kinetics of the absorption bands corresponding to the electronic transitions of chromium at 350 nm follows an exponential law as a function of time which consolidates the idea of formation of an insoluble complex between the polymer and the metal. . A more detailed study of the kinetics of chromium adsorption on the polymer-

covered anode leads to second-order kinetics because the $1/C_t - 1/C_0$ curve as a function of time is strictly linear with an equation of the form. y= 7.2 t and a correlation coefficient of the order of $r^2 = 0.993$ (Figure 8). Therefore, we obtained a rate constant $k_2 = 7.2 \pm 0.4$ L mol^{-1} s^{-1}.

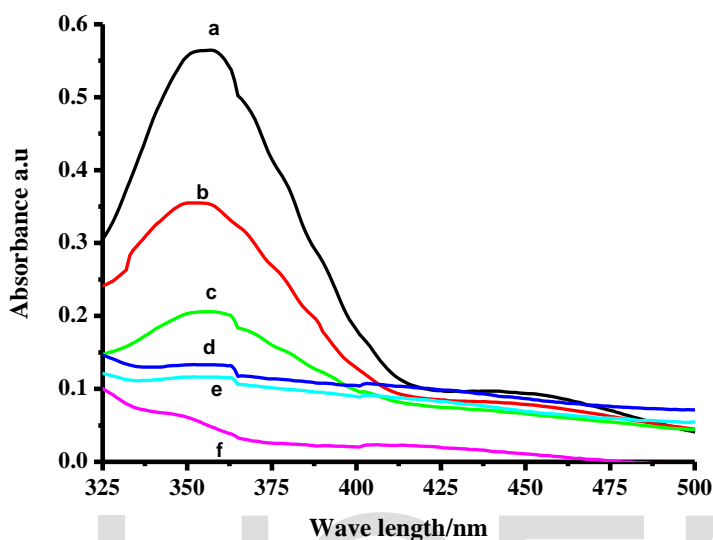**Fig. 5**: Evolution of the UV-VIS absorption spectra of a chromium solution (50 mg L^{-1} $K_2Cr_2O_7$) as a function of AHNSA-poly(Py) polymer impregnation time
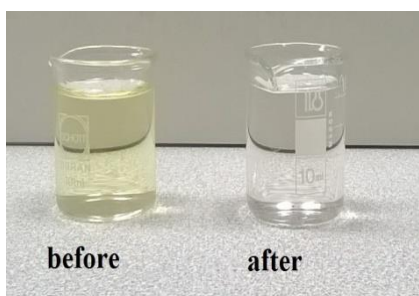

Fig. 6: Image of the potassium dichromate solution 50mg/L before and after contact with the polymer PPy-AHNSA
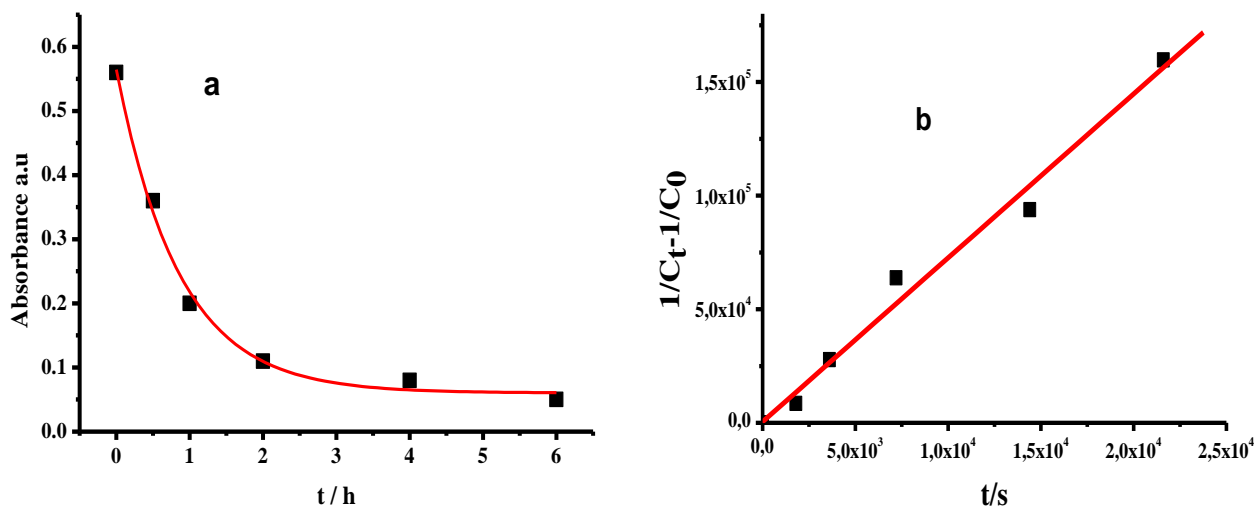
Fig. 7 : Study of the kinetic of adsorption of Cr(VI) by PPy-AHNSA, using a polymer-covered anode (m (polymer) = 80 mg) in optimized experimental conditions. **a** Decay curve of the Cr(VI) 350-nm absorption band vs. time. **b** Determination of the apparent second-order rate constant

The decrease in the absorbance of the 350 nm bands assigned to the VI chromiums shows that PPy-AHNSA is capable of adsorbing hexavalent chromium.

3.4. Amount of adsobed chromium

Using equation (2): $q_t = [(C_0-C_t) / m] \times V$, we also calculated the adsorption capacity of PPy-AHNSA (in mg / g), which corresponds to the amount of chromium adsorbed per gram of polymer [10]. Thus on the basis of our absorption spectra obtained in **Figure 5**, we calculated the amounts of chromium adsorbed as a function of the immersion time of the polymer in the optimized chromic solution that we have shown in **Figure 8**.
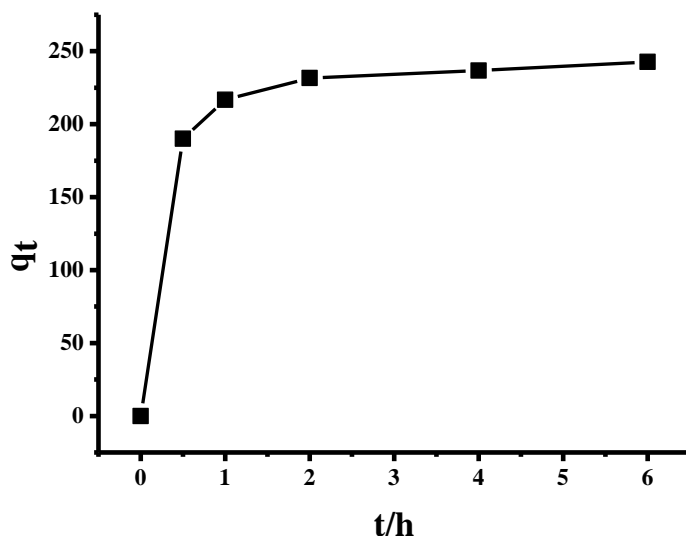
Fig. 8: Evolution of the chromium quantity (qt), adsorbed by the PPy-AHNSA polymer (m = 80 mg), as function of the impregnation time in a 400-mL pH 2 potassium dichromate aqueous solution

The exploitation of this Figure shows that the amount of chromium adsorbed per gram of polymer increases significantly with the immersion time of the polymer, then reaches a plateau beyond 10 hours, this small variation in the quantity absorbed reaches a limit value of 224. mg per g from 48 hours. Beyond these two days, the amount of chromium absorbed per gram of polymer remains a constant, thus noting that this value is the maximum limit obtained by our PPy-AHNSA-based polymer. Moreover, our qt values obtained are higher than to those found by Bhaumik et al [18] with nanofibers of polypyrrole-polyaniline (227 mg / g at 25 ° C) and those of Ballav et al. [19] (217.4 mg / g at 25 ° C), with polypyrrole doped with glycine. However, they are lower than those obtained by Kera et al [20] (303 mg / g (25 ° C)).

We compared the adsorption capacity of our PPy-AHNSA with others obtained with polypyrrole composites in order to highlight the performance of our adsorbent. These results are listed in the table below. From this table it emerges that only Kera et al [20] have obtained a greater adsorption capacity than ours with polypyrrole/ ADABS composite. That shows that the PPy-AHNSA is very efficient for the removal of hexavalent chromium.

Table : Comparison of adsorption capacity of the PPy-AHNSA with other adsorbents for Cr(VI) removal at 25 $\circ$ C.

Adsorbents	q_m (mg/g)	Optimum pH	References
PPy-AHNSA electrosynthesized	224	2	26
Ppy-glycine	217	2	19
Polypyrrole/wood sawdust	3.4	5	27
Polypyrrole-polyaniline nanofibers	227	2	18
polypyrrole/ ADABS composite	303	2	20
Polypyrrole/Fe$_3$O$_4$ magnetic nanocomposite	169.4	2	28
PPy-AHNSA chemically synthesized	242	2	This work

3.5. Influence of the absorption of the chromium on the FT-IR spectrum of the polymer

We compared the IRTF absorption spectra of the AHNSA-poly (Py) polymer before and after immersion in a solution of potassium dichromate at pH 2 (concentration = 50 mg / L) for 48 hours (Figure 9). We observed several important changes in the post-immersion polymer spectra, such as the appearance of two relatively strong bands at 786 and 920 cm-1, respectively corresponding to the deformation vibrations γCr-O and γCr = O [10; 21]. Several bands were also displaced after immersion: for example, the 1,555 cm-1 band was moved to 1,565 cm-1 (due to aromatic δ C-H deformation vibrations), and we also note the disappearance of the band at 3400 which shows that the OH group of AHNSA is involved in the chelation of chromium. These spectral variations can be attributed to the interactions between chromium and the polymer, which confirms the binding of chromium to polypyrrole-AHNSA.
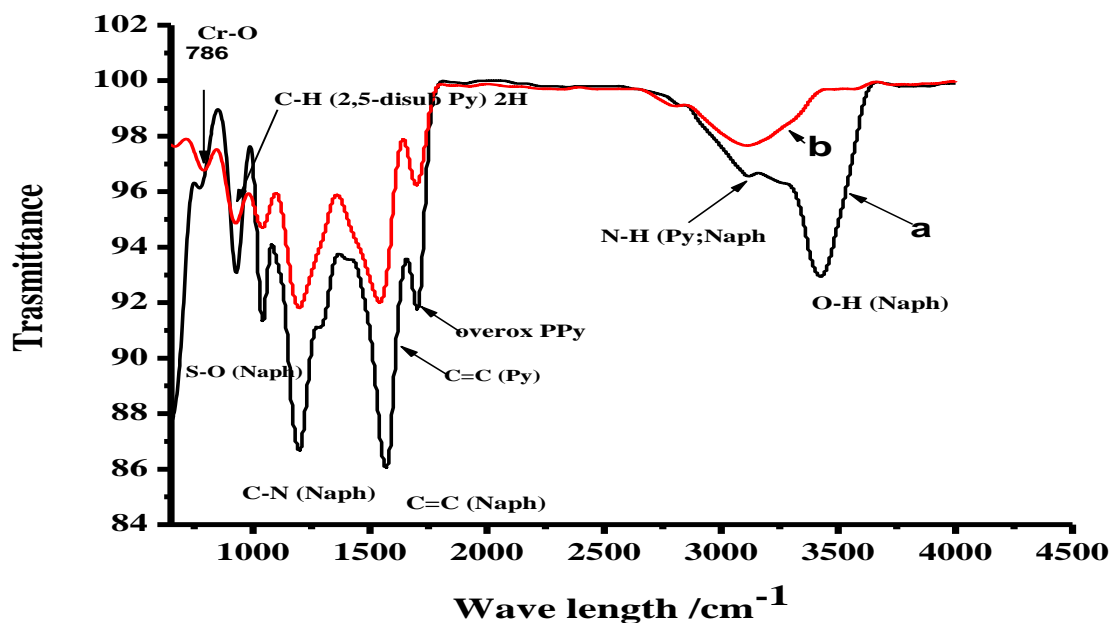
Fig. 9 : FT-IR spectra of the PPy-AHNSA polymer **a** before immersion and **b** after immersion in a pH 2 potassium dichromate solution (50 mg L−1) during 6 h

4. Conclusion

In this work we have synthesized for the first time a polypyrrole doped with 4-amino-3-hydroxynaphthalene-1-sulfonic acid. The polymer powder obtained was characterized by FTIR which polymerization of pyrrole the insertion of ANNSA into the polymer chain.

This PPy-AHNSA was immersed in a $K_2Cr_2O_7$ solution of 50 mg/L, we obtained a considerable drop in the absorbance of Chrome VI. After a work of optimization of the polymer mass (m = 80 mg) and the pH (pH = 2), a chromium removal percentage of the order of 96% and a quantity of 242 mg of chromium absorbed by gram of polymer were obtained. These high values of R and qt, judged to be better than those already described in the literature, made it possible to say that this polymer can be used effectively in the treatment of waters containing the chromic ions.

We also compared the FTIR spectra of the polymer before and after immersion in the metal solutions. We found new bands characteristic of Cr-O, Cr = O and the displacement of some bands of Ppy-AHNSA in the spectra obtained after immersion, confirmed the fixation of chromium, lead or cadmium on the polymer.

Acknowledgements

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