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Chemical and electrochemical Chromium (VI) recovery process by conducting composite, olive pomace/PANI-HCL

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ABSTRACT/RESUME

Abstract: *The aim of this study is the use of a new conducting composite material which was prepared from an agricultural by-product "olive pomace (OP)" and a polymer "polyaniline doped with a chlorhydric acid (PANI-HCl) and used for the fabrication of electrode, which was then used as substrate for the recovery of chromium hexavalent to an aqueous solution through chemical adsorption and electrosorption tests. We used the spectral analysis techniques such as FT-IR to characterize the material as well as scanning electron microscopy (SEM) to show that the PANI was successfully attached to OP. We carried out adsorption in batch system and electrosorption tests in acid medium within an electrochemical cell at a potential of +800 mV imposed and we compared the recovery with chemical adsorption at open circuit under the same conditions.*
For batch adsorption tests of Cr (VI) on olive pomace, PANI-HCl and the composites material prepared; the effect of several parameters such as the contact time, and the pH of the solution were studied.
For the électrosorption tests, the results demonstrated that the electrosorption capacity of Cr (VI) is superior to the adsorption, which is due to the excellent electrical conductivity and mechanical properties of OP/PANI composite electrode.

I. Introduction

The increasing global interest in the preservation of the environment by the authorities requires the industrialists to find the technical means to valorize the solid waste resulting from the various activities of human transformation. In the case of lignocellulosic residues (fruit cores, almond hulls, and olive pomace etc.), manufacturers have found applications in the production of activated carbon. [1, 2].
To optimize the high cost of producing activated carbon, researchers are working on the recovery of this waste in the native state. This waste has a good adsorption property, even in the native state, because of functional groups that exist on the surface [3, 4].However, to improve their properties; several researchers have thought to make a composite based on these materials [5].
Among the areas of application of composites, electrochemical techniques that have many advantages and fit perfectly into the framework of sustainable development technologies.
Among these techniques, the adsorption supported by the application of potential difference called electrosorption, which can be considered one of the best methods of recovery of Cr (VI) knowing that the methods implemented today to treat the discharges polluted by chromium (VI) generally aims to recover this metal, in order to reuse it and thus reduce its eco-toxicological impact.
Electrosorption is an important technology for the removal of heavy metal ions from wastewater, [6, 7] during which an electric field is applied on solid adsorbents to enhance their adsorption capacity and

facilitate their subsequent regeneration by electro-desorption. [8] Diverse materials as the cellulose, the rubber, the plastic and the textile were used as good supports for the electrosorption because of their distinguished physical properties. Our choice is concerned a new material which was not still applied in this domain and which is the olive pomace. Olive pomace is one of the most abundant materials in nature; it possess several advantages such as low cost, low density, non-toxicity, renewable nature, biodegradability.[9] It was been reported to be a suitable adsorbent material. [10] However, to achieve electrosorption with natural material, we must make it conductive. To this end, the conductive polymer is used.

Among various conducting polymers, polyaniline (PANI) is considered as promising candidate for practical applications owing to its high environmental stability and easy control of electrical properties. [11, 12] The main objective of this work is to fabricate a composite based on olive pomace, to make it conductive and to study its applicability in the electro-enhanced removal of chromium hexavalent from aqueous solution.

II. Materials and methods

II.1. Synthesis procedure of Olive Pomace-PANi composite

The production process of the olive oil, are washed at first several times in the tap water then in the distilled water. They are then exhausted by the hexane to eliminate the residual oil, washed with some hot distilled water, dried and Crushed in a diameter between 500 µ and 1000 µ [13, 14, 15].

Aniline monomer and Ammonium persulphate (APS) was purchased from Biochem Chemopharma. Hydrochloric acid (HCl), was obtained from Chem-lab.

For the preparation of the olive pomace–PANI composite, 2 g olive pomace was added to 2.0 mol/L HCl solution dissolving aniline monomer (10:1 by molar ratio) and stirred for 50 mn. After, 0.025 mol.L^{-1} APS aqueous solution was added dropwise to oxidatively polymerize aniline. [9] The mixture was stirred for 20 h at ice temperature. [10] The reaction product was filtred and washed with 0.2 mol.L^{-1} Hydrochloric acid solution, [16] and then with absolute ethanol till the filtrate became colorless. The composites were dried at 40 °C in an air oven for 5 h.

II.2. Material characterization

A study of the structure of the composites was carried out by infrared spectroscopy with an EQU INOX-SS FT-IR spectrometer (Bruker lazer). Their surface morphology was examined by SEM on Philips ESEEM XL 30 SEM, JEOL, Inc., JSM-6500F) . Their conductivity was measured by cyclic voltammetry (CV) by the four-point-electrode method. The samples were compressed to13 mm diameter and 0.08–0.2 mm thickness pellets for the measurements.

II.3. Cr (VI) adsorption

A solution of Cr (VI) ($C_{Cr\,(VI)}$ = 20 mg L^{-1} , pH = 5,45) was prepared for the adsorption investigation. Five olive pomace–PANi composites with different ratios between the aniline and the olive pomace were prepared. The reaction solution was filtered after adsorption to determine the remaining Cr (VI) by colorimetry. The best of the Cr (VI) adsorbing composites was chosen for the electrosorption tests.

II.4. Cr (VI) electrosorption

An experiment on adsorption/electrosorption kinetics were carried out starting with the same initial chromium salt concentration of about 20 mg L^{-1} of chromium (VI) with an electrode area of 13.2 cm^2 at room temperature and recorded the adsorption at open circuit (OC) and electrosorption under 800 mV polarization. The exact speciation of the chromium ions depends upon pH, temperature, concentration and the presence of other ions. However according to different authors, [17,18], the Cr (VI) is in the form of $HCrO_4^-$, CrO_4^{2-}, or $Cr_2O_7^{2-}$ .The Cr (VI) forms would be drawn to the anode. Since these ions are already in a high oxidation state, complexation at the anode, without anodic oxidation is expected. To this effect we apply a positive polarization (anodic potential) to promote electrosorption chromium Cr (VI), in order to efficiently investigate on the relation between the developed conductor material (Olive pomace-PANI composite) and the effect of the electrochemical polarization on the adsorption rate (which is necessary for the accurate design and modelling of adsorption processes).

III. 3. Results and discussion

III.3.1. Material characterization

III.3.1.1 FT-IR analysis

Figure 1 shows the FTIR spectra of olive pomace, PANI and OP/ PANI composites where some vibration bands are revealed. According to the results found in previous works our results of olive pomace confirm the existence of superficial functions including oxygen. The 1031cm^{-1} band indicates the presence of the stretching bonds C-OH primary alcohol and C-N. The 1234cm^{-1} band corresponds to the vibrations of the OH and NO2 function, and the 1730cm^{-1} band indicates the presence of the C = O lactones groupment [19] also The band 3330cm^{-1} corresponds to the vibrations of the OH function [19, 20]. The characteristic bands of the polyaniline are observed at 470cm^{-1}, 594cm^{-1}, and 770cm^{-1} indicating the presence of the N-H and C-H stretching bonds, which makes it possible to identify the type of substituted benzene. The 1079cm^{-1} band indicates the elongation bonds primary alcohol C-OH and C-N. The 1278cm^{-1} band corresponds to off-plane -NH flexion and elongation vibrations of the phenolic C-O bond and C-N relative to the benzoide cycle [21], and the 1457cm^{-1} band is attributed to the elongation vibration of the aromatic C-C bond of the benzoic rings. There is also a 1557cm^{-1} band, which is attributed to the elongation vibration of the conjugated aromatic C = C bond relative to the quinoid cycle [22, 23]. The 1730cm^{-1} band is characteristic of the conductive form of the PANI while the 3269cm^{-1} and 3448cm^{-1} bands are characteristic of N-H and O-H elongation bonds.

The characteristic bands of the GON / PANI-HCl composite (39%, 23%, 19% and 8%) are identified with different intensities at 497cm^{-1} and 790cm^{-1} corresponding to the C-H and C-N bonds. These bands are due to the para distribution of the aromatic cycle. The 1079cm^{-1} band corresponds to the binding elongation of C-OH primary alcohol while 1287cm^{-1} band is attributed to the stretching vibration of the C-N bond on the benzoide cycle. There is also a band at 1457 cm^{-1} which is attributed to the C-H bond, C = O amide and N-H. and a 1730cm^{-1} band that is characteristic of the conductive form of PANI [24]. These results allow us to observe that the majority of characteristic bands of the olive pomace spectrum disappeared after mixing with polyaniline. For the bands characterizing the PANI, some have disappeared such as the band 3269cm^{-1} and 3448cm^{-1} and others have moved slightly or their intensity has decreased. For the PANI 4% composite, it is found that the characteristic bands of olive pomace are all present, whereas the majority of the bands representing the PANI are absent except for some that are present with very low intensity such as the 1278cm^{-1} band, which corresponds to off-plane –NH flexion and elongation vibrations of phenolic C-O bond and C-N relative to the benzoide cycle. [21], and the 1457cm^{-1} band is attributed to the elongation vibration of the aromatic C-C bond of the benzoide cycles. There is also the presence of the 1557cm^{-1} band, which is attributed to the elongation vibration of the conjugated aromatic C = C bond relative to the quinoid cycle [22, 23].

It can be said that the PANI exists on the surface of the GO which explains the absence of some bands characterizing the GO and the displacement and intensity decrease of some other bands for the two components of the composites which confirms that There was a reaction between the functions of GO and PANI. The FT-IR spectrum of OP/PANI indicates that the compositing of OP and PANI is successful.

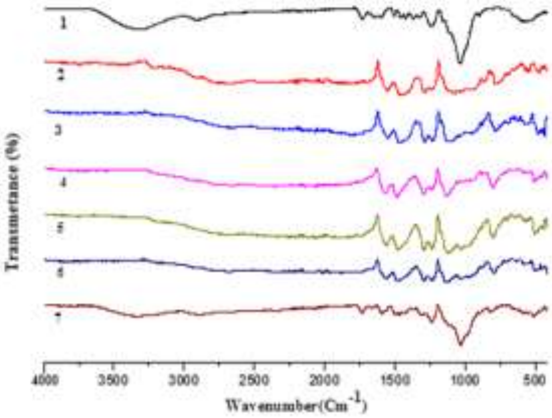

Figure 1. *FT-IR spectra of olive pomace (1), PANI-HCl (2) and OP/PANI-HCl composite with 39% (3), 23% (4), 19% (5), 8% (6) and 4% (7) of PANI.*

III.3.1.2. Scanning electron micrographs analysis (SEM)

The percolation limiting the composite is related to the homogeneity of the mixture of the constituents. The above results can be explained according to the composites morphology, based on the characterization by SEM microscopy. Different images were taken. Figure 2 shows the image of olive pomace (OP) witch, taken at SEM shows a heterogeneous surface and geometry. Thus we observe the appearance of macro and micropores.

For figure 3 of 100% PANI, there is an heterogeneous size and form of PANI particles, with a majority smooth surface.

The prepared composite figures (4, 5, 6, 7 and 8) show the presence of smooth surface on a granular surface and which becomes less extensive until almost absent depending on the percentage of aniline.

We note the persistence of OP macropores which concludes that the bonding PANI on the OP is successful while keeping free surfaces of the latter.

The microanalysis (EDX) of the different samples enabled us to characterize qualitatively and quantitatively the elements of the materials (OP, PANI-HCl) as well as the composites (39% PANI, 23% PANI, 19% PANI, 8% PANI and 4% PANI). EDX spectra of olive pomace, indicates a majority presence of carbon (60.81%), followed by Oxygen (39.19). For PANI-HCl there is a predominant presence of oxygen (43.1%) followed by nitrogen (35.83%), chlorides (17.6) Sulfur (2.63) and Aluminum (0.8%).

The EDX spectra of different composite indicates a presence with varying rates of major elements of the two materials (OP, PANI-HCl) for composite to another.

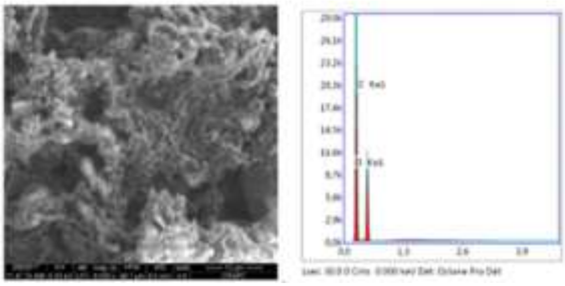

Figure 2. *Scanning Electron Micrographs and Energy Dispersive X-ray analysis of olive pomace*

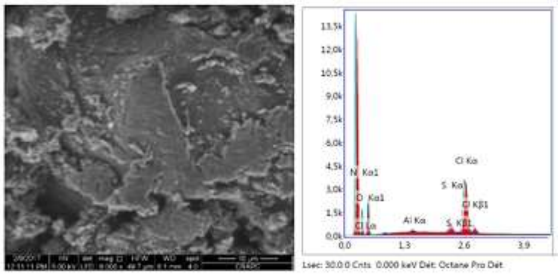

Figure 3. *Scanning Electron Micrographs and Energy Dispersive X-ray analysis of 100% PANI*

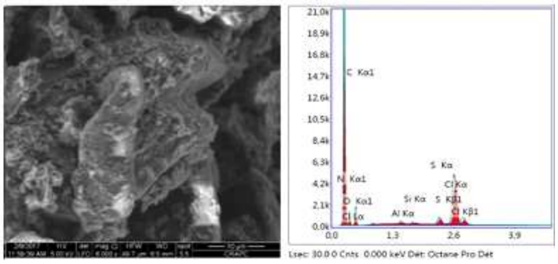

Figure 4. *Scanning Electron Micrographs and Energy Dispersive X-ray analysis of 39% OP/PANI composite*

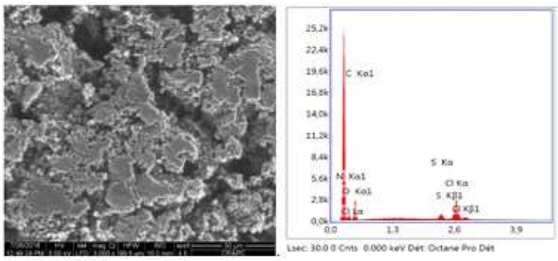

Figure 5. *Scanning Electron Micrographs and Energy Dispersive X-ray analysis of 23% OP/PANI composite*

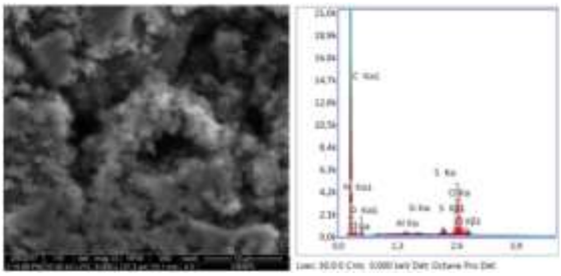

Figure 6. *Scanning Electron Micrographs and Energy Dispersive X-ray analysis of 19% OP/PANI composite*

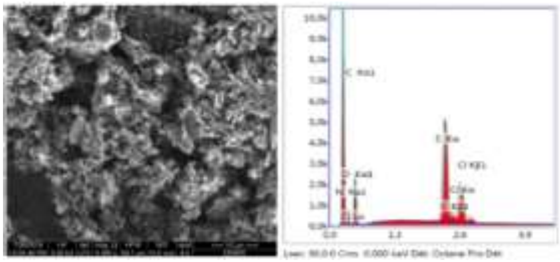

Figure 7. *Scanning Electron Micrographs and Energy Dispersive X-ray analysis of 8% OP/PANI composite*

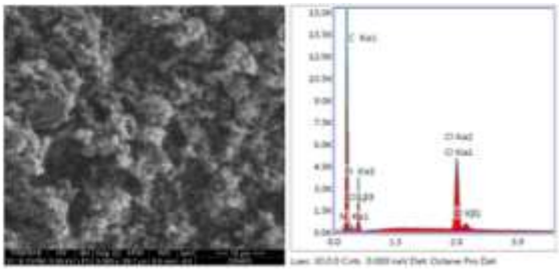

Figure 8. *Scanning Electron Micrographs and Energy Dispersive X-ray analysis of 4% OP/PANI composite*

III.3.2. Electrical analysis

III.3.2.1. The electrical conductivity (EC) caractérisation (four point méthod)

The electrical conductivity parameter was measured in the case of PANI and the OP/PANI composite prepared with different percentages of PANI, the results are shown in table 01

Table 1. *Values of conductivity of OP/PANI-HCl composite*

% PANI	σ **(S/cm)**
4.63	$1.23.10^{-4}$
8.23	$1.02.10^{-3}$
19.18	$1.5.10^{-3}$
23.23	$2.13.10^{-3}$
28.15	$8.81.10^{-3}$
39.42	$3.20.10^{-2}$
100	$6.90.10^{-2}$

According to the results found, we note that the value of the conductivity obtained (σ = 0.06 S/cm) for the synthesized polyaniline,is close to that given in the literature, taking into account the same operating conditions.

The insertion of the polyaniline in the olive pomace by the method of in-situ polymerization, confers a conducting appearance. Even low-PANI, composites already express a conductivity of about $1{,}23.10^{-4}$ S/cm. The samples percolation threshold is observed in the range [25%, 40%] by weight of PANI; it reflects the formation of conjugated system.

III.3.2.2. Static adsorption tests

In this part, we will study the adsorption capacity of hexavalent chromium by olive pomace, PANI-HCl and the various prepared composites (OP/PANI-HCl), in batch system.

III.3.2.2.1. effect of contact time on the hexavalent chromium adsorption

The contact time chosen was between 0 and 300 min at an ambient temperature of 27.2 ° C. The initial pH measured was 5.45 and was kept constant throughout the test. The adsorbate concentration was 20 mg l^{-1} and the adsorbent dose was 1g l^{-1}.

Figure 9 represents the adsorbed quantity (qt) of Cr (VI) on the various adsorbents as a function of timeindicates slow adsorption kinetics in the case of olive pomace with a very low adsorbed amount (1,816 $mg.g^{-1}$) reached around 60 minutes corresponding to a removal rate of the order of 10.081%. For PANI-HCl a very fast kinetics is observed, the equilibrium is reached in the first ten minutes with an optimal adsorption quantity of 17,809 $mg.g^{-1}$ corresponding to a removal rate of 99%. This rapid kinetics can be explained by the availability of active sites on PANI-HCl. Then there was a slowdown until equilibrium reached; this may be due to the decrease in the contact area after occupation of the majority of the active sites by the Cr (VI) ions. For the various composites prepared, there is a decrease in the adsorption kinetics as well as the adsorbed amount of Cr (VI) with the decrease of the percentage of PANI-HCl introduced into the composite.

The adsorbed amount in the case of 39% of PANI was 17.809 $mg.g^{-1}$ corresponding to 98.86% removal. In the case of 23%, 19% 8% and 4% of PANI, adsorbed quantities of 17.91 $mg.g^{-1}$, 17.05 $mg.g^{-1}$, 12.68 $mg.g^{-1}$ and 5.93 mg g-1are noted respectively. These results show the effect of adding PANI-HCl to olive pomace even at low percentages. It should be noted that from 60 min, no further improvement in the amount of adsorption was observed. 120 min of adsorption time were selected so that the adsorption equilibrium of Hexavalent chromium by the various adsorbents prepared is reached.

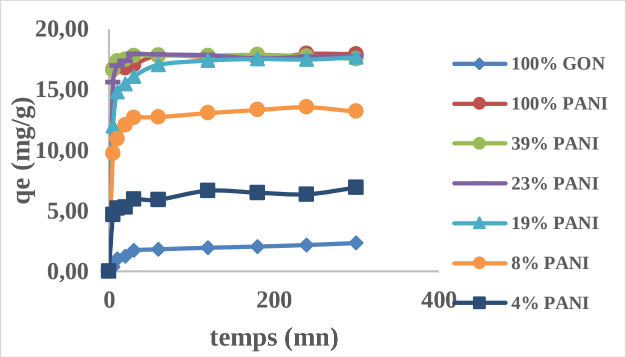

Figure 9. *Effect of contact time on the adsorption capacity of Hexavalent chromium on the various prepared materials, (adsorbent dose = 1 $g.L^{-1}$, pH = 5.45, C_o = 20 mg / l, W = 300 rpm, T = 27 ° C).*

III.3.2.2.2. effect of the solution pH of on the adsorption of hexavalent chromium

The pH of the solution has an important role in the adsorption of metal ions on the adsorbent surface [25] [26]. It also affects the ionization degree of the Hexavalent Chromium. To optimize the pH, a study of the Cr (VI) adsorption as a function of the pH variation ranging from 2 to 10 was carried out with an initial concentration of 20 mg L^{-1} and a dose of the adsorbent of 1 g. L^{-1}.

Figure 10 shows the evolution of the amount of Cr (VI) adsorbed as a function of the pH of the solution at equilibrium. As shown in the figure, the adsorption capacity did not change significantly by alternating the pH value. It is quite clear that the adsorption capacity of PANI-HCl is higher compared to that of olive pomace and consequently even with regard to the composites prepared it decreases with the decrease of the percentage of PANI-HCl. HCl.

In the case of olive pomace the evolution of the amount of Cr (VI) adsorption goes through two successive stages: growth and decay with increasing pH in the indicated range. With the initial pH increase from 2 to 4, the adsorbed amount of Cr (VI) increases to 12.51 mg g-1 corresponding to 69.44% and the optimum pH value is 4. It falls beyond of pH = 4 and reaches a value of 9.75 mg g-1, (54.14%) at pH = 6.

L'adsorption maximale de Cr (VI) autour de pH = 4 est expliquée par la protonation de l'adsorbant et la forme sous laquelle existe le Cr (VI).

At low pH, the proton concentration is high and the negative charges at the pore surface of the adsorbent are neutralized and new sites will be developed with positive charges [27].

According to BRITO et al. (1997a) [28], COTTON et al. (1972) [29], Cr (VI) in solution, exists in different ionic forms: chromate (CrO_4^{-2}), dichromate ($Cr_2O_7^{-2}$), hydrogénochromate ($HCrO_4$) ou chromic acid (H_2CrO_4) according to equation 1. The molecules of the $HCrO_4$ are the most numerous in the solution compared to those of $Cr_2\ O_7^{-2}$ at pH = 2,6 and $HCrO_4$ ions have smaller size than those of the $Cr_2\ O_7^{-2}$ ions [28]. As a result, monovalent $HCrO_4$ ions diffuse and adsorb more easily and in greater amounts to the surface of pores than $Cr_2\ O_7^{-2}$ ions.

There is a re-increase in the amount of Cr (VI) adsorbed at pH 10 and which is 12.087 $mg.g^{-1}$, corresponding to 67.1% elimination. This indicates that the adsorption of Cr (VI) on olive pomace may not only be chemical but also physical.

As for the PANI-HCl, it is found that the pH variation has no significant influence on the adsorption capacity because the results indicate a stability to pH 2 at pH 10, the optimal adsorption capacity noted is 17.9 mg g^{-1}, corresponding to 99% elimination. When the PANI exists in salt form, it is good for the adsorption of Cr (VI) of the solution, because of the exchange of anions between Cl^{-} and $Cr_2O_7^{-2}$ [30].

For the various composites prepared, it is noted that their behavior with respect to Cr (VI) is similar to that of olive cranberries; only what changes is the adsorbed quantity, which depends on the percentage of PANI introduced. When it is low, the amount adsorbed is close to that of olive pomace (8% and 4% of PANI) and when it is high, the adsorbed quantity is close to that of the PANI (19%, 23% and 39%). This allows us to conclude that PANI did not influence or change the active sites of olive pomace responsible for the fixation of Cr (VI) so it did not completely coat the olive pomace (pores that are remained free) but it has reinforced by its criteria the adsorption capacity of the material.

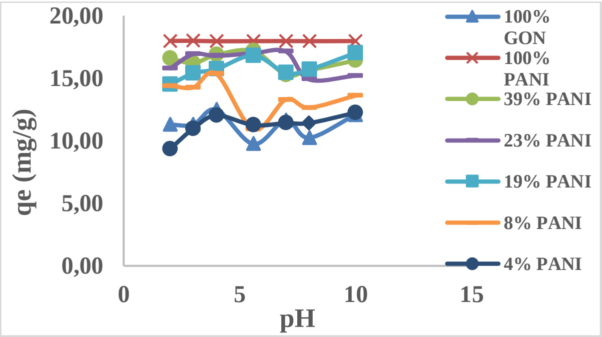

Figure 10. *Effect of pH on the adsorption capacity of Hexavalent Chromium on the different materials prepared, (adsorbent dose = 1 $g.L^{-1}$, C_O = 20 $mg.L^{-1}$, W = 300 rpm, t = 120 min, T = 27 ° C).*

III.3.2.3. Electrosorption behavior

For the electrosorption tests, our choice of composite materials was focused on 39% PANI given its acceptable electrical conductivity while preserving the characteristics of the two basic materials (GON and PANI-HCL) according to the characterization and the tests in system batch realized.

In order to effectively examine the relationship between the developed conductive composite material (olive pomace / PANI-HCl) and the effect of electrochemical polarization on the adsorption rate (necessary for the accurate design and modeling of the processes of adsorption); an electrochemical characterization by cyclic voltammetry and Chrometerometry was performed followed by an open-circuit adsorption / polarization electrosorption experiment of less than 800 mv from the same initial chromium salt concentration (approximately 20 mg / L) with an electrode area of 13, 2 cm^2 and at room temperature.

III.3.2.3.1. Electrchemical caracterization

a) Cyclic Voltammetry (VC)

The procedure is carried out by applying a cyclic potential scan, that is to say a potential varying linearly with time in a positive manner from t_0 to t_1 and inversely varying after t1 until it returns to Ei. At the same time, the response of the system is recorded by a curve i = f (E) characteristic of the electroactive species.

A preliminary study conducted by cyclic voltammetry is devoted to the electrochemical behavior of the substrate. Indeed, figure 11 shows a typical voltammogram of our composite electrode (OP/PANI-HCl) in a solution of potassium dichromate at 20 $mg.L^{-1}$, plotted in a potential range of -1 , 2 to +1.2 V / ECS.

The curve deviates from the ideal two-dimensional rectangular shape with respect to certain functional groups at the surface of the composite electrode and shows no obvious oxidation / reduction peak, suggesting an ideal Electrical Double Layer (EDL) capability that appeared on the surface of the electrode. Therefore, the electrode is supposed to be feasible for the electrosorption of Cr (VI) [31].

We observe that during the forward scan, the reduction of Cr (VI) ions starts at a potential of +0.5 V/SCE and gives a wide cathode wave at +0.8 V/SCE.

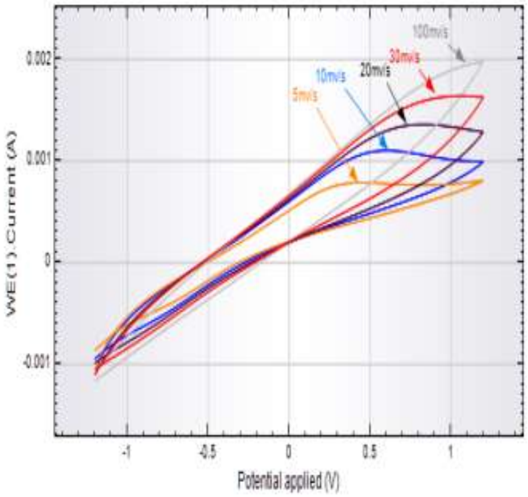

Figure 11. *Cyclic voltammogram of a composite electrode (GON / PANI-HCL) in Cr (VI) solution at 20 mg / L as a function of the potential sweep rate*

b) Chronoamperometry

By exploiting the results of voltammetry we could choose the potential to apply (E = +0.8 V / ECS).

The curve current density versus time (i = f (t)) resulting from this electrosorption gives, according to its appearance, indications on the mechanisms operating through the composite electrode / blocking layer / Cr (VI) solution). It is observed that the chronoamperogram is subdivided into three parts.

The first part, which starts from the beginning of the process until the beginning of the current rise, corresponds to the discharge of the double layer and the time necessary to form the seeds.

The curve then shows an increase in the current density to the maximum imax = 29.7x10-5 mA / cm2, during tmax = 137 seconds, this zone corresponds to the zone of the double layer and the time necessary to form the seeds , (forming a film).

There is again a decrease in the current which corresponds to the growth of the germs and therefore to the increase of the active surface area on the electrode. This third zone reflects the fact that the diffusion of the ions in the solution becomes the limiting step for the growth reaction of the deposit. This evolution of the current density is characteristic of the growth of a deposit of Cr (VI) (figure12).

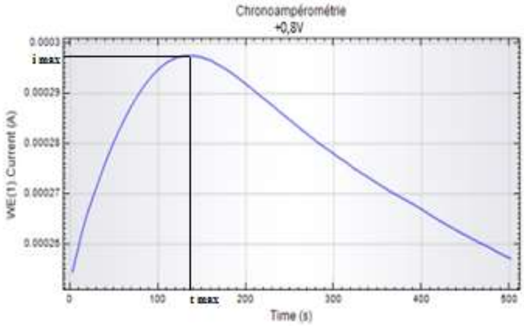

Figure 12. *Amperometric curve (E imposed = +0.8 V / ECS, ω = 20 mv / s)*

III.3.2.3.2 adsorption / electrosorption tests in an electrochemical cell

The adsorption tests at open circuit (OC) and electrosorption under 800 mV polarization are realized. The concentration of the remaining Hexavalent chromium is measured on a sample taken as a function of time, by UV-visible spectrophotometry. As shown in Figure 13 it is found that the retention rate of hexavalent chromium by the electrosorption method is greater than that of adsorption. It reaches 86% whereas it is only 17% in the case of adsorption.

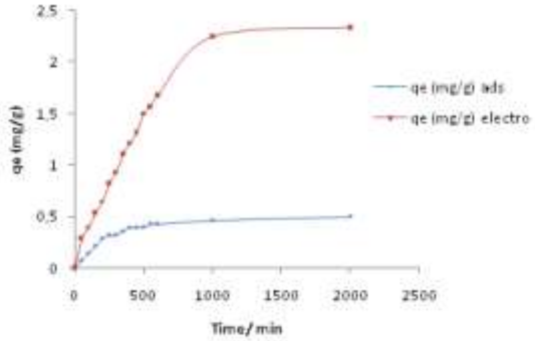

Figure 13. *Adsorption kinetics at open circuit (OC) and electrosorption under 800 mV polarization at C0: 20 mg/L, T: 25°C, pH: 2.6.*

IV. Conclusion

Olive Pomace /PANI conductive composites were prepared by chemical oxidative polymerization of aniline with natural olive pomace. The FT-IR spectrum of OP/PANI composites indicates that the compositing of OP and PANI is successful. On the other hand SEM-EDX of OP/PANI-HCl composites reveals that the bonding PANI on the OP is successful while keeping free surfaces of the latter witch confirms results obtained by FT-IR analysis. These results indicate that the PANI is successfully fixed on the OP. The conductive composite was used in the chemical and electrochemical removal of Cr (VI) from aqueous solutions. The Cr (VI) is in the form of $HCrO_4^-$, CrO_4^{2-}, or $Cr_2O_7^{2-}$, they would be drawn to the anode. Since these ions are already in a high oxidation state, complexation at the anode, without anodic oxidation is expected. To this effect we apply a positive polarization (anodic potential) to promote electrosorption chromium Cr (VI).

The retention rate of hexavalent chromium by the electrosorption method is greater than that of adsorption. It reaches 86% whereas it is only 17% in the case of adsorption.

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