ELECTROCHEMICAL CHROMIUM (VI) RECOVERY PROCESS BY CONDUCTING COMPOSITE, OLIVE POMACE/PANI

Naouel BABAKHOUYA,[a,b*] Mohamed ABDOUNI[a] and Krim LOUHAB[a]

[a] Food Technology Research Laboratory (LRTA), Faculty of Sciences Engineer
University of M'hamed Bougara, Boumerdes, BP 70, 35000 Boumerdes – Algeria
[b] Scientific and Technical Research Center of Physico-chemical Analysis, BP 384, Siège ex-Pasna Zone Industrielle,
Bou-Ismail CP 42004, Tipaza, Algérie

We examined the use of a new conducting composite material which was prepared from olive pomace (OP) and polyaniline, developed and used for the fabrication of electrode, which was then used as substrate for the recovery of chromium hexavalent to an aqueous solution through electrical conductivity tests. We used the spectral analysis techniques such as FT-IR and X-ray diffraction (XRD) to characterize the material as well as Laser Particle Size and scanning electron microscopy (SEM) to show that the PANI was successfully attached to OP. We carried out 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. The results demonstrated that the electrosorption of Cr (VI) is superior to the adsorption, which is due to the excellent electrical conductivity and mechanical properties of OP/PANI composite electrode. Through the electrosorption and electrodesorption we studied the possibility of regeneration of our electrode.
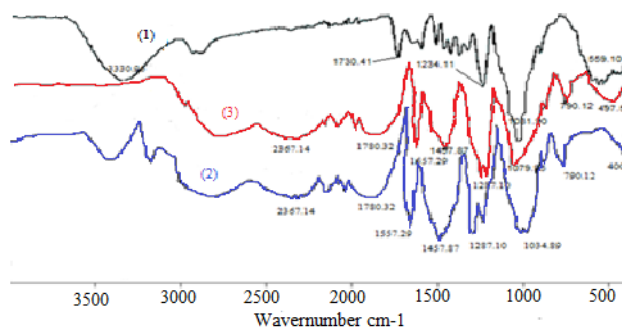
INTRODUCTION

Electrosorption is an important technology for the removal of heavy metal ions from wastewater,[1,2] during which an electric field is applied on solid adsorbents to enhance their adsorption capacity and facilitate their subsequent regeneration by electrodesorption.[3] 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.[4] It has been reported to be a suitable adsorbent material.[5] However, to achieve a 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.[6,7] 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.

---

* Corresponding author: nawelamini@yahoo.fr

EXPERIMENTAL

1. Materials and methods

The olive pomace results from seeds crushed during 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.[8-10] Aniline monomer and Ammonium persulphate (APS) was purchased from Biochem Chemopharma. Hydrochloric acid (HCl), was obtained from Chem-lab.

2. Synthesis of olive pomace–PANI composites

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 APS aqueous solution was added dropwise to oxidatively polymerize aniline.[4] The mixture was stirred for 20 h at ice temperature.[5] The reaction product was filtred and washed with 0.2 mol/l Hydrochloric acid solution,[11] and then with absolute ethanol till the filtrate became colorless. The composites were dried at 40 °C in an air oven for 5 h. As shown in table, 6 samples are prepared.

3. Characterization

The Fourier transform infrared spectra (FT-IR) of samples were recorded in the range of 4000-400 cm-1 by using the EQU INOX-SS FT-IR spectrometer (Bruker lazer). The X-ray diffraction (XRD) of the composite samples were recorded in the range from 5° to 120° by using the DMAX-Ultima III X-ray diffractometer. Finally, scanning electron microscopy (Philips ESEEM XL 30 SEM, JEOL, Inc., JSM- 6500F) was used to characterize the surface morphology and structure of the samples. The electrical conductivity (EC) of the composites was measured at room temperature by the standard four-probe method. The samples were compressed to13 mm diameter and 0.08–0.2 mm thickness pellets for the measurements.

RESULTS AND DISCUSSION

1. Structure and morphology analysis

1.1. FT-IR characterization

The Fig.1 shows the FT- IR spectra of olive pomace (1), PANI-HCl (2) and olive pomace – PANI composite (3). The characteristic broad band for O–H group (being in presence of H-band) of olive pomace appears at 3330 cm^{-1},[12–14] a peak around 1730cm^{-1} due to functional group C=O of lactones[12] and the band 1234cm^{-1} corresponds to the vibrations of the function OH and NO_2. So the band 1031cm^{-1} indicates the presence of the connections of strain C- OH primary alcohol and C-N. The broad absorption band between 1200 and 935 cm^{-1} is attributed to the contribution of various functional groups, such as C–O and C–O–C. The

typical feature of pure PANI is also well known in literature. The peaks corresponding to out of bending vibration of N–H and C–H band of p-di-substituted benzene appears at 497 cm^{-1} and 790 cm^{-1}. The band 1079 cm^{-1} indicates the presence of the connections of strain C-OH primary alcohol and C-N. The 1278 cm^{-1} band corresponds to an NH bending out of plane and stretching vibrations of C-O phenolic bond and C-N on the benzoide cycle.[14] The peaks around 1457 and1557 cm^{-1} result from stretching vibration of N–A–N and N=B=N structures, respectively (where –A– and =B= stand for benzenoid and quinoid moieties in the PANI chains).[15,16] The 1780 cm^{-1} band is characteristic of the conducting form of PANI. The characteristic absorptions of pure cellulose (3331, 1234 and 1031cm^{-1}) and PANI (1780, 1557, 1457 and 1278 cm^{-1}) have been both present in the spectrum of the composite.[17] The FT-IR spectrum of OP/PANI indicates that the compositing of OP and PANI is successful.

1.2. X-ray diffraction characterization

Fig. 2 shows XRD patterns of pure olive pomace, PANI-HCl and OP/PANI-HCl composite. The diffractogram of olive pomace exhibits a crystalline major peak at 2θ=22.4°,[18,19] corresponding to the (200) crystallographic plane which is attributed to typical cellulose I structure also called native cellulose constituting the crystalline part of cellulose.[20,21] The other constituents of olive pomace are predominantly amorphous which is explained by the appearance of the spectrum from 2θ=22.4°. For the plane PANI, the major diffraction peaks at 2θ=18.5°, 18.6° and 25.2° are consistent with (020) and (200) crystal planes respectively.[22,23] Similar to the PANI prepared by conventional methods,[8] the peaks of our PANI 2θ=18.5°, 18.6° and 25.2° are ascribed to the periodicity parallel and perpendicular to the polymer chains of PANI respectively, which indicates that PANI is partially crystalline as previously reported.[4] This crystallinity is also dependent on the acid used for synthesis and the degree of doping.[24] However XRD of OP/PANI-HCl composite reveals broad diffraction peaks typical to those obtained from the pure PANI (at 2θ=25.51°) and the pure olive pomace (at 2θ=22.28°) indicating a successful coating of PANI over olive pomace.[24] From the graph, the emergence of an additional peak at 15.87° corresponds to the orientation (010).[25]

Table 1

Samples prepared by *in situ* polymerisation

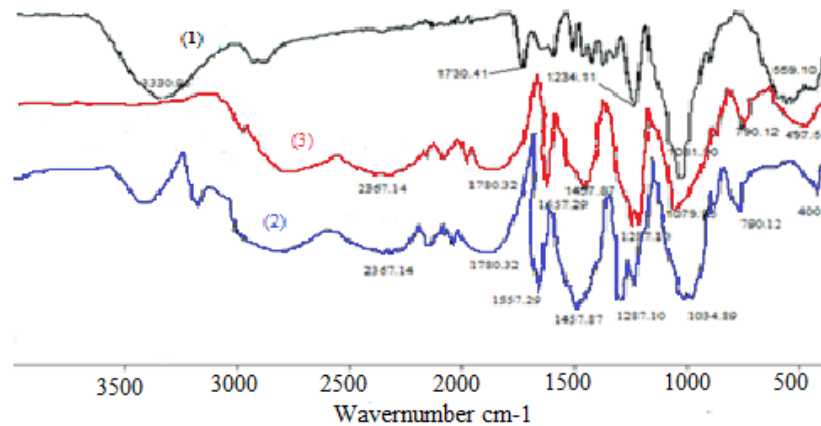| Samples	Amount of aniline (mmole)	Amount of HCl (mmole)	Amount of Persulfate d'Ammonium APS (mmole)	Amount of olive pomace (g)
1	2	20	2.5	2
2	4	40	5	2
3	8	80	10	2
4	12	120	15	2
5	16	160	20	2
6	20	200	25	2

Fig. 1 – FT-IR spectra of olive pomace (1), PANI-HCl (2) and OP/PANI-HClcompositewith39,42% of PANI (3).
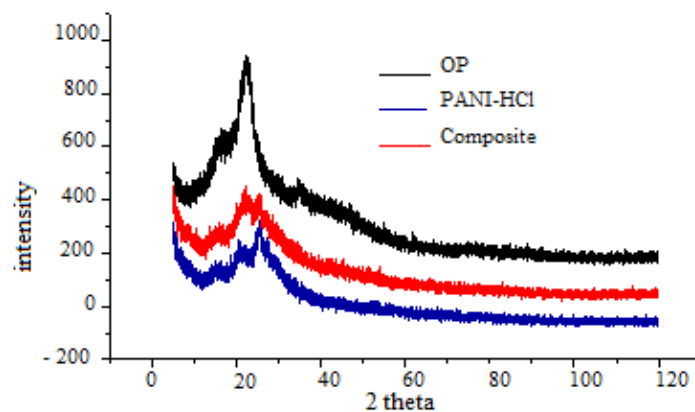

Fig. 2 – X-ray diffraction patterns of olive pomace, PANI and OP/ PANI composite with39.42% of PANI.

1.2. Scanning electron micrographs characterization (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. Fig. 3 shows an image resulting from SEM-microscopy method. In this image, the spectra (a) of olive pomace, shows heterogeneous size distribution. Particle geometry is variable. Thus we observe the emergence of apparently well-crystallized grains coexisting with fine powder clusters. For the spectra (b) of PANI, there is a heterogeneous size and form of particles of PANI, as it establishes the existence of a cylindrical form with a smooth surface. The spectrum (c) shows typical SEM images of the surface of the OP/ PANI composite. We note an apparent uniformity of the surface which leaves us assume that our adsorbent is homogeneous. Also there is an increase in the size of the particle and some resemblance in the form and smoothness of the surface in comparison with the SEM images of PANI and those of composite. This confirms the results obtained by analysis of Infrared indicate that PANI was able to bind to the surface of olive pomace.[26]
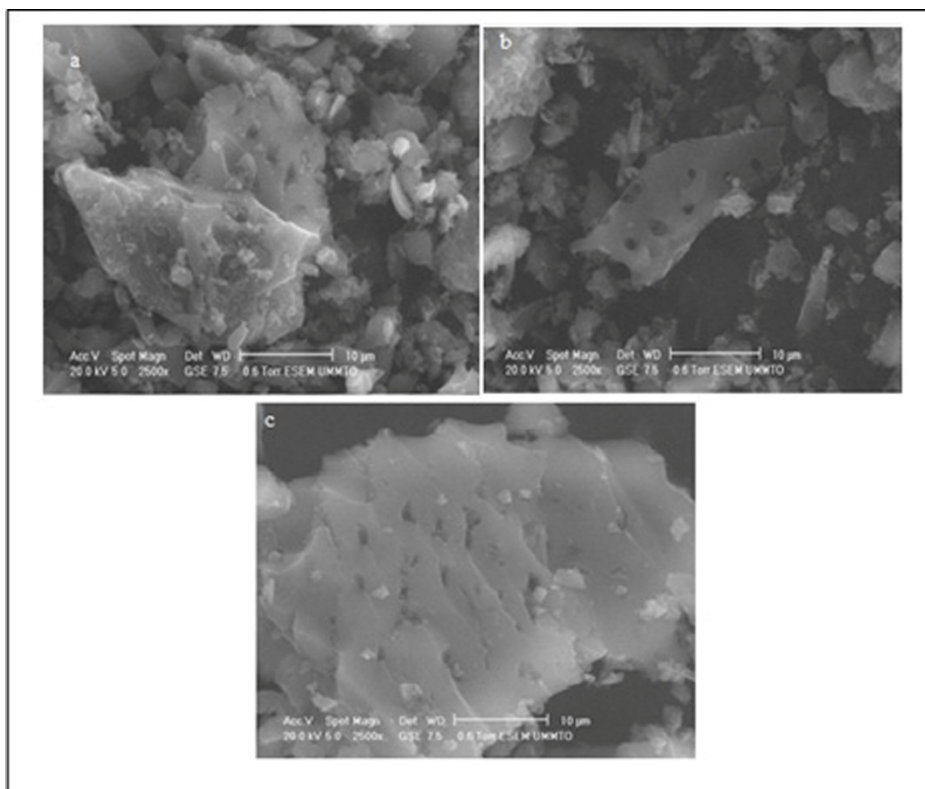
Fig. 3 – Scanning electron micrographs of (a) olive pomace (b) polyaniline, and (c) PO/PANI composite.

Table 2

Values of electrical conductivity of the PANI-HCL

Sample	e (mm)	I (µA)	V (volt)	Resistivity (Ohm.cm)	Conductivity (S/cm)
PANI	0.53	1.989	$1.20.10^{-4}$	14.4851	$6.90.10^{-2}$

2.1. Electrical analysis

2.1.1. 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 2.

The value of the conductivity obtained ($\sigma = 0.06$ S/cm) for the synthesized polyaniline is close to that given in the literature, taking into account the same operating conditions.

Table 3

Values of conductivity of OP/PANI-HCl composite

% PANI	σ(S/cm)	Log σ (S/cm)
4.63	1.23.10-4	-3.91
8.23	1.02.10-3	-2.99
19.18	1.5.10-3	-2.82
23.23	2.13.10-3	-2.82
28.15	8.81.10-3	-2.05
39.42	3.20.10-2	-1.49

According to the results found, we note that 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.

ELECTROSORPTION BEHAVIOR

Batch mode electrosorption experiments were performed to investigate the application of the electrosorption process for the removal of chromium (IV) from aqueous solutions, using an Olive pomace-PANI composite with an (PO/PANI) electrode. In the first step we apply a adsorption tests at open circuit. We recorded the evolution in potential of the electrode in function of time. As the pH is the most important factor in

this case having regard to its effect on the surface and equilibrium between $Cr_2O_7^{2-}$ and CrO_4^{2-} and the dedopage of our electrode which is in a basic medium (pH>7). We chose adsorption test in two acidic pH as shown in Fig. 4.

In the second step, an experiment on adsorption/electrosorption kinetics were carried out starting with the same initial chromium salt concentration of about 20 mg/L of chromium (IV) with an electrode area of 13.2 cm² at room temperature and recorded the adsorption at open circuit (OC) and electrosorption under 800 mV polarization as shown in Fig. 5. The exact speciation of the chromium ions depends upon pH, temperature, concentration and the presence of other ions. However according to different authors,[27,28] 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).
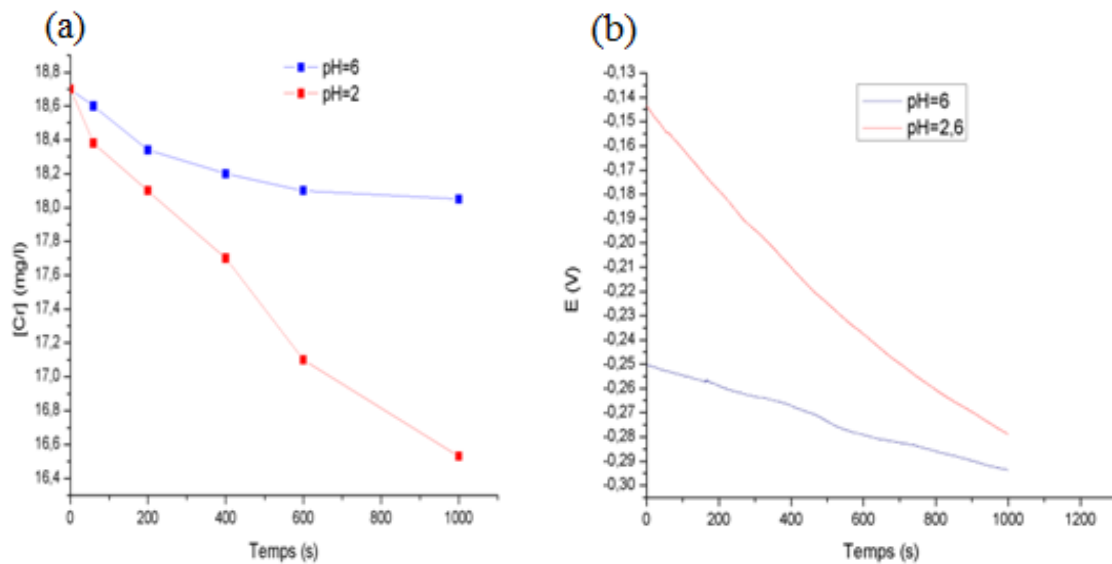

Fig. 4 – adsorption tests at open circuit: (a): effect of different acidic pH, (b): evolution of electrode potential.
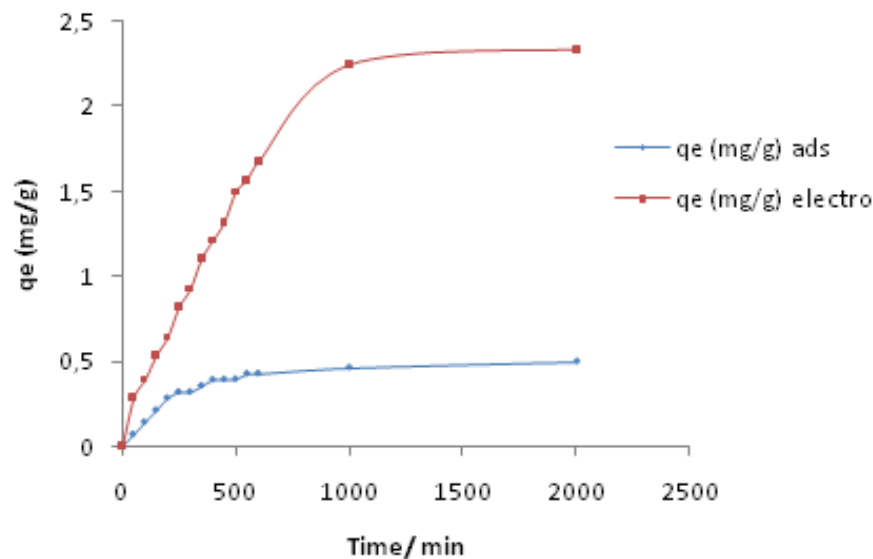

Fig. 5 – Adsorption kinetics at open circuit (OC) and electrosorption under 800 mV polarization at C_0: 20 mg/L, T: 25°C, pH: 2.6.
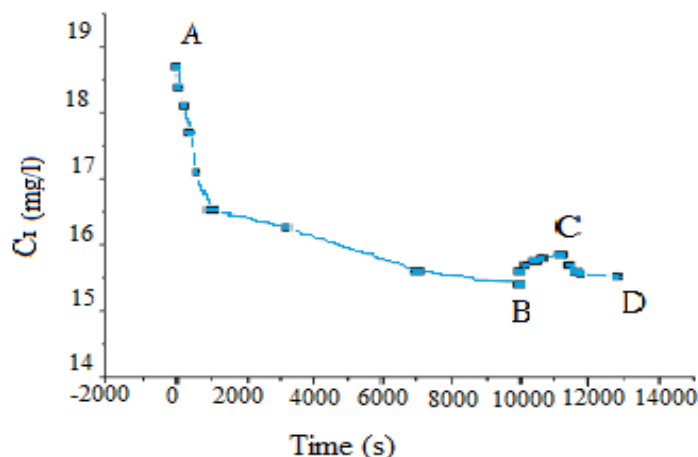
Fig. 6 – Successive electrosorption/ electrosdesorption (from A to D), electrosorption (from A to B) at +400 mV, electrodesorption (from B to C) at -400 mV polarization, and electrosorption (from C to D); mass of OP/PANI electrode was 0.2 g.

In order to determine the capacity for electrosorption and regenerability after electrosorption on Olive pomace-PANI composite we have carried another experiment. In this latter, the electrosorption run from adsorbate solution according to desorption run. The electrosorption data were recorded upon polarization by applying -400 mV for the first 10000 s followed by electrodesorption upon polarization by applying +400mV for the next 12000 s for the possible regeneration of Olive pomace-PANI composite. Then polarization direction was reversed in order to observe the electrosorption. The results are shown in Fig. 6.

The electrosorption takes place from A to B upon +400 mV. A decrease is observed in solution concentration of chromium, resulting in electrosorption of almost 25% of chromium in the first 10000s. When the polarization direction is reversed (-400 mV) at point B to C during 1200 s as shown in Fig. 6, a small amount of Cr (VI) was released during this step. During regeneration step at – 400 mV polarisation, an amount of 0,5 mg g⁻¹of electrosorbed chromium was electrodesorbed into 800 mL of $K_2Cr_2O_7$ solution in 20 min period, corresponding to about 18,5% of the amount of chromium electrosorbed. The remainder is absorbed. A reverse polarization at -1.2 V was required for the partial release of bound Cr (VI). This electrosorptive behavior of chromium not only can be linked to the electrostaticinteractions between Chromium species in solution and charged Olive pomace-PANI composite surface in the double layer but also chemical complexation between the dichromate oxyanions with functional groups on the Olive pomace-PANI composite surface, where the relative irreversibility Cr (VI)

electrosorption. It is evident that Cr (VI) anions such as dichromate are not removed from the solution by a simple electrostatic (capacitive charging) mechanism. The electrosorption process involves some type of bond formation. Reverse polarization at -400 mV caused cathodic reduction at the electrode complexed with the Cr (VI) species, there by destroying the Olive pomace-PANI composite Cr (VI) bonds. After the regeneration, the polarization direction is reversed (+ 400 mV) at point C, the concentration starts to decreases sharply as a result of electrosorption of chromium. However, the adsorbed amount is similar with that previously regenerated.

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 indicates that the compositing of OP and PANI is successful. On the other hand XRD of OP/PANI-HCl composite reveals broad diffraction peaks typical to those obtained from the pure PANI and the pure olive pomace indicating a successful coating of PANI over olive pomace. Scanning electron micrographs characterization (SEM) confirms results obtained by FT-IR and DRX Laser granulometry 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 electro-sorption chromium Cr (VI). Finally an experiment was carried out in which electrosorption run from adsorbate solution were followed by a desorption run indicating that this electrosorption behavior of chromium can also be linked to the chemical complexation between the dichromate oxyanions with functional groups on the Olive pomace-PANI composite surface.

REFERENCES

1. E. J. Bain, J. M. Calo, R. Spitz-Steinberg, J. Kirchner and J. Axen, *Energ. Fuel.,* **2010,** *24,* 3415–3421.
2. X. Q. Wang, J. S. Lee, C. Tsouris, D. W. DePaoli and S. Dai, *J. Mater. Chem.*, **2010,** *20*, 4602–4608.
3. A. Ban, A. Schafer and H. Wendt, *J. App. Electrochem.,* **1998,** *28*, 227–236.
4. U. M. Casado, M. I. Aranguren and N. E. Marcovich, *Ultrason. Sonochem.*, **2014,** *21*, 1641–1648.
5. N. Babakhouya, S. Boughrara and F. Abad, *Am. J. Environ. Sci.*, **2010,** *6*, 470-476.
6. J. Stejskal, M. Exnerova, Z. Moravkova, M. Trchova, J. Hromadkova and J. Prokes, *Polym. Degrad. Stab.,* **2012,** *97*, 1026-1032.
7. S. Bhadra, D. Khastgira, N. K. Singhaa and J. H. Lee, *Prog. Polym. Sci.*, **2009,** *34*, 783-790.
8. S. J. R. Prabakar and S. S. Narayanan, *Talanta,* **2007,** *72*, 1818-1824.
9. N. Abed, N. Babakhoya and S. Boughrara, *Algerian J. Env. Sc. Tech.*, **2015,** *1*, 4-8.
10. N. Babakhouya, S. Boughrara, F. Abed, N. Abai and S. Midoune, *Algerian J. Env. Sc. Tech.,* **2015,** *1*, 3-9.
11. W. Hu, S. Chen, Z. Yang, L. Liu and H. Wang, *J. Phys. Chem-Us.* **2011,** *B 115,* 8453–8457.
12. F. Sheimann, "An introduction to spectroscopic methods for the identification of organic compounds", Perg. Press, 1998.
13. L. J. Bellamy, "The infrared spectra of complex molecules", Ch., London, 1975, Vol. 1.
14. M. Hesse, H. Meir and B. Zeeh, "Méthodes Spectroscopiques pour la chimie organique", Masson, Paris, 1997.
15. Z. Xuan and L. Lu, *Mater. Lett.*, **2011,** *65,* 754-756.
16. M. Ayad, G. El-Hefnawy and S. Zaghlol, *Chem. Engin. J.* **2013,** *217*, 460-465.
17. Z.-L. Mo, Z.-L. Zhao, H.Chen, G.-P. Niu and H.-F. Shi, *Carbohyd. Polym.,* **2009,** *75*, 660-664.
18. E. Malkoc, *J. Hazard. Mater.,* **2006,** 142–151.
19. D. Trache, A. Donnot, K. Khimeche, R. Benelmir and N. Brosse, *Carbohyd. Polym.,* **2014,** *104*, 223–230.
20. M. H. Schneider and K. I. Brenbner, *Wood Sci. Technol.,* **1985,** *19*, 67-73.
21. F. Zhang, Z. Pang, C. Dong and Z. Liu, **2015,** *132*, 214–220.
22. F. Yang, M. Xu, S.-J. Bao, H. Wei and H. Chai, *Electrochim. Acta,* **2014,** *137*, 381–387.
23. M. Kumar, K. Singh, S. K. Dhawan, K. Tharanikkarasu, J. S. Chung, B.-S. Kong, E. J. Kim and S. H. Hur, *Chem. Eng J.,* **2013,** *231*, 397–405.
24. A. Mekki, S. Samantaa, A. Singh, Z. Salmia, R. Mahmoud, M. M. Chehimia, D. K. Aswal, *J. Colloid. Interf. Sci.,* **2014,** *418*, 185–192.
25. P. Dallas, N. Moutis, E. Devlin, D. Niarchos and D. Petridis, *Nanotechnol.,* **2006,** *17*, 5019.
26. S. De Bondt, L. Froyen and A. Deruyttere, *J. Mat.Sci*., **1992,** *27*, 1983.
27. D. Lindsay, K. J. Farley, R. F. Carbonaro, "Oxidation of CrIII to CrVI During Chlorination of Drinking Water, Electronic Supplementary Material (ESI) for Journal of Environmental Monitoring", The Roy. Soc. Ch., 2012.
28. E. L. Hawley, R. A. Deeb, M. C. Kavanaugh and R. G. James Jacobs, Treatment Technologies for Chromium (VI), *L1608_C08.fm* **Friday, July 23, 2004,** *5:46,* 273.