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Removal of chromium from tannery wastewater by electrosorption on carbon prepared from peach stones: effect of applied potential

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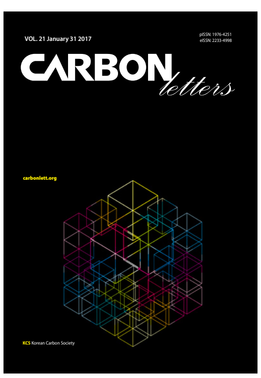

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Abstract

The objective of this study is the removal of chromium from tannery wastewater by electrosorption on carbon prepared from lignocellulosic natural residue "peach stones' thermally treated. The followed steps for obtaining coal in chronological order were: cleaning, drying, crushing and finally its carbonization at 900°C. The characterization of the carbon material resulted in properties comparable to those of many coals industrially manufactured. The study of the dynamic adsorption of chromium on the obtained material resulted in a low removal rate (33.7%) without applied potential. The application of negative potentials of -0.7 V and -1.4 increases the adsorption of chromium up to 90% and 96% respectively. Whereas a positive potential of +1.4V allows desorption of the contaminant of 138%.

Key words: chromium, coal, electrosorption, peach stones, tannery wastewater

1. Introduction

The growing global interest in environmental sustainability has motivated industrialists to find technical ways to reduce or reclaim resources from the solid waste left by various human activities and processes. In the case of lignocellulosic residues (e.g., olive stones, peach stones, and almond hulls), manufacturers have found applications for the activated carbon produced from these wastes/resources [1,2]. Such charcoals are used in water treatment systems, purification products, gas adsorption, and in many other ways [3]. The use of these filter media or adsorbents in the areas mentioned, requires knowledge of the structure and texture of the manufactured material; namely qualities such as the ash content, surface area, and pore volume. Knowledge of these characterization parameters helps to explain the phenomena that govern the efficiency and sustainability of the charcoal used [4].

In order to convert local waste materials to activated carbon, we used as raw material peach stones thermally treated at 900°C. This type of treatment has been successfully applied to improve the texture parameters (exchange surface area and porous volume) of several materials [5,6].

After physico-chemical characterization, the charcoal obtained was used in tests of its ability to remove chromium from tannery wastewater. Tanneries use as tannery agent a solution of almost 32% chromium [7,8]. In addition, according to Tiravanti et al. [9], 50% of the chromic salts are discharged with the waste water. Therefore, the tanning process is an important source for the discharge of this pollutant into the environment. In addition, the cost of metallic chromium is significant and it is possible to recover it from the wastewater [10]. Therefore, the elimination of this pollutant using a low-cost, effective, easy application, such as adsorption on activated carbon made from waste materials of natural origin, could prove very important in the current context of environmental sustainability. However, regardless of the charcoal used, its saturation is unavoidable; hence the need to regenerate the charcoal in the case of an industrial application.

The regeneration of saturated activated carbon is conventionally achieved chemically or by heating at high temperature. The latter is a very expensive operation because of the energy consumption. The approaches of some authors (Strohl and Dunlap [11] or Alkire and Eisinger [12]) utilize a completely different method of regeneration by providing electrochemical potential in situ electrochemically. Indeed, the good electrical conductivity of the charcoal and its high overvoltage in the electrolysis reactions of water, allows the possibility to use it as an electrode in solid aqueous phase. By applying a suitable potential to charcoal, we can change its adsorption capacity or induce desorption of the pollutant (regeneration), this phenonmenon is called electrosorption.

The objective of this study was to use peach stones as the raw material from which to manufacture activated carbon suitable for use in electrosorption of chromium from tannery wastewater. It is thus possible to vary (in situ) the adsorption capacity of the activated carbon: to increase the amount of the target product adsorbed, or to reverse the process and release the adsorption target, thereby achieving regeneration of the charcoal.

2. Experimental Procedure

2.1. Sampling Method of Wastewater

The main collector tannery output was selected as the sampling point. It is the meeting place of all emissions including from the river workshops, and the tanning and retanning operations. Sampling was performed manually using a bucket with a depth of meshing of about 1.5 m. The samples were stored in containers in a dark, cool place (4°C) to minimize chemical modification. The chromium concentration was analyzed by atomic absorption (AA spectrometer; Solaar Thermo Elemental, USA).

2.2. Preparation of activated carbon from peach stones

The peach stones taken as raw material do not have a charcoal structure or texture (specific surface area, surface functions, porosity) that would make them capable of adsorbing any pollutant. Therefore, thermal and/or chemical activation must be performed to change (in an irreversible manner) the surface of the raw material to permit retention by adsorption of organic and inorganic substances. For a pollutant and a material, several activation variations can be made: thermal (choice of steam or carbon dioxide as an oxidant) and/or chemical (in the presence of inorganic acids and metal oxide) [13,14]. In this study, the peach stones were ground then sieved (0.5–2.0 mm). The grains retained were thermally activated by direct pyrolysis at 900°C in a tubular oven (Cyol), under a nitrogen stream, for a period of 3 hours of contact time. This produed a dry residue free of resins or other non-carbon compounds.

Any residual carbonization was then removed by extensive washing with hydrochloric acid (10%) and distilled water under reflux until the rinsing water showed a neutral pH. The protocol used by Anundo Polania [15] helped to clean the micro-pores of an activated carbon made from coconut. Before undertaking its use in adsorption of polyphenols testing, the treated charcoal was dried in an oven at 105°C to constant weight, for at least 8 h.

2.2. Physico-chemical characterization of the obtained coal

The physico-chemical characterization of the prepared charcoal required the use of several analytical methods. The surface area was determined by the Brunauer-Emmett-Teller (BET) method, using the ASAP 2010 type apparatus (Micromeritics, USA). The porous volume was deduced from the adsorption isotherm of nitrogen in the capillary condensation zone. Zeta potential or potential of hydrodynamic shear, defining free water and bound water in a particle, was measured using a 3000 HS zétamètre (Malvern, UK). The measurements were performed on samples of 200 mg of powdered activated carbon in 50 mL of distilled water at 25°C. Elemental analysis of carbon, hydrogen, nitrogen, and sulfur was performed by photoemission spectroscopy induced X-ray. The preparation of the acidic and basic sites on the charcoal surface was performed using the titrimetric acid-base method proposed by Boehm [16]. Acid sites (carboxylic acids, lactones, phenols and quinones) are prepared in succession by mixing 1 g of charcoal in a volume of 50 mL of each of the bases ($NaHCO_3$, Na_2CO_3, NaOH, and $NaOC_2H_5$) at a concentration of 0.1 N. These four solutions were stirred simultaneously for 24 h at 20°C. After filtration of each mixture, the acid sites were dosed using 0.1 N HCl. Similarly, the basic surfaces were assayed by contact of 1 g of charcoal with 50 mL of 0.1 N HCl. After 24 h of stirring at 20°C, 10 mL of filtrate was dosed with 0.1 N NaOH. In order to detect differences in morphology related to details of the production of charcoal, photos were taken using an electronic microscope JEM-100B (JEOL, Japan) with a scanning accessory (ASID, JEOL), and energy dispersivex-ray analysis analyzer.

2.3. Development of the Electrosorption Method

For our study of electrosorption, it was necessary to plan and build an experimental setup to measure the concentration of the product percolated through the electrochemical cells filled with granular activated carbon to which an electrical potential could be applied.

Installation of electrosorption–the experiments were performed according to the diagram shown in Fig. 1. The electrosorption cells (E) were inspired by the model of Alkire and Eisinger [12]. Each cell is made of two concentric tubes, between which circulates water with temperature measured via thermostat (T). The used activated carbon was dried at 105°C to constant weight before being placed inside the inner tube.

The feed solution (waste water), contained in a reserve, is introduced into the two columns. The one to the left (N°, I) serves as a control while that to the right (N°, II) is used to perform the

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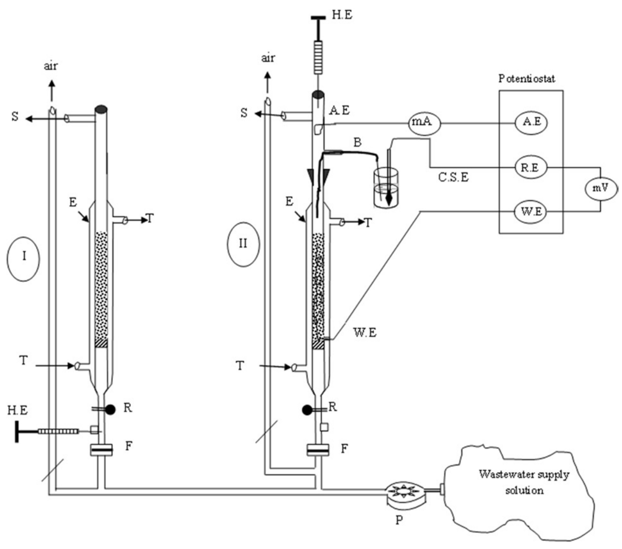

Fig. 1. Simplified diagram of the electrosorption set-up.

electrosorption experiments.

The sampling was done using a syringe (H.E.) above the charcoal. A filter (F) with pore size of 0.22 μm was used to eliminate bacteria that could grow in the power circuit. A potentiostat controls the potential imposed on the activated carbon using a three-electrode system: 1) working electrode (WE): a platinum wire in contact with the activated carbon, 2) saturated calomel electrode (SCE): for reference (ER), connected to the cell by a bridge with agar-agar (B) saturated with potassium nitrate, and 3) platinum auxiliary electrode (AE).

The potential difference applied at the granular activated carbon, between the working electrode and the reference electrode, was measured using a millivolt meter (mV) (AX 502). A milliamp meter (mA) (SkyTronic 600, 527, Nijverdal, Netherlands) was used to measure the current in the electrode circuit; it was placed in the auxiliary electrode circuit to prevent the voltage drop across its terminals and to avoid subtracting it from the set potential. The advantage of this three-electrode assembly is the ability to avoid ohmic drops and current flow in the reference electrode.

Each cell contained 3.5 g of prepared charcoal. The chromium was adsorbed on this granular activated carbon with or without applied potential (0, −0.7, −1.4, and +1.4) V/SCE. The different adsorption and electrosorption tests were made at a percolation rate of 130 mL/h and free pH.

The calculated reduction rate of chromium, expressed as a percentage T (%), was based on the following formula:

$$TX(\%) = \frac{(C_iX - C_fX)}{C_iX} \times 100 \quad (1)$$

C_i and C_f are the initial and final concentration of chromium before and after electrosorption.

3. Results And Discussion

3.1. Characterization of the tannery wastewater

The physico-chemical analysis of the studied tannery wastewater shows that the chromium content was 236.62 mg/L, this concentration greatly exceeds the Algerian standard for discharge of industrial liquid effluent. This element is a metal known to be highly toxic to many plant and animal species, including humans. The removal of this pollutant by electrosorption on carbon prepared from lignocellulosic natural residue peach stones, thermal treated was required.

Physicochemical characterization of activated carbon

Knowledge of the physico-chemical characteristics of activated carbon is necessary to understand many of its qualities (e.g., adsorption, desorption, and ion exchange) [4]. Table 1 shows the main physic-chemical characteristics of charcoal prepared from peach stones. The results show that the charcoal is mainly composed of carbon and oxygen; other hetero-elements (e.g., nitrogen and sulfur) can coexist according to the raw material used [17].

The pH of the prepared charcoal was almost neutral (6.93). The moisture content and the textural parameters of primary importance for industrial use (namely the surface area and porosity) are suitable for an industrial operation. For example, the specific surface area is on the order of 623 m^2/g. This is comparable with the results of other authors. Duranoğlu et al. [18] showed that the specific surface area of activated carbon made from peach stones thermally treated at 800°C, was 608 m^2/g.

Moreover, it was noted that the zeta potential was negative. This is related to the phenomenon of compression of the double layer of the particles and the zeta potential reduction or cancellation. The zeta potential of the activated carbon particles thus enables an estimate of the surface charge carried by this, and therefore can lead to an interpretation of the results obtained during the adsorption of pollutant.

Analysis of the charcoal surface showed more basic surface

Table 1. Physico-chemical characteristics of the prepared charcoal

Parameter	Value
C (%)	83.1
H (%)	6.7
O (%)	28.0
N (%)	3.2
S (%)	1.5
pH	6.93
Humidity rate (%)	0.6
Specific surface (m^2/g)	623
Porous volume (cm^3/g)	0.63
Zeta potential (mV)	–21.96
Total of acid functions (meq/g)	1.80
Carboxylic function	0.15
Lactones function	0.32
Phenol function	0.50
Quinone function	0.83
Total basic functions (meq/g)	2.43

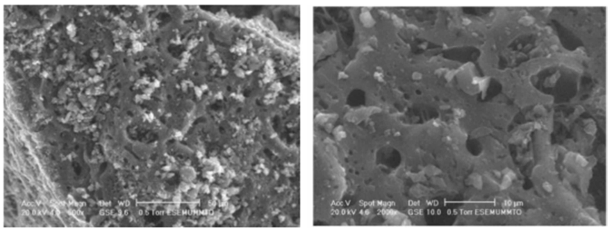

Fig. 2. Scanning electron microscope images of the prepared charcoal.

oxides than acid, due to the pyrolysis at 900°C. Remember that this surface effect has long been known [14]. The observed low concentrations of carboxylic acid are probably due to the charcoal pyrolysis temperature. Julien [19] found that these surfaces were virtually eliminated with an activated carbon prepared from coconut for pyrolysis at 600°C.

The images of charcoal by scanning electron microscope (Fig. 2) show a well-developed porosity over the entire surface of the activated carbon with some heterogeneity. In addition, there may also be the presence of a multitude of fine particles attached to the activated carbon. These particles can be attributed to both a reminiscence of vegetable origin of charcoal and impurities formed during its preparation.

Results for the electrosorption of chromium on activated carbon prepared from peach stones

The focus of this section was to optimize the electrosorption by studying the influence of applied potential. The results are shown in the figures that present the adsorption in dynamic or breakthrough curves, with and without applied potential.

3.2. Influence of the applied potential

Fig. 3 shows the efficiency processing values obtained as a function of time of treatment or percolation, for potential values of (0, −0.7, and −1.4) V/SCE. At −0.7 V, the rate of reduction of chromium in tannery watewater was on the order of 90%; whereas at −1.4 V, the removal rate was approximately 96%. The effectiveness of treatment at zero potential (dynamic adsorption on activated carbon) hardly reached 33%.

The variation of adsorption capacity was related to the intense electric field in the double layer and to low electrolysis.

Several authors reported that the charcoal adsorption capacity increased when an electric potential was applied [20]. When the electrosorption process is applied in the treatment of solutions containing ionic species, these can be electrostatically adsorbed in the double electric layer of the electrode without phase change.

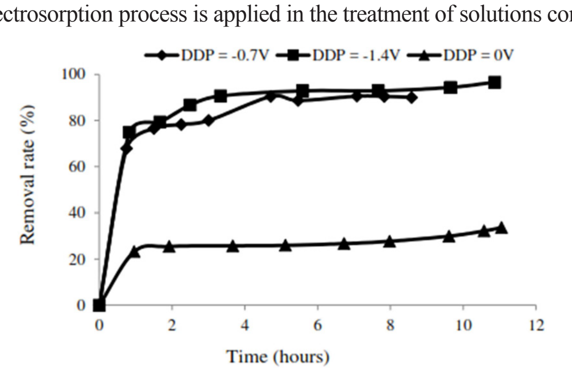

Fig. 3. Influence of voltage clamp on electrosorption of chromium in tannery waste water on activated carbon.

As shown in Table 1, the active carbon prepared from peach stones has various functional groups that are amphoteric, providing the possibility of cation-exchange.

The protonation/deprotonation equilibium that is generally used to describe the development charge to a surface containing an amphoteric oxygenate group can be written as follows [21]:

$$MOH_2^+ \longrightarrow MOH + H^+ \quad (2)$$

$$MOH \longrightarrow MO^- + H^+ \quad (3)$$

where in MOH represents the oxygenated group on the charcoal surface.

During application of negative polarization to the electrode of charcoal, the reduction of water causes the formation of hydrogen gas and hydroxylions on the surface of the charcoal:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad (4)$$

Due to the porous texture of the activated carbon, the OH^- ions diffuse slowly into the solution. Consequently, the pH increases locally and the surface groups are differentiated according to their strength.

In the case of carboxyl groups, for example, the trapping mechanism of chromium (III) is as follows:

$$C^*{-}COOH + OH^- \longrightarrow C^*{-}COO^- + H_2O \quad (5)$$

$$3C^*{-}COO^- + Cr^{3+} \longrightarrow (C^*{-}COO^-)_3Cr^{3+} \quad (6)$$

wherein C* the coal matrix.

3.3. Desorption of chromium

Regeneration of the adsorbent, which is an attractive aspect of the electrosorption process, can be carried out by reversing the potential imposed on the electrode (activated carbon). The application of a positive potential (+1.4 V) after saturation of the active carbon with chromium (Fig. 4) causes its desorption of chromium (recovery rate up to 138%). This can be explained by the fact that when the potential is reversed, It could be considered that the surface functional group of the activated carbon was removed by a partial reaction and then the property of the electrode surface was changed, activated

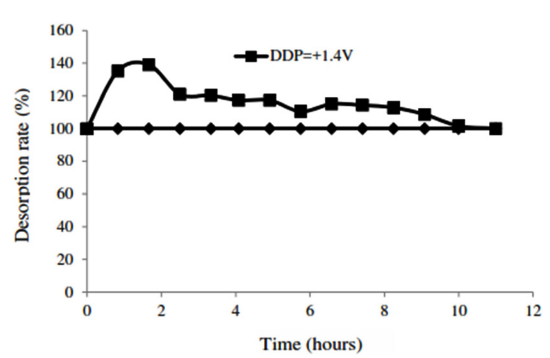

Fig. 4. Electrodesorption of chromium retained on active carbon.

carbon acts as an anode and oxidation of water produces dioxygen and the protons which decrease the pH of the surface [22]:

$$2H_2O \longrightarrow 4H^+ + O_2 + 4e^- \quad (7)$$

Then the adsorbed ions of chromium (III) are released, giving a neutral surface group:

$$(C^*{-}COO^-)_3\,Cr^{3+} + H^+ \longrightarrow C^*{-}COOH + Cr^{3+} \quad (8)$$

4. Conclusion

The characterization of tannery wastewater showed a significant pollutant load characterized in particular by chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), high turbidity, and chromium. This work had the objective of recovering the chromium, reputed to be a very toxic pollutant, from a real sample of tannery wastewater by electrosorption on activated carbon prepared from peach pits.

The preparation of peach stones (or other lignocellulosic residues) by thermal treatment at 900°C yielded a charcoal with physicochemical and structural properties comparable with those found in the literature, but created from other natural materials. Adsorption results of chromium on the activated carbon material obtained, gave a low removal rate (33.7%) in the absence of applied electrical potential. The application of negative potential (−0.7 V and −1.4 V) increases the adsorption of chromium up to (90% and 96%), respectively. On the other hand, a positive potential (+1.4 V) allows desorption of up to 1.38× the contaminant absorbed.

Finally, we can say that the treatment method chosen in this study provides very acceptable chromium removal efficiency. Improved results obtained by adjustment of the process conditions might make it possible to get even more utility from this natural waste.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

References

[1] Kobya M, Demirbas E, Senturk E, Ince M. Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Bioresour Technol, **96**, 1518 (2005). https://doi.org/10.1016/j.biortech.2004.12.005.

[2] Calero M, Hernáinz F, Blázquez G, Martín-Lara MA, Tenorio G. Biosorption kinetics of Cd (II), Cr (III) and Pb (II) in aqueous solutions by olive stone. Braz J Chem Eng, **26**, 265 (2009). https://doi.org/10.1590/S0104-66322009000200004.

[3] Derbyshire F, Jagtoyen M, Andrews R, Rao A, Martin-Gullón I, Grulke EA. Carbon materials in environmental applications. Chem Phys Carbon, **27**, 1 (2000).

[4] Cases JM, Villiéras F, Michot L. Les phénomènes d'adsorption, d'échange ou de rétention à l'interface solide-solution aqueuse. 1. Connaissance des propriétés structurales, texturales et superficielles des solides. C R Acad Sci Ser IIa: Sci Terre Planetes, **331**, 763 (2000). https://doi.org/10.1016/S1251-8050(00)01495-6.

[5] Suhas, Carrott PJM, Ribeiro Carrott MML. Lignin–from natural adsorbent to activated carbon: a review. Bioresour Technol, **98**, 2301 (2007). https://doi.org/10.1016/j.biortech.2006.08.008.

[6] Baccar R, Bouzid J, Feki M, Montiel A. Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions. J Hazard Mater, **162**, 1522 (2009). https://doi.org/10.1016/j.jhazmat.2008.06.041.

[7] Verheijen J, Vogg H. Metal extraction from flyash. Proceedings of the International Municipal Waste Incineration Workshop, Montreal, QC, 381 (1987).

[8] Walsh AR, O'Halloran J. Chromium speciation in tannery effluent. II: speciation in the effluent and in a receiving estuary. Water Res, **30**, 2401 (1996). https://doi.org/10.1016/0043-1354(96)00174-1.

[9] Tiravanti G, Marani D, Passino R, Santori M. Synthesis and characterization of cellulose xanthate chelating exchangers for heavy metal removal and recovery from wastewaters. Stu Environ Sci, **34**, 109 (1988). https://doi.org/10.1016/S0166-1116(08)71283-4.

[10] Esmaeili A, Mesdaghi nia A, Vazirinejad R. Chromium (III) removal and recovery from tannery wastewater by precipitation process. Am J Appl Sci, **10**, 1471 (2005). https://doi.org/10.3844/ajassp.2005.1471.1473.

[11] Strohl JH, Dunlap KL. Electrosorption and separation of quinones on a column of graphite particles. Anal Chem, **44**, 2166 (1972). https://doi.org/10.1021/ac60321a012.

[12] Alkire RC, Eisinger RS. Separation by electrosorption of organic compounds in a flow-through porous electrode : I. mathematical model for one-dimensional geometry. J Electrochem Soc, **130**, 85 (1983). https://doi.org/10.1149/1.2119688.

[13] Donnet JP, Hueber F, Reitzer C, Odoux J, Riess G. Etude de l'action chimique des oxydants sur le noir de carbone. Bull Soc Chim Fr, **294**, 1727 (1962).

[14] Steenberg B. Adsorption and Exchange of Ions on Activated Charcoal, Almqvist and Wiksell, Uppsala (1944).

[15] Anundo Polania L. Contribution à L'étude de la Fixation du Cyanure d'or et de Potassium sur les Charbons Actifs, Université de Haute-Alsace, Mulhouse, PhD Thesis (1986).

[16] Boehm HP. Chemical identification of surface groups. Adv Catal, **16**, 179 (1966). https://doi.org/10.1016/S0360-0564(08)60354-5.

[17] Mattson JS, Mark HB. Activated Carbon: Surface Chemistry and Adsorption from Solution, Marcel Dekker, New York (1971).

[18] Duranoğlu D, Trochimczuk AW, Beker Ü. A comparison study of peach stone and acrylonitrile-divinylbenzene copolymer based activated carbons as chromium(VI) sorbents. Chem Eng J, **165**, 56 (2010). https://doi.org/10.1016/j.cej.2010.08.054.

[19] Julien F. Contribution à L'étude des Mécanismes de L'adsorption de Molécules Organiques sur Différents Types de Charbons Actifs, Université de Poitiers, Poitiers, PhD Thesis (1994).

[20] Seron A, Benaddi H, Beguin F, Frackowiak E, Bretelle JL, Thiry MC, Bandosz TJ, Jagiello J, Schwarz JA. Sorption and desorption of lithium ions from activated carbons. Carbon, **34**, 481 (1996). https://doi.org/10.1016/0008-6223(95)00200-6.

[21] Kim JS, Jung CH, Oh WZ, Ryu SK. Electrosorption and separation of Co^{2+} and Sr^{2+} ions from decontaminated liquid wastes. Carbon Sci, **3**, 6 (2002).

[22] Alfarra A, Frackowiak E, Béguin F. Mechanism of lithium electrosorption by activated carbons. Electrochim. Acta **47**, 1545 (2002).