ELECTROCHEMICAL DECONTAMINATION OF CREOSOTE EFFLUENT LOADED WITH POLYCYCLIC AROMATIC HYDROCARBONS

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Summary

Creosote wastes contain toxic and carcinogen compounds, namely polycyclic aromatic hydrocarbons (PAHs). One concern involved in the use of creosote is the long-term release of organic toxic compounds into the environment. The treatment of creosote oily effluent has been carried out using electrochemical treatment. Different types of electrolytic cells (parallelepipedic and cylindrical cells) comprising of different electrode material (Ti/SnO_2, Ti/IrO_2 and Ti/RuO_2) were use. Current density and retention time played important roles for PAHs degradation efficiency, whereas circulation flow rate and oxygen injection slightly influenced the removal efficiency. Finally, the best and simplest operating conditions (82-84% of PAHs removal) determined for PAHs degradation in COE were obtained at a current density of 15 mA/cm^2 through 90 min of treatment with a recycling rate of 3.6 L/min but without O_2 injection in the close loop.

1. Introduction

Creosote oil is an industrial product that used as wood preservative. Creosote-treated woods are widely used as railway sleepers and pole for the transport of electricity or for telephone lines and as exterior wood for use in garden (Becker *et al*., 2001; Engwall *et al*., 1999; Gouvernement du Canada, 1993; Ikarashi *et al*., 2005). Creosote treated wood has been classified as dangerous waste because the presence of PAHs (up to 85%) in creosote solution (Engwall *et al*., 1999; Mueller *et al*., 1989). Most of these PAHs are stable and difficult to oxidize by the traditional biological methods and require chemical or physico-chemical treatments.

Electrochemical oxidation treatment can be used as an alternate method for PAHs degradation. Electro-oxidation process opens new ways and can advantageously replace or complete already existing processes. Hydroxyl radicals are the most oxidative species and they have been shown to degrade many organic compounds including PAHs. There are two types of anodic oxidations that are indirect oxidation process and direct oxidation (Martinez-Huitle and Ferro, 2006; Drogui *et al*., 2007). The latter may be achieved through mineralization with hydroxide radical ($OH^\bullet$) produced by dimensionally stable anodes having high oxygen overvoltage, such as SnO_2, PbO_2 and IrO_2 (Comninellis, 1994; Comninellis and Pulgarin, 1991; Panizza *et al*., 2000).
The former (indirect oxidation) may be achieved through electrochemical generation of a mediator in solution (such as, HClO, HBrO, H_2O_2, $H_2S_2O_8$, and others) to convert toxic organics to a less harmful product by using graphite or noble metal anodes (Drogui *et al*., 2001; Rajeshwar and Ibanez, 1997).

The main objective of the present study was to examine the feasibility of electro-oxidation process in treating creosote solution and to determine the optimal operational conditions to efficiently remove PAHs using Ti/RuO_2 expanded, Ti/IrO_2 and Ti/SnO_2 circular or cylindrical mesh anode. The creosote effluent was a synthetic solution prepared from a commercial creosote solution in the presence of an amphoteric surfactant. Effectiveness was measured in terms of reduction in PAHs, carbon oxygen demand (COD), carbon organic total (TOC), oil and grease (O&G) and petroleum hydrocarbon (C_{10}-C_{50}). Finally, the reduction in toxicity of the solution to two different micro-organisms (*Vibrio Fischeri* and *Daphnia*) was measured. From that, expanded capacity to detoxification of creosote treated wood waste.

2.   Methodology
2.1   Electro-oxidation

Electrochemical conversion only transforms the non-biodegradable organic pollutants into biodegradable compounds, whereas electrochemical combustion yields water and carbon dioxide and no further treatment is then required. In this study, a particular attention is given to direct anodic oxidation. It has been admitted that the direct anodic oxidation is carried out using two steps (Comninellis, 1994; Gandini *et al*., 1998). The first reaction (Equation 1) is the anodic oxidation of water molecule leading to the formation of hydroxyl radicals ($OH^\bullet$) adsorbed on active sites on the electrode "*M*":

$$H_2O + M \rightarrow M[OH^\bullet] + H^+ + e- \tag{1}$$
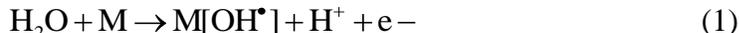
Subsequently, the oxidation of organics "*R*" is mediated by adsorbed hydroxyl radicals (Equation 2) and may result in fully oxidized reaction product as CO_2 (Equation 3).

$$R + M[OH^\bullet] \rightarrow M + RO + H^+ + e- \tag{2}$$

$$R + M[OH^\bullet] \rightarrow M + mCO_2 + nH_2O + H^+ + e- \tag{3}$$
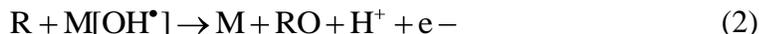
Where "*RO*" represents the oxidized organic molecule, which can be further oxidized by hydroxyl radical while it is continuously produced at anode electrodes. The accumulation of $OH^\bullet$ radicals favors the combustion reaction (Equation 3). The hydroxyl radicals are species capable of oxidizing numerous complex organics, non-chemically oxidizable or difficulty oxidizable (Pulgarin *et al*., 1994). They efficiently react with the double bonds -C=C- and attack the aromatic nucleus, which are the major component of refractory PAH. However, during direct anodic oxidation of organic pollutant, competitive reactions (parasitic reactions) can take place and limit hydroxyl radical formation, such as molecular oxygen formation (Equation 4):

$$H_2O + M[OH^\bullet] \rightarrow M + O_2 + 3H^+ + 3e- \tag{4}$$

Equation 4 can be minimized by using appropriate electrodes, such as over-potential electrodes. Graphite, noble metals, Pt, PbO_2, Ti/SnO_2, Ti/RuO_2, Ti/Pt and Ti/IrO_2 are commonly used as anode materials (Comninellis, 1994; Morao *et al*., 2004; Panizza *et al*., 2001).

2.2   Preparation of creosote oily effluent

Commercially-available creosote used in this study was provided by Stella-Jones Inc. (Montréal, QC, Canada). It was comprised of 50% (v v^{-1}) of creosote and 50% of petroleum hydrocarbons. The creosote effluent was prepared in a 100 mL glass-tank containing 30 to 50 g of oily-creosote in which 2 to 5 g of an amphoteric surfactant, CAS (Chemron, Ohio, USA) was added. Conditioning was carried out at a speed of 750 rpm for a period of time of 24 h. The mixing was achieved by a Teflon-covered stirring bar installed at the bottom of the 250 mL beaker. At the end of the conditioning stage, the suspension was transferred into a 20 L polypropylene tank containing 10 L of distilled water (final concentration = 3.0 to 5.0 g creosote L^{-1}). The resulting suspension constituted the synthetic COE, which was then subjected to settling for at least 24 h in order to separate the insoluble and suspended solids before electrochemical treatment.

2.3   Experimental setup and operation
2.3.1   Electrolytic cell C$_1$

The first, electrochemical degradation of PAHs in COE was carried out in a batch electrolytic cell made of acrylic material with a dimension of 12 cm (width) x 12 cm (length) x 19 cm (depth) (Figure 1a). The electrode sets (anode and cathode) consisted of ten parallel metal pieces with a distance inter-electrode of 1 cm. Five anodes and five cathodes alternated in the electrode pack. The electrodes were placed in stable position and submerged in COE. The anodes are presented in the form of expanded titanium (Ti) covered with ruthenium oxide (RuO$_2$), each one having a solid surface area of 65 cm^2. The cathodes are plate stainless steel (SS, 316L) and having a surface area of 110 cm^2 (10 cm width x 11 cm height). The electrodes were placed 2 cm from the bottom of the cell. Mixing in the cell was achieved by a Teflon-covered stirring bar installed between the set of electrodes and the bottom of the cell. For all tests, a working volume of 1.5 L of COE was used. The anodes and cathodes were connected respectively to the positive and negative outlets of a DC power supply Xantrex XFR 40-70 (Aca Tmetrix, Mississauga, ON, Canada) with a maximum current rating of 70 A at an open circuit potential of 40 V. Current was held constant for each run.

a) C$_1$ **b) C$_2$**   **c) C$_3$ and C$_4$**
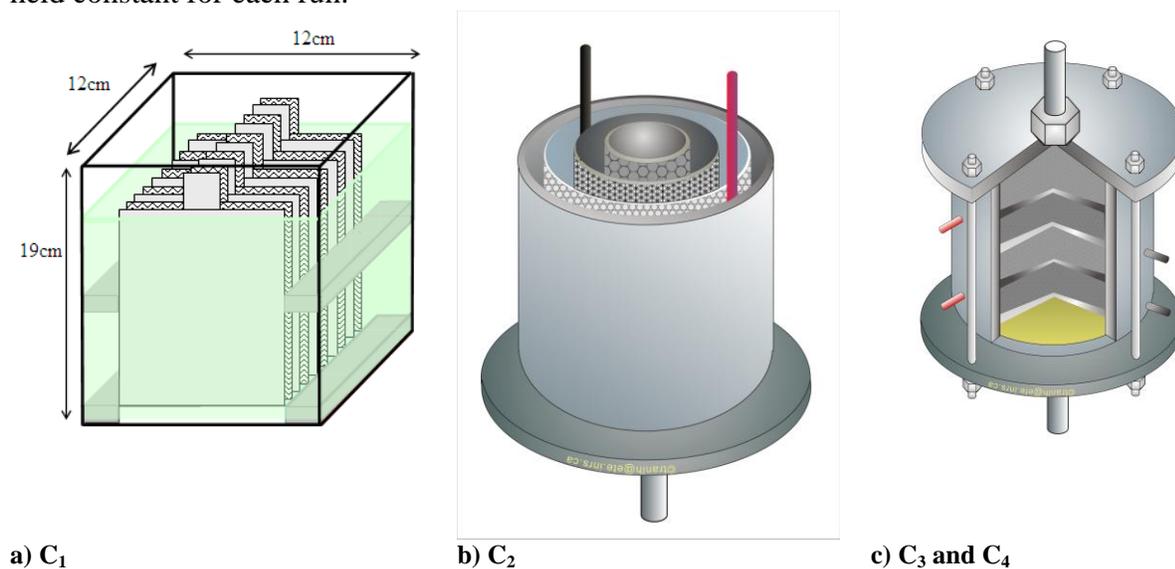
Figure 1   Electrolytic cells
1a) Using expanded electrodes C_1 (anode: Ti/RuO$_2$; cathode: Inox);
1b) Using cylindrical electrodes C_2 (anode: Ti/IrO$_2$; cathode: Ti);
1c) Using circular electrodes C_3 (anode: Ti/IrO$_2$; cathode: Ti) and C_4 (anode: Ti/SnO$_2$; cathode: Ti)

The first set of electro-degradation experiments consisted to test successively different operating parameters such as, current densities (3.08 to 12.3 mA cm^{-2}), retention times (20 to 180 min), initial pH (2.0 to 9.0), initial PAH concentration (240 to 540 mg L^{-1}), concentration of electrolyte (500 to 4000 mg Na$_2$SO$_4$ L^{-1}) and temperature (4 to 35°C) in view of determining the optimal conditions (reduce COEt and increase effectiveness) for treating COE. The pH was adjusted using sulphuric acid (H$_2$SO$_4$, 5 mol L^{-1}) or sodium hydroxide (NaOH, 2 mol L^{-1}). Sodium sulphate, sodium hydroxide and sulphuric acid were analytical grade reagent and supplied by Fisher Scientific. During these assays, only the residual PAH concentrations were measured to evaluate the performance of the experimental unit in oxidizing these refractory organic compounds. Once the appropriate values of these parameters were determined, the optimal conditions were repeated in triplicate to verify the effectiveness and the reproducibility of the electro-oxidation process. In addition to residual PAHs analyzed during the second set of experiments, DOC, TOC, O&G and C$_{10}$-C$_{50}$ were simultaneously measured. Likewise, biotests (Microtox and *Daphnia* tests) were carried out to have information about the toxicity of the initial and treated solution under optimum experimental conditions.

2.3.2   Electrolytic cell C_2, C_3 and C_4

Three cylindrical electrolysis cells (C2, C3 and C4), each having 2 L of capacity, were operated. The cells were made of PVC material with a dimension of 15 cm (height) x 14 cm (diameter) and all electrodes were presented in the form of expanded metal. The electrolytic C2 was comprised of two concentrically electrodes (Figure 1b).
The cylindrical anode electrode (14 cm height x 10 cm diameter x 0.1 cm thick) was titanium coated with iridium oxide (Ti/IrO$_2$) having a solid surface area of 270 cm^2 and a void area of 170 cm^2. The cylindrical cathode electrode (14 cm height x 12 cm diameter x 0.1 cm thick) was made of titanium (Ti) having a solid surface area of 325 cm^2 and a void area of 202 cm^2. A perforated cylindrical weir (2 mm diameter of holes) made of PVC material, was placed in the centre of the C_2 cell and allowed uniformly distributing the effluent toward the concentrically electrodes. Likewise, the cylindrical weir allowed wastewater to remain in the cell for a certain period. The weir had a diameter of 4.0 cm and a height of 14 cm.
By comparison, inside both electrolytic C_3 and C_4, the electrodes were circular disks (12 cm diameter) and titanium (Ti) was used as cathode with a solid surface area of 65 cm^2 and a void surface area of 45 cm^2 (Figure 1c). Circular Ti/IrO$_2$ and Ti/SnO$_2$ electrodes were respectively used as anode electrode in C_3 and C_4 cells with a solid surface area of 65 cm^2. The inter-electrode gap was 10 mm in the three electrolytic cells. The circular electrodes were supplied by Electrolytica Inc (Amherst, NY, USA), whereas the cylindrical electrodes were provided by Electech (Chardon, Ohio, USA).
The assays were carried out in a closed loop, depicted schematically in Figure 2. A one litre PVC reservoir (4), a centrifugal gear pump (6) and the electrolytic cell (1) (fully detailed in

Figure 1b,c) constitute the loop. The first assays were conducted in batch recirculation mode with a flow of wastewater entering the bottom of the cell. The recycle flow rate (varying from 1.8 to 7.3 L/min) was measured using a flow-meter (13). It is worth noting that the recycle flow (Q_R), induced by the centrifugal pump maintained the liquid phase in sufficient mixing. A needle valve (2) installed before a manometer (3) allowed controlling the hydrostatic pressure inside the cell. To be able to impose the desired liquid flow rate, a constant hydrostatic pressure of 0.2 PSI was imposed during the recirculating batch tests. The apparatus included oxygen injection (8) in the closed loop in order to favour the hydroxyl radical at anode electrode. The rate of oxygen injected was measured using a flow-meter (7). An oxygen probe (9) was connected to an oxymeter and installed in the pipe to measure dissolved oxygen concentration (8.0 to 20 mg/L) during electrolysis. The excess of oxygen was rejected out of the system by means of a venting pipe (10) fixed on the 1-litre PVC reservoir. At the start of each assay, the raw effluent was injected in the experimental unit by means of a funnel (14) installed in the pipe and connected to a peristaltic pump, which allowed adding a working volume of 4.5 L. An addition of sodium sulphate (0.5 g/L of Na_2SO_4) was necessary to increase the electrical conductivity. The electrochemical cells were operated under galvanostatic conditions, with current densities varying from 4.0 to 23 mA/cm^2 imposed during a period of treatment ranging from 10 to 180 min. While the experimental unit operated in continuous mode, valve 15 was closed, whereas valves 11 and 12 were opened. However, in the batch mode, valves 11, 12 and 15 were closed. Prior to continuous mode operation, the apparatus was initially operated in batch recirculation mode until the steady sate for PAHs degradation was reached, followed by feeding the electrolytic cell with untreated and freshly creosote effluent by means of peristaltic pump. The inlet (Q_E) and outlet (Q_S) flow rates were quite the same and ranged between 50 and 100 mL/min. It is worth noting that during the continuous mode operation, the centrifugal pump was closed and the recycling flow (Q_R) was null.

(1) : Electro-oxydation cell
(2) : Needle valve (0-5 bars)
(3) : Manometer
(4) : PVC tank (1 L)
(5) : Exhaust pipe
(6) : Centrifugal Pump
(7) : Air and O_2 flowmeter
(8) : Oxygen bottle
(9) : Oxygen probe
(10) : Venting pipe

(11) : Valve (Outlet of water in continuous operation mode)
(12) : Valve (Inlet of water in continuous operation mode)
(13) : Water flowmeter
(14) : Funnel for filling in effluent the experimental unit
(15) : Valve

Figure 2:   **Schematic view of the electro-oxidation cell with a recirculation loop**

2.4   Extraction and analysis of PAHs

Analyses of PAHs were carried out after extraction and purification on a solid phase using polypropylene-cartridges (Enviro-Clean sorbents, United Chemical Technology Inc.). The Enviro-Clean polypropylene-cartridge was successively conditioned by rinsing with 10 mL of dichloromethane (99.9% ACS reagent, EMD chemicals Inc., USA), 10 mL of methanol (99.8% reagent, Fisher Scientific, Canada) and 10 mL of distilled water. Subsequently, 500 mL of sample (creosote-oily solution) containing 10 mL of methanol was loaded onto the cartridge where it is entirely filtered drip. PAHs retained on the polypropylene-cartridge were then eluted with 10 mL of dichloromethane. After elution, the sample was transferred into a filter containing anhydrous $MgSO_4$ (EMD chemicals Inc., USA) in order to eliminate all traces of water, followed by evaporation of dichloromethane using a rotary evaporator (Büchi Rotavapor-R, Rico Instrument Co.). PAHs were quantified using a Perkin Elmer 500 gas chromatograph (GC) on a VF-5MS-FS column (0.25 mm diameter, 30 m long and 0.25 μm film thickness) coupled to a Perkin Elmer, model Clarus 500, mass spectrometer detector operated with a mass range between m/z 50 and 450. The GC column temperature was programmed as follows: it was first

maintained at 80°C for 2 min, then heated at a rate of 15°C min^{-1} up to 220°C and then heated at a rate of 5°C min^{-1} up to 320°C, after which it was held at this temperature for 5 min. The injection temperature was maintained at 250°C. The carrier gas was helium and column flow was maintained at 2.0 mL min^{-1}. A PAH mixture containing 44 PAHs at a concentration of 1000 mg L^{-1} in dichloromethane-benzene (3:1) (Supelco, Canada) was used as a standard for PAHs.

2.5   Organic measurements

COD determination was made by the Hach COD method (HACH, 1995) and a reading spectrophotometer Carry UV 50 (Varian Canada Inc.). TOC was measured using a Shimadzu TOC 5000A analyzer (Shimadzu Scientific Instruments Inc.) equipped with an autosampler. Samples BOD determinations with required controls were made by Standard Methods (APHA, 1999). The quality of the treated-solution was also measured in terms total O&G and C_{10}-C_{50} petroleum hydrocarbons. O&G were determined by gravimetric method which consisted in extracting fat and grease from sample with hexane at pH below 2.0 followed by the evaporation of the organic solvent. The concentration of petroleum hydrocarbons present in the samples was determined by comparing the total area of group of peaks of n-C_{10} to n-C_{50} with area of the standard curves obtained under similar reaction conditions.

2.6   Toxicity tests

The quality of treated-solution (versus untreated solution) has been evaluated using a biotest battery to have information about its toxic effect. Microtox and *Daphnia* bioassay tests were applied. Microtox analysis is a standardized toxicity test using the luminescent marine, *Vibrio fisheri* (Software MTX6, version 6.0, Microbics Corporation) (Environment Canada, 1992; USEPA, 1993). This test consisted of one control and six serial dilutions of each sample (1.5, 3.0, 6.25, 12.5, 25.0, and 50% v v^{-1}). The endpoint of Microtox test is the measurement of bioluminescence reduction. The bioluminescence emitted by *V. fisheri* was first measured after 10 min of incubation (without adding any sample, control assay), after which the creosote-solution (treated or untreated-solution) was added to the bacterial suspension. The bioluminescence reduction was determined after a 5, 15 and 30 min exposure to the contaminant. The toxicity effects were monitored as the average percentage of light emission inhibition compared to the control assay. By comparison, *Daphnia* bioassay test consisted in determining the lethal concentration for which at least 50% of mortality of crustacean *Daphnia magna* is observed after 48 h exposure to the contaminant. This test consisted of one control and five serial dilutions of each sample (6.25, 12.5, 25.0, 50.0, and 100% v v^{-1}). After 48 h exposure, the survival and death organisms was counted and the toxicity effect was evaluated using a statistic calculation software (Computer Basic, Spearman Karber tests, version 2.01, Microsoft) (Environnement Canada, 2000; Ministère de l'environnement du Québec, 2000).

3.   Results and Discussion
3.1   Creosote effluent characteristic

3.2   Electrochemical oxidation of PAHs in creosote solution

Several batch electrolytic tests were performed in order to determine economical and optimal conditions for PAH degradation in COE. Majors operating conditions investigated included: (i) current density; (ii) retention time; (iii) initial pH; (iv) electrolyte concentration; and (iv) temperature.

3.2.1   Effect of current density

Current density is one of the most important parameters that can affect organic removal. Table 3 indicates the initial untreated COE and residual PAH concentrations after treatment while imposing different current densities (3.08, 4.62, 6.15, 9.23 and 12.3 mA cm^{-2}) for 180 min. The control assay consisted only in agitating the COE in the electrolytic cell without imposing any current density. The yields of PAH degradations were obtained by subtracting the residual PAH concentration from the initial value recorded in COE and the resulting operation was divided by the same initial concentration of PAHs. A total PAH concentration of 476 mg L^{-1} was measured in the initial solution. By comparison, a concentration of 418 mg L^{-1} was recorded in the control assay and corresponded to an abatement of 13.2% of PAHs. The decrease in PAH concentration during the control assay was probably attributed to the volatilization of the fraction of the molecular organic while agitating the solution. For instance, some compounds such as, PYR, FLE, MEN were more sensitive to the volatilization than CAN, NAP and CHR. While the current density was imposed the degradation of PAHs increased from 72 to 82%. Considering the possible volatilization of some organic compounds, the real contribution of electro-oxidation for PAH degradation can be obtained by subtracting the yields of PAH removal (while imposing current density) from the yields recorded without current density. Thus, in our experimental conditions, the real yields of PAH degradation varied from 59 and 69%. The yields of PAH degradation increased with current density until 9.23 mA cm^{-2} and then remained quite stable at 12.3 mA cm^{-2}. Similar results have been recorded while studying electrochemical oxidation of phenol by using ruthenium mixed metal oxide electrode (Yavuz and Kaporal, 2006). Phenol removal of 47, 67 and 78% were obtained with current densities of 10, 15 and 20 mA cm^{-2}, respectively for a charge loading of 269 F m^{-3}. Using a current density of 9.23 mA cm^{-2}, the rates of PAH degradation (around 81 to 84%) were quite similar regardless of the number of aromatic rings (2-, 3-, 4-, 5- and 6-ring PAHs) of the compounds. Finally, the current density of 9.23 mA cm^{-2} was retained for the next step of the study. The power consumption was 78 kWh m^{-3} while the current density of 9.23 mA cm^{-2} was held constant for a period of treatment of 180 min.

Table 1   **PAH concentration (mg L^{-1}) before and after treatment using different current densities[a]**

PAHs	Initial solution	Control	Current densities (mA cm^{-2})				
		0.00	3.08	4.62	6.15	9.23	12.30
NAP	70.9	70.1	22.5	21.7	21.7	13.6	11.5
MEN	64.1	53.7	13.1	13.0	11.6	8.83	7.30
ACN	3.91	3.02	1.98	1.52	1.08	0.68	0.66

ACA	62.8	57.1	12.3	12.2	11.1	9.40	9.59
FLU	45.3	38.8	10.0	9.87	10.1	9.51	9.12
PHE	90.4	84.4	22.7	22.4	21.9	17.7	18.2
ANT	16.3	15.3	4.11	4.09	4.21	2.95	3.63
FLE	53.2	40.5	10.8	10.7	10.6	8.42	8.99
PYR	41.3	31.5	8.74	8.55	8.07	5.91	5.53
BAA	8.00	6.02	2.37	2.29	2.28	1.26	1.76
CHR	9.48	8.31	2.48	2.26	2.48	1.78	1.94
BJK	6.29	5.86	1.50	1.43	1.37	1.25	1.24
BAP	2.51	2.23	0.63	0.62	0.55	0.47	0.49
DAN	1.21	1.09	0.31	0.28	0.25	0.20	0.21
INP	0.18	0.17	0.08	0.08	0.06	0.05	0.05
BPR	0.53	0.43	0.19	0.17	0.16	0.08	0.08
Σ PAHs (mg L^{-1})	476	418	114	111	108	82.1	80.4
Removal (%)	-	13.4	72.0	73.5	75.7	82.1	81.6

[a]   Operating conditions: treatment time = 180 min, without initial pH adjustment (pH_i = 6.0), $[Na_2SO_4]$ = 0 mg L^{-1}, T = 21°C.

3.2.2   Effect of treatment time

In view of reducing the power consumption and further optimizing the electrochemical oxidation of COE, additional experiments were conducted by testing different retention times. During these assays, the current density of 9.23 mA cm^{-2} was imposed. During the first set of experiments a total PAH concentration of 513 mg L^{-1} was measured in the initial solution. By comparison, 474, 364 and 299 mg L^{-1} were recorded while imposing 0, 10 and 20 min, respectively. The PAH degradation yield increased with the retention time. However, it is surprising to see that, the initial concentration of PAHs recorded in the untreated solution was different to that measured at t = 0 min (i = 0 mA cm^{-2}) in the electrolytic cell. In fact, before each assay, 10 L of COE was prepared in a 20 L cylindrical tank from which 1.5 L was withdrawn and transferred into the electrolytic cell. PAH concentrations in the initial solution were measured using a sample obtained from the 20 L cylindrical tank, whereas the initial values measured at t = 0 min were obtained from a sample withdrawn in the electrolytic cell. Thus, this discrepancy can be attributed to two main factors. Firstly, the initial solution was not very homogenous, and secondly a fraction of PAHs could be deposited on the wall on the tank or on the electrode material, so that PAH concentrations initially measured in both tanks (cylindrical tank and electrolytic cell) were different. It was the reason for which, at the start of each set of experiment (before imposing the current density), a sample of COE (untreated sample) was withdraw from the cell and analyzed. During the 2nd set of experiment, a total concentration of 525 mg PAH L^{-1} was measured in the untreated solution. The application of electro-oxidation process allowed reducing PAH content and the residual concentration varied from 88.5 to 143 mg L^{-1} and contributed to removal of about 74 to 83% of PAHs depending on the retention time imposed. Figure 2 shows the changes in PAH degradation yield as a function of charge loading. Two different regions could be distinguished. When the charge loading is below 1 A.h L^{-1}, the yield of PAH degradation increased linearly with charge loading. Beyond 1 A.h L^{-1}, the rate of PAH degradation remained quite stable. These results are consistent with those obtained by Chen and Chen (2006) while oxidizing orange II dye molecular on titanium (Ti) recovered with boron-

doped diamond (BDD) electrode. The anodic oxidation of pollutant occurs heterogeneously. First, organic pollutants must be transported toward the anode electrode surface, and then be oxidized there. The organic pollutant degradation may be subjected either to current control or mass transfer control. In fact, at the start of the electrolysis, the PAH concentration was relatively high, and accordingly the PAH reduction rate was subjected to current control. As the PAH concentration was lowered to a certain level, the PAH reduction rate was subjected to the mass transfer control (Panizza *et al*., 2001). In that case, only a fraction of current intensity (or charge loading) supplied was used to oxidize pollutants, while the remaining charge loading was wasted for generation of oxygen. It was the reason for which the yields of PAH degradation remained stable in spite of high charge loading applied. Figure 3 presents also the change in energy consumption as a function of charge loading. The energy consumption varied in a linear fashion between 0.0 and 6.0 A.h L^{-1}, from 0.0 to 78 kWh m^{-3}. Since the maximum increase in PAH reduction rate was reached between 1.0 and 3.0 A.h L^{-1}, the energy consumption could be reduced by curtailing the charge loading at 3.0 A.h L^{-1}. Indeed, a charge loading of 3.0 A.h L^{-1} was selected (rather than 1.0 A.h L^{-1}) to further oxidize by-products resulting from PAH oxidation and, render the treated-solution less toxic. A charge loaded of 3.0 A.h L^{-1} corresponded to a period of treatment time of 90 min and the energy consumption was reduced to 41 kWh m^{-3} (rather than 78 kWh m^{-3}) as expected.
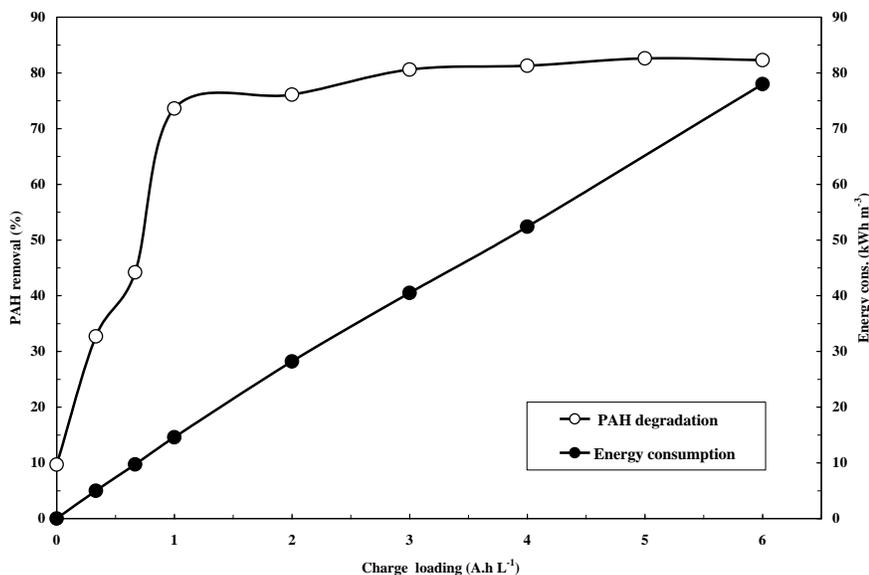
Figure 3   **Effect of charge loading on the yields of PAH degradation and on energy consumption (current density = 9.23 mA cm-2, without initial pH adjustment (pHi = 6.0), [Na2SO4] = 0 mg L-1, T = 21°C)**

3.2.3   Effect of initial pH

In order to know if the electrolysis cell could work well in oxidizing PAHs in a wide pH range, the removal efficiency at four different initial pH values (2.0, 4.0, 7.0, and 9.0) was investigated. Initial pH of the solution was adjusted using sulfuric acid (H_2SO_4, 5 mol L^{-1}) and sodium

hydroxide (NaOH, 2 mol L^{-1}). In addition, a control assay was carried out without pH adjustment (original pH was around 6.0). During these assays, the current density was maintained at 9.23 mA cm^{-2} and a retention time of 90 min was imposed. It was found that COE having an initial pH closed to the neutral value (pH 6.0 and 7.0) was more favorable for PAH reduction (PAH removal of 81 and 84% were recorded, respectively). This is consistent with the results of Yavuz and Kaporal (2006) while oxidizing phenol using ruthenium mixed metal oxide electrode. They reported that electro-oxidation without initial pH adjustment (initial pH around 7.0) was more effective in removing phenol, compared to pH 3.0 and pH 11.0. However, one study showed that the pH effect is not significant while oxidizing orange II dye on Ti/BDD anode at a current density imposed of 200 mA m^{-2} (Chen et Chen, 2006). The COD reduction (nearly 100%) at pH 1.2 was comparable with that at pH 12.0. Another study showed that the current efficiency increased from 3.0 to 13% as pH increased from 2.0 to 11.0 while oxidizing aniline on PbO_2 anode (Kirk *et al*., 1985). PAHs electro-oxidation rate variations with pH recorded in the present study are contradictory with those obtained by the authors mentioned above. This may be associated with the differences in properties of chemical compounds tested and the anodic electrode used. Finally, as the highest PAH removal yield (84%) recorded at pH 7.0 was quite similar to that measured (81%) without pH adjustment (original pH 6.0), it was not necessary to modify the initial pH before treatment.

3.2.4   Effect of supporting electrolyte

The addition of an electrolyte in solution during electrolysis can influence the treatment since it modifies the conductivity of the solution and facilitates the passage of the electrical current. Thus, various concentrations of sodium sulfate (Na_2SO_4 used as electrolyte) were added to the system and changes in PAH reduction rate were noted. The current density of 9.23 mA cm^{-2} was held constant over the retention time of 90 min without initial pH adjustment. The PAH degradation yields (80 to 83%) were quite similar regardless of supporting electrolyte concentration imposed. There was not a significant effect of electrolyte concentration on the oxidation efficiency in the investigated range of 500 to 4000 mg Na_2SO_4 L^{-1}. This is consistent with the results of Chen and Chen (2006) while oxidizing orange II dye synthetic solution. The same trend has also been recorded by Fernandes *et al*. (2004). However, these results are not consistent with those obtained by Alcàntara *et al*. (2008) while studying a two stage process combining soil electrokinetic remediation and liquid electrochemical oxidation for the remediation of polluted soil with organic compounds using phenanthrene-spiked kaolinite. The liquid from the cathode chamber was treated in an electrochemical cell with graphite electrode by applying a 5 V direct current. The addition of Na_2SO_4 (0.1 M Na_2SO_4) clearly increased the degradation rate about 6-7 fold compared to the experiment without electrolyte. In our experimental conditions, even if the supporting electrolyte (Na_2SO_4) had not an effect on the performance of PAH degradation, it was interesting to add a certain quantity of electrolyte in order to reduce the power consumption and consequently, to reduce the COEt related to the electrochemical treatment. For instance, for the same oxidation efficiency of 80% recorded, the treatment COEt (including only, energy and electrolyte COEt) was estimated to 1.32 US\$ m^{-3} while adding 500 mg Na_2SO_4 L^{-1} in COE, compared to 2.52 US\$ m^{-3} recorded without any addition of supporting electrolyte.

3.2.5 Effect of temperature

The effect of the temperature on PAH degradation was examined by controlling the temperature of the solution in a water bath. Figure 3 shows residual PAH concentration of different number of aromatic rings (2-, 3- and 4-ring PAHs) at different temperatures (4, 21 and 35°C). These results compare the untreated-solution (initial solution maintained at the desired temperature without current imposition) with electro-oxidation of solution (treated-solution). Firstly, considering the untreated-solution subjected but maintained only, at different temperatures, it can be seen that residual 2-ring PAH concentrations increase slightly while increasing the temperature from 4 to 21°C. The same trend could be observed for 4-ring and 3-ring PAHs. The temperature of 21ºC enhanced PAH solubilization. However, while maintaining the temperature to 35°C, residual PAH (2-, 3- and 4-ring) concentrations decreased compared to that recorded at 4°C or at 21°C. For instance, at 21°C, the 2-ring PAH concentration measured was 26.0 mg L^{-1}. When the temperature increased to 35°C, the residual 2-ring PAH concentration was lowered to 14.9 (42.9% 2-rings PAH reduction). It is believed that, from a certain level of temperature, the heat induced a loss of a fraction of PAHs either by volatilization or by PAH deposition on the wall of the electrolytic cell so that PAH concentrations in solution were reduced. Considering now the effectiveness of electro-oxidation process at different temperatures imposed, it can be seen that about 50% of PAHs was oxidized at 4°C. However, the yields of PAH removal increased to around 80% while increasing the temperature either at 21 or 35°C. The increase of the temperature accelerates the electrochemical decomposition of PAHs.
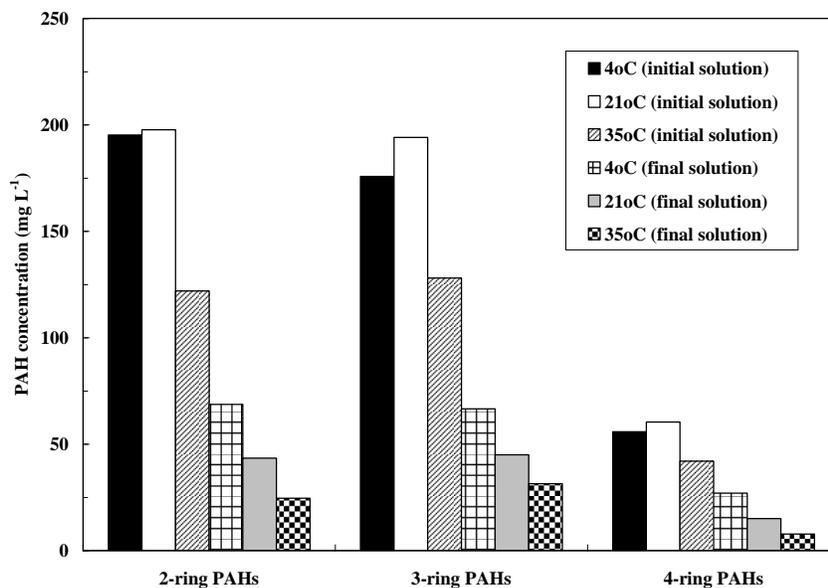
Figure 4 :   **Effect of temperature on the residual PAH concentrations (current density = 9.23 mA cm^{-2}, treatment time = 90 min, without initial pH adjustment (pH$_i$ = 6.0), [Na$_2$SO$_4$] = 500 mg L^{-1})**

These results were consistent with several works mentioned in the literature (Chen and Chen, 2006; Sharifian and Kirk, 1986; Tahar and Savall, 1998; Yavuz and Kaporal, 2006;). Since the

temperature of the solution naturally (without temperature control) increased from about 20 to 25°C during electrolysis, it was not necessary to adjust the temperature to have its beneficial effect on PAH degradation.

3.3   Organic and toxicity reduction

In addition to PAH measurements, other parameters such as O&G, C_{10}-C_{50}, COD and TOC related to the organics were also measured in the initial and treated-solution. The results are summarized in Table 9. The residual O&G and C_{10}-C_{50} concentrations recorded at the end of the treatment were 290 mg L^{-1} and 27 mg L^{-1}, respectively, compared to 940 mg O&G L^{-1} and 170 mg O&G L^{-1} measured in the initial solution. A yield of 69% of O&G removal was recorded, whereas 84% of C_{10}-C_{50} was removed.

On the other hand, reduction in COD and TOC were 62% and 27%, respectively. The residual concentrations recorded at the end of electro-oxidation were 809 mg COD L^{-1} and 174 mg TOC L^{-1}. By comparison, 2109 mg L^{-1} and 237 mg L^{-1} were measured respectively in the initial solution. The relatively low yield of TOC removal (27%) compared to 62% of COD removal, indicated that only a small fraction of PAH was completely oxidized into water and carbon dioxide, the majority of the pollutants being transformed into small molecules that reduce the oxygen demand in the treated-solution. The residual molecules in COE required less oxygen for oxidation and should be more easily degradable by a subsequent biological treatment (Comninellis and Pulgarin, 1993; Panizza *et al*., 2006). It is the reason for which the COD was reduced from 2109 mg L^{-1} to 809 mg L^{-1} after electrolysis. In fact, the electrolytic cell broke the double bonds producing smaller molecules. It is worth noting that, during electrolysis, organic pollutants can be subjected to two different paths in anodic oxidation: electrochemical conversion or electrochemical combustion (Comninellis, 1992; Drogui *et al*., 2001). Electrochemical conversion only transforms the non-biodegradable organic pollutants into biodegradable compounds, whereas electrochemical combustion yields water and carbon dioxide and no further treatment is then required. In the present study, electrochemical conversion was the predominant reaction. Electrochemical oxidation was also investigated by Panizza *et al*. (2000) for the treatment of real chemical wastewater containing naphthalene- and anthraquinone sulphonic, by combining direct and indirect electro-oxidation. Three types of anode electrodes were used (Ti/Pt, Ti-Ru-Sn-SbO_2 and carbon felt) either in the presence of a supporting electrolyte NaCl (1.0 to 10 g/L) or without addition of electrolyte at a current density of 50 mAcm^{-2}. It was found that the Ti/Pt anodes offered better performance in the presence of 5.0 g/L of NaCl. For instance, about 67 % of COD was removed at a 7.0 Ah L^{-1}, whereas only 40 % of COD was reduced without addition of electrolyte. In spite of combining both direct and indirect effect of electrical current during electrolysis, COD abatement (67 %) recorded by Panizza et al. (2000) was quite similar to the value measured (62 %) while treating COE by means of only direct anodic oxidation. Likewise, the current density (50 mAcm^{-2}) and the charge loading (7.0 Ah L^{-1}) applied by Panizza *et al*. (2000) were respectively 5 and 2 times higher than the values imposed during electrochemical oxidation of COE (9.23 mA.cm^{-2} and 3.0 Ah L^{-1}, respectively). In fact, the effectiveness of the electro-oxidation process in removing organics

depends on the composition of effluent and, more importantly, on the criteria design and operating condition of the electrolytic cell.

Microtox and *Daphnia* bioassay tests were carried out to estimate the toxic effect of the initial and treated solutions under optimum experimental conditions. The Microtox test used the luminescent marine bacterium (*Vibrio fisheri*) and the toxicity results effects were monitored as the average percentage of light emission inhibition. The *Daphnia* test consisted in determining the lethal concentration for which at least 50% of mortality of crustacean *Daphnia magna* is observed after 48 h exposure to the contaminant. The results are given in toxicity unit (TU) and are summarized in Table 2. The comparison of the results shows a reduction of the toxicity while applying electro-oxidation treatment. Thus, relatively high toxicity of 4762 TU was measured for crustacean *Daphnia* and 1000 TU was recorded for luminescent bacterium *Vibrio fisheri* in the initial solution. By comparison, only 453 TU and 200 TU were recorded after treatment, respectively. It corresponded to 91% of toxicity reduction on crustacean *Daphnia*, whereas 80% of toxicity reduction was accomplished on luminescent bacterium *V. fisheri.*

Table 2   Concentrations of parameters related to the organics and toxicity measurements before and after treatment in optimal conditions[a]

Parameters		Solution		Removal
		Initial	Final	(%)
Organics	O&G (mg L^{-1})	940	290	69.2
	(C$_{10}$–C$_{50}$) (mg L^{-1})	170	27	84.1
	COD (mg L^{-1})	2102	809	61.5
	TOC (mg L^{-1})	237	174	26.6
Toxicity	*Daphnia magna* test (TU)	4,762	453	90.5
	Vibrio fischeri test (Microtox) (TU)	1000	200	80.0

[a]   Operating conditions: current density = 9.23 mA cm^{-2}, treatment time = 90 min, without initial pH adjustment (pH$_i$ = 6.0), [Na$_2$SO$_4$] = 500 mg L^{-1}, T = 21°C.

3.4   Comparison between different types of electrochemical cells and electrode materials

According to the results mentioned above, the electrolytic cell C$_1$ operated at current density of 9.23 mA cm^{-2} through 90 min of treatment in the presence of 500 mg L^{-1} of Na$_2$SO$_4$ but without pH and temperature adjustment gave the best performance of electro-oxidation of COE. In this part, different electrolytic cells and electrode materials were evaluated for capacity of PAH deduction by electro oxidation.

The assays were carried out using electrolytic cells made up of either Ti/IrO$_2$ or Ti/SnO$_2$ anode electrodes at current densities of 9.0 mA/cm^2 and 12 mA/cm^2 for 90 min.

Table 3   **Treatment of creosote oily effluent using different electrolytic cells**

Parameters	Electrolytic cells					
	C_2		C_3		C_4	
Anodic current density (mA/cm^2)	9	12	9	12	9	12
Current intensity (A)	2.4	3.2	1.2	1.6	1.2	1.6
Anode electrode	Ti/IrO$_2$	Ti/IrO$_2$	Ti/IrO$_2$	Ti/IrO$_2$	Ti/SnO$_2$	Ti/SnO$_2$
Cathode electrode	Ti	Ti	Ti	Ti	Ti	Ti
Geometric form	concentric	concentric	circular	circular	circular	circular
Recycling rate (L/min)	3.6	3.6	3.6	3.6	3.6	3.6
Treatment time (min)	90	90	90	90	90	90
Average voltage (V)	7.4	9.5	7.1	9.7	9.8	10.5
Initial pH	6.0	6.0	6.0	6.0	6.0	6.0
Final pH	6.9	7.1	7.8	7.3	7.3	7.5
Energy cons. (kWh/m^3)	6.14	9.50	3.09	5.54	4.33	6.00
Energy cost ($/m^3)	0.37	0.57	0.19	0.33	0.26	0.36
Electrolyte cost ($/m^3)	0.15	0.15	0.14	0.14	0.14	0.14
Total cost ($/m^3)	0.52	0.72	0.33	0.48	0.40	0.50
Σ PAHs (before treatment)	146	140	146	146	155	155
Σ PAHs (after treatment)	43.0	33.4	27.9	28.0	44.5	32.2
Removal (%)	67.3	73.5	79.8	78.0	74.8	82.4

Table 3 presents initial and final conditions of each test as well as PAHs degradation rates obtained during treatment using different electrolytic reactors, C_2, C_3 and C_4. The initial pH was around 6.0, whereas at the end of the treatment the values varied from 6.9 to 7.8. The power consumption has been evaluated between 3.09 and 9.50 kWh/m^3, and the highest consumption was obtained for C_1 (6.14 and 9.50 kWh/m^3) comprising of cylindrical electrodes. This was mainly due to higher current intensities imposed to reach the desired current densities with regard to high surface area of cylindrical anode in the C_2. For instance, for the same current density of 9.0 mA/cm^2 and the same nature of electrode of Ti/IrO$_2$ imposed (comparison between C_2 and C_3), the current intensities required were 2.4 A and 1.2 A, respectively, whereas the average voltage was around 7.1 or 7.4 using either the C_2 or the C_3. However, considering the energy consumption, it can be seen that the electrical energy (6.14 kWh/m^3) using C_2 was approximately twice higher than that (3.09 kWh/m^3) recorded with C_3. This confirms that the parameters that influenced the energy consumption during assays using C_2 and C_3 is the current intensity and hydrodynamic conditions. The efficacy of the electro-oxidation process in terms of PAHs removal from COE using different electrolytic cells was in the following order: C_4 (75 to 82%) $\geq$ C_2 (78 and 80%) > C_1 (67 to 74%). In fact, the electrolytic cells (C_3 and C_4) including circular electrodes were more effective than the other one comprised of cylindrical electrodes. Considering both electrolytic cells (C_2 and C_3) for which the same material anode electrode (i.e., Ti/IrO$_2$) was used, it can be seen that the PAHs removal yields (80 and 78%, respectively) using the C_3 were better than those recorded (67 and 74%, respectively) using the C_2 while imposing respectively 9.0 and 12 mA/cm^2 of current densities. This can be attributed to the different hydrodynamic conditions (or mass transfer coefficient) imposed inside the cells. It is well-known that, hydrodynamic conditions inside the reactors are greatly linked to the cell configuration or

cell design (Kim *et al.* 2003; Rajeshwar and Ibanez, 1997; Wendt and Kreysa, 2001; Chen, 2004). Indeed, in the direct anodic oxidation, the oxidation of pollutants occurs heterogeneously. Pollutant must be transported to the electrode surface first, and then be oxidized there owing to hydroxyl radical formation (OH$^{\bullet}$) (Drogui *et al.*, 2001; Grimm *et al.*, 1998; Martinez-Huitle and Ferro, 2006). In the C_3, the liquid arrived rapidly and directly on the anode material and passed through the cathode material, followed by the circulation through a second anode and cathode electrodes. By comparison, in the C_2 comprised of cylindrical electrodes, the liquid firstly arrived in the centre of the cell inside a perforated cylindrical weir, before being distributed gradually and successively toward the anode and cathode electrodes. From the hydrodynamic descriptions (mentioned above), it is believed that the mass transfer between electrode and electrolyte was better inside the C_3, resulting in an increase in PAHs oxidation rates by comparison to the C_2. On the other hand, in view of putting into evidence the influence of anode electrode material on PAHs removal from COE, additional experiments were conducted by using Ti/SnO$_2$ circular electrodes (C_4). The hydrodynamic conditions and the configuration of the C_3 and C_4 were the same; all parameters were kept constant with the exception of the anode material. For the relatively high current density of 12 mA/cm^2 imposed, the highest yield of PAHs degradation (82.4%) was recorded using Ti/SnO$_2$ anode electrode installed in the C_3 in comparison to 78% PAHs removal obtained with Ti/IrO$_2$ anode using the C_2 for the same current density imposed. As reported by Comninellis and Nerini (1995), Comninellis (1992) and Feng *et al.* (2003), tin oxide is one of the noble metal oxides having a better performance for organic compounds degradation in comparison to traditional electrodes (Pt, IrO$_2$ and RuO$_2$). This is attributed to the highly crystalline nature of tin oxide, which catalyzes the reaction of electrochemical oxidation (Comninellis, 1992). In fact, the nature of the electrode material strongly influences both the selectivity and the efficiency of the direct oxidation process. Based on the Comninellis model, two types of anode electrodes can be distinguished: *actives electrodes* and *non-active electrodes* (Comninellis, 1994). In both cases, the first reaction (Equation 1) occuring in the direct oxidation process is the oxidation water molecules leading to the formation of adsorbed hydroxyl radicals. Indeed, with *active electrodes* there is a strong interaction between the electrode (M) and the hydroxyl radical (OH$^{\bullet}$). Adsorbed hydroxyl radicals may interact with the anode, forming a so-called higher oxide MO (Equation 5):

$$M(OH^{\bullet}) \rightarrow MO + H^+ + e- \qquad (5)$$

Using such electrodes, the redox couple MO/M acts as a mediator in the oxidation of organic pollutants R (present in aqueous solution). This reaction is in competition with the side reaction of oxygen evolution, which is due to the chemical decomposition of the higher oxide:

$$MO + R \rightarrow M + RO \qquad (6)$$

$$MO \rightarrow M + \frac{1}{2}O_2 \qquad (7)$$
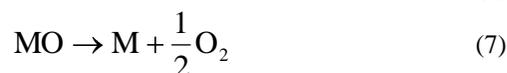
It is to be noted that the oxidative reaction with the surface redox couple MO/M is much more selective than the reaction directly involving hydroxyl radicals (Martínez-Huitle and Ferro, 2006; Martínez-Huitle and Brillas, 2009).

In contrast, with a *non-active electrode*, weak interactions exist between hydroxyl radical and the surface, so that that the oxidation of organics is mediated by hydroxyl radical and may results in fully oxidized reaction products such as follows:

$$R_{(aq)} + xM(OH^\bullet)_{ads} \rightarrow xM + Mineraliza\,tion\,(products) + yH^+ + ye- \qquad \textbf{(8)}$$

Where "x" and "y" are the stoichiometric coefficients. This reaction is in competition with the side reaction of the anode discharge of these radicals to oxygen.

$$M(OH^\bullet)_{ads} \rightarrow M + \frac{1}{2}O_2 + H^+ + e- \qquad \textbf{(9)}$$
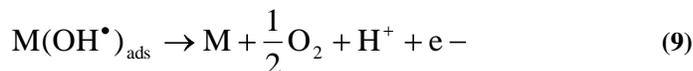
Several authors argue that, direct oxidation by Ti/IrO_2 anodes occurs through the formation of a higher oxide $M-O_{x+1}$ in the lattice rather than hydroxyl radicals owing to a higher adsorption enthalpy of the M-OH (Kapalka *et al.*, 2008; Martínez-Huitle and Ferro, 2006; Martínez-Huitle and Brillas, 2009). By comparison, on Ti/SnO_2 anodes, hydroxyl radicals play an important role due to the weak interaction between the hydroxyl and the electrode surface. As a general rule, the weaker the interaction, the higher is the anode reactivity for organics oxidation. This difference in the two types of electrodes (Ti/IrO_2 and Ti/SnO_2) explains the difference observed in the direct oxidation efficiency recorded.

3.5   Combining successively batch and continuous electro-oxidation treatment of creosote oily effluent

Three sets of experiments were performed to evaluate the performance of the electro-oxidation process while combining successively batch and continuous mode operations. During these assays, a constant current density of 15 mA/cm^2 was imposed for various inlet flow rates (50, 75 and 100 mL/min). The experimental conditions are summarized in Table 4. For the first set of experiments, the electrochemical system was previously maintained in the recirculating batch test (run A, 3.6 L/min of recycling flow rate) for 90 min, followed by the continuous mode operation (runs B to F) by imposing a constant inlet flow rate at 50 mL/min, which corresponded to 90 min of HRT (hydraulic retention time). By comparison, during the second set of experiment (runs H to K) 60 min of HRT was imposed in continuous mode operation by imposing a constant inlet flow of 75 mL/min, whereas the system was previously maintained in the recirculating batch test (run G, 3.6 L/min of recycling flow rate) for 90 min. Similarly to the 1st and 2nd set of experiments, a recirculating batch test (run L) was carried out prior to continuous mode operation (runs M to O) during the third set of experiment where 45 min of retention time (100 mL/min of inlet flow rate). The interest of imposing recirculating batch tests (Runs A, G and L) was to maintain initially a steady state inside the cell prior to start the continuous run tests. The results are presented in Table 4. This table compares sum of PAHs concentration measured in the inlet solution versus those recorded in the outlet solution. As expected, the best performance of the electrolytic C_4 operated in continuous mode was obtained while a HRT of 90 min was imposed. Residual PAHs concentration varied from 19.1 to 34.4 mg/L compared to 150 mg/L of PAHs continuously injected inside the electrochemical system. By comparison, while decreasing HRT (60 or 45 min), residual PAHs concentration increased rapidly and residual concentrations up to 80 and 90 mg/L could be recorded in the outlet solution (compared to 176 mg/L injected in the system). Fig. 5 represents the change in PAHs degradation with reaction time for various HRT. The values reported correspond to the values obtained after a period of time equal at least to three HRT (i.e. when the initial effluent

electrolyzed in the recirculating batch test was completely replace by freshly effluent). The percentage of PAHs oxidized remained in a steady state (around 85%) for a long period of time (from 300 to 1 200 min), then slightly decreased to 79% of total PAHs removal. The slight decrease of degradation efficiency can probably due the formation of organic substances on the electrode surface that reduce its electrode active surface. Nagata *et al*. (2006) analyzed the electrode surface (Ti/Pt anode electrode) before and after the continuous electrochemical by using X-ray photoelectron spectrometry (XPS). Before treatment, a big Pt peak, a small oxygen and carbon were observed, translating to the fact that electrode surface was comprised a clean Pt. However, after treatment a big carbon peak was observed instead of the Pt peak, meaning that the electrode surface was covered with organic substances that were formed during the treatment of organic-containing effluent. A similar behaviour has been observed for the oxidation of other aromatic compounds (Panizza and Cerisola, 2008; Gherardini *et al*. 2001; Iniesta et al. 2001; Canizares *et al*. 2004). From Fig. 5, it can be seen that PAHs degradation efficiency decrease rapidly using 60 min of HRT (with a relatively high slope). Degradation efficiency passed from 77% to 54% between 360 min and 1 080 min of treatment period. In fact, the formation of organic substances on the electrode surface increased while HRT decreased to 60 min. Otherwise, while further decreasing HRT, the percentage of PAHs degradation was low, but it remained quite stable around 50%, meaning that the process of the formation of organic substances on the electrode surface decreased owing to a relatively high linear velocity of liquid. In all case, during continuous treatment, the electrode surface can be easily recovered with organics dependently on HRT imposed. This situation may affect the treatment performance in a long term experiment. To overcome this process, the polarity inversion during the treatment could be one of the easier and feasible regeneration methods of the electrode surface.

Table 4   **Combining batch and continuous mode operations for the treatment of COE using experimental C$_3$ (Ti/SnO$_2$)**

Experim ental runs	Operating mode	Current density (mA/cm^2)	Recycling flow rate (L/min)	Inlet flow rate (mL/min)	Outlet flow rate (mL/min)	Retention time (min)	Treatment time (min)	Σ PAH inlet conc. (mg/L)	Σ PAH outlet conc. (mg/L)
A	Batch	15	3.6	0.0	0.0	90	90	150	30.2
B	Continuous	15	0.0	50	50	90	60	150	25.4
C	Continuous	15	0.0	50	55	90	300	150	19.1
D	Continuous	15	0.0	50	55	90	360	150	21.2
E	Continuous	15	0.0	50	54	90	1080	150	23.5
F	Continuous	15	0.0	50	52	90	1440	150	34.4
G	Batch	15	3.6	0.0	0.0	90	90	176	27.6
H	Continuous	15	0.0	75	75	60	60	176	38.1
I	Continuous	15	0.0	75	77	60	360	176	40.8
J	Continuous	15	0.0	75	76	60	720	176	60.2
K	Continuous	15	0.0	75	76	60	1080	176	80.0
L	Batch	15	3.6	0.0	0.0	90	90	176	26.6
M	Continuous	15	0.0	100	100	45	60	176	65.7
N	Continuous	15	0.0	100	100	45	360	176	84.5
O	Continuous	15	0.0	100	100	45	720	176	90.2
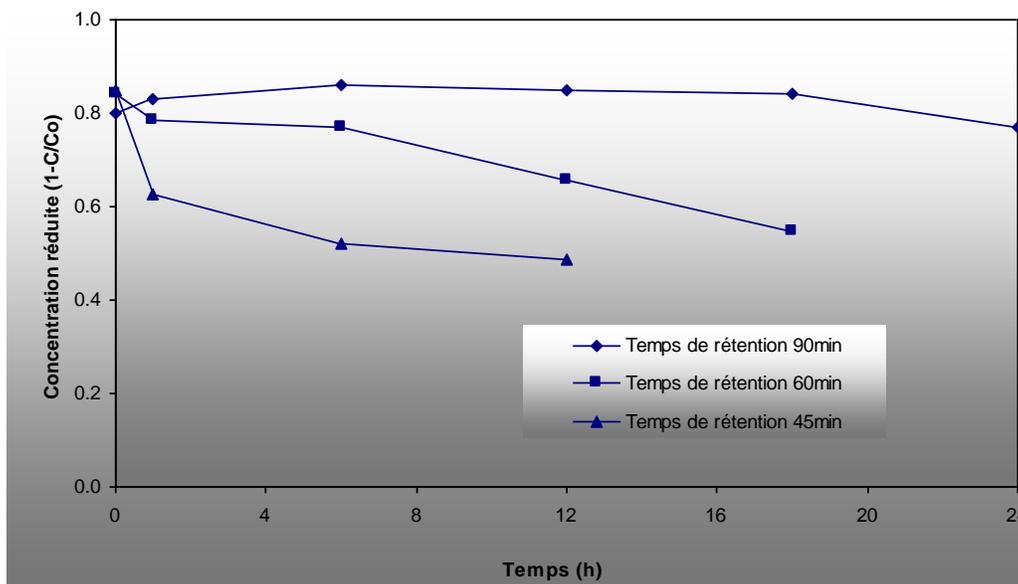
Figure 5   **Variation of normalized concentration with the reaction time using the electrochemical C_4 during continuous mode operation at different HRT (operating conditions: current density: 15 mA/cm^2). Values reported after a period of time equal to three HRT**

4.   Conclusions

This study investigated creosote oily effluent containing PAHs using Ti/IrO$_2$, Ti/RuO$_2$, and Ti/SnO$_2$ circular and cylindrical mesh electrode systems. The degradation of PAHs by electrochemical oxidation was greatly affected by the operating conditions such as current density and treatment time, whereas recirculation flow rate and oxygen injection slightly influenced the removal efficiency. The best and simplest operating conditions (82-84% of PAHs removal) for PAHs degradation in COE were obtained at a current density of 15 mA/cm^2 through 90 min of treatment. The electrooxidation technique could form the basis of a process capable of removing refractory organic compounds from many industrial wastes and (creosoted wastes, aluminium wastes, polluted soils, etc.).

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