



Coupling extraction–flotation with surfactant and electrochemical degradation for the treatment of PAH contaminated hazardous wastes

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ABSTRACT

The performance of a two-stage process combining extraction of polycyclic aromatic hydrocarbons (PAHs) with an amphoteric surfactant (CAS) followed by electro-oxidation of PAH-foam concentrate was studied for the decontamination of aluminum industry wastes (AIW) and polluted soils. The PAH suspensions extracted from AIW and soils were treated in a 2L-parallel-plate electrolytic cell containing Ti/RuO₂ anodes and stainless steel cathodes. Current densities varying from 4.6 to 18.5 mA cm⁻² have been tested with and without addition of a supporting electrolyte (6.25 to 50 kg Na₂SO₄ t⁻¹ of dry waste). The best performance for PAH degradation was obtained while the electrolytic cell was operated during 90 min at a current density of 9.2 mA cm⁻², with a total solids concentration of 2.0%, and in presence 12.5 kg Na₂SO₄ t⁻¹. The application of the process on AIW (initial PAH content: 3424 mg kg⁻¹) allowed extracting 42% of PAH, whereas 50% of PAH was electrochemically degraded in the resulting foam suspensions. By comparison, 44% to 60% of PAH was extracted from polluted soils (initial PAH content: 1758 to 4160 mg kg⁻¹) and 21% to 55% of PAH was oxidized in the foam suspensions. The electrochemical treatment cost (including only electrolyte and energy consumption) recorded in the best experimental conditions varied from 99 to 188 USD \$ t⁻¹ of soils or AIW treated.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are chemical compounds having two or more fused aromatic rings produced by incomplete combustion of organic material such as coal, diesel, wood and vegetation. They are generally found from both natural and industrial sources. In particular, they are found in soils and sediments that are contaminated by oil, coal, tar or by industrial activities [1]. Industrial wastes especially aluminum wastes have high PAH contamination. The PAH contamination from the aluminum industry wastes (AIW) results from the Söderberg technology for transformation of alumina to aluminum. PAH are present as products in the pitch and coke which is used in the construction of the anodes of electrolytic cells during the electrolytic reduction of alumina to aluminum. The PAH are generally associated with fine particles, and are mainly localized in the by-products originating from the cleaning systems of air purification and ventilation in the industry [2].

There is interest in these compounds because of their toxic, mutagenic and carcinogenic properties [3]. Consequently, it is important to prevent the transport of these pollutants into environment. PAH are hydrophobic compounds and their persistence in

the environment is mainly due to their low solubility. Due to their low solubility they have a tendency to strongly bind with the particles (clay minerals and organic matter) present in the contaminated wastes (e.g. soils, aluminum waste). Therefore, the extraction with surfactant could be considered as the first stage to enhance PAH solubility [4–8]. The PAH are desorbed with surfactant and PAH present in the solution could be degraded in a second stage using an appropriate treatment.

Once PAH solubilized and entered into wastewater, it is often difficult to remediate by conventional water treatment method, as they are recalcitrant and non-reactive in water [9]. It is a reason for which many research efforts have been carried out to find suitable methods for remediation of contaminated wastes (including soils and AIW) and water environments contaminated with PAH. PAH degradation can be achieved through some treatment methods, such as chemical advanced oxidation [10–13], electrochemical oxidation [14–16], or biological oxidation using micro-organisms [17–18]. Among these methods, an environmentally friendly approach for PAH degradation in aqueous solution could be based on the use of electrochemical oxidation, which has been widely applied for the treatment of different effluents: textile effluent [19], landfill leachate [20], olive oil wastewater [21], sewage sludge [21], tannery effluent [22–23] using different electrode materials. Electrochemical treatment is generally characterized by simple equipment, easy operation, brief retention time and negligible equipment for adding chemicals. According

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Nomenclature

ACA	acenaphtene
ACN	acenaphtylene
AIW	aluminum industry wastes
ANT	anthracene
BAA	benzo(a)anthracene
BAP	benzo(a)pyrene
BJK	benzo(b,j,k)fluoranthene
BPR	benzo(ghi)perylene
CAS	cocamidopropylhydroxysultaine
CHR	chrysene
CMC	critical micellar concentration
COD	chemical oxygen demand
DAN	dibenzo(a,h)anthracene
E_c	energy consumption
E_s	specific energy consumption
FCO	foam concentrate suspensions
FLE	fluoranthene
FLU	fluorene
I	current intensity
INP	indeno(1,2,3-c,d)pyrene
MEN	2-methyl naphthalene
NAP	naphthalene
O&G	oil and grease
PAH	polycyclic aromatic hydrocarbons
PHE	phenanthrene
PW	process water
PYR	pyrene
SRE	non-floating material – solid residue
TS	total solids
Uc	electrolytic cell votage
USD \$ t ⁻¹	US dollars per metric ton of soils or AIW treated.

to Rajeshwar and Ibanez [24] benefits from using electrochemical techniques include: environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation and cost effectiveness. Previous work in our laboratory [25] demonstrated that electro-oxidation process could be effectively used for treating oily-cresote effluent strongly loaded with PAH. The sum of PAH concentrations could be optimally diminished up to 80–82%, whereas 84% of petroleum hydrocarbons (C₁₀–C₅₀) was removed. Removal yields of 69% and 62% have also been measured for O&G and COD, respectively.

The objective of the present study is to evaluate a method of treatment consisting of two combined techniques: extraction of PAH from AIW and polluted soils by an adequate surfactant previous selected, followed by electrochemical degradation of PAH compounds collected in the previous extraction stage. The flowsheet of the process is shown in Fig. 1. To our knowledge, no study has been conducted to investigate PAH extraction from AIW in the presence of surfactant followed by electro-oxidation of PAH. Primarily, the selection of the adequate surfactant (CAS: cocamidopropyl hydroxysultaine) and its concentration was based on previous studies [25–27]. Secondly, the electrochemical degradation process was conducted with foam concentrate suspensions (FCO) loaded with PAH. The effects of current density, supporting electrolyte and total solids (TS) concentration on PAH degradation were examined while treating AIW. The best conditions determined while treating the FCO from AIW were then applied for decontaminated FCO from three polluted soils.

2. Materials and methods

2.1. Aluminum waste samples

The aluminum industry wastes (AIW) were obtained from an aluminum industry located in the province of Québec (Canada). This AIW is considered as hazardous waste. The sampling was carried out using a shovel into polypropylene containers of 20 L capacity. The sampling was collected under vacuum filter and contained 5% of moisture (95% TS), 225 g Al kg⁻¹ and 76 g C kg⁻¹. Other inorganic elements such as sulfur (2.1 g kg⁻¹), calcium (18.1 g kg⁻¹) and sodium (29 g kg⁻¹) were also measured. Various collected samples were stored in the dark and at ambient temperature throughout the study awaiting complementary analyses in terms of PAH content. The samples were subjected to particle size analysis. The analysis was carried out using a dry sieving apparatus of Ro-Tap horizontal jolts and the separation of the residues was accomplished in five different particle size categories (5–50 mm, 2–5 mm, 1–2 mm, 500–1000 μm and <500 μm). In this work, the fraction of particles smaller than 2 mm and larger than 0.5 mm has been used.

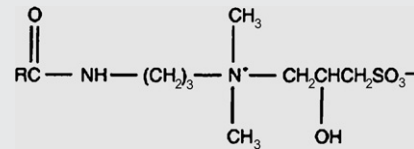
2.2. Soil samples

The three types of soils (Medric soil (Soil-1), Black soil (Soil-2) and CEMRS soil (Soil-3)) used in this study were obtained from different sites located in the province of Québec (Canada). Each sample was taken out from a confidential site and information related to the contamination history was not available. Prior to the PAH extraction procedure, the samples were subjected to a screening of coarser particles using a screen having a pore size of 2.0 mm. The soil samples had a moisture content varying from 3.2% to 12.5% (w/w), and a density ranging between 2.7 and 3.2 g cm⁻³.

2.3. PAH extraction with surfactant

The PAH extraction from AIW and soils was performed in a Denver flotation cell (Joy Manufacturing Company, Denver, Colorado, USA), containing 400 g of polluted wastes mixed with 4.0 L of tap water (process water, PW1). The homogenization of the pulp obtained (10% TS (w/v)) was carried out by mixing for 10 min at a speed of 1800 rpm at room temperature. Thereafter, the pulp conditioning was carried out by addition of an amphoteric surfactant (CAS, Chemron Co., Ohio, USA) at a concentration of 0.20% (w/w). The properties of the CAS are summarized in Table 1. At the end of the conditioning stage, flotation was carried out at the time of the opening of the air valve in the cell. Air flow rate within pulp was adjusted to 1 mL min⁻¹. The foam was formed and moved up to the surface of the pulp. After each flotation step, the flotation concentrate (comprised of foam and fine particles) named as

Table 1
Properties of the CAS surfactant [42–43].

Names	Cocoamidopropyl hydroxysultaine (CAS)
Molecular structure	
Formula	CH ₃ (CH ₂) ₁₃ -N(OH)-(CH ₂) ₃ -N ⁺ (CH ₃) ₂ -CH ₂ -CHOH-CH ₂ SO ₃ ⁻
Molecular weight (g mol ⁻¹)	452
Density (g mL ⁻¹)	1.11
CMC (M)	5 × 10 ⁻⁵
Biodegradability (%)	96

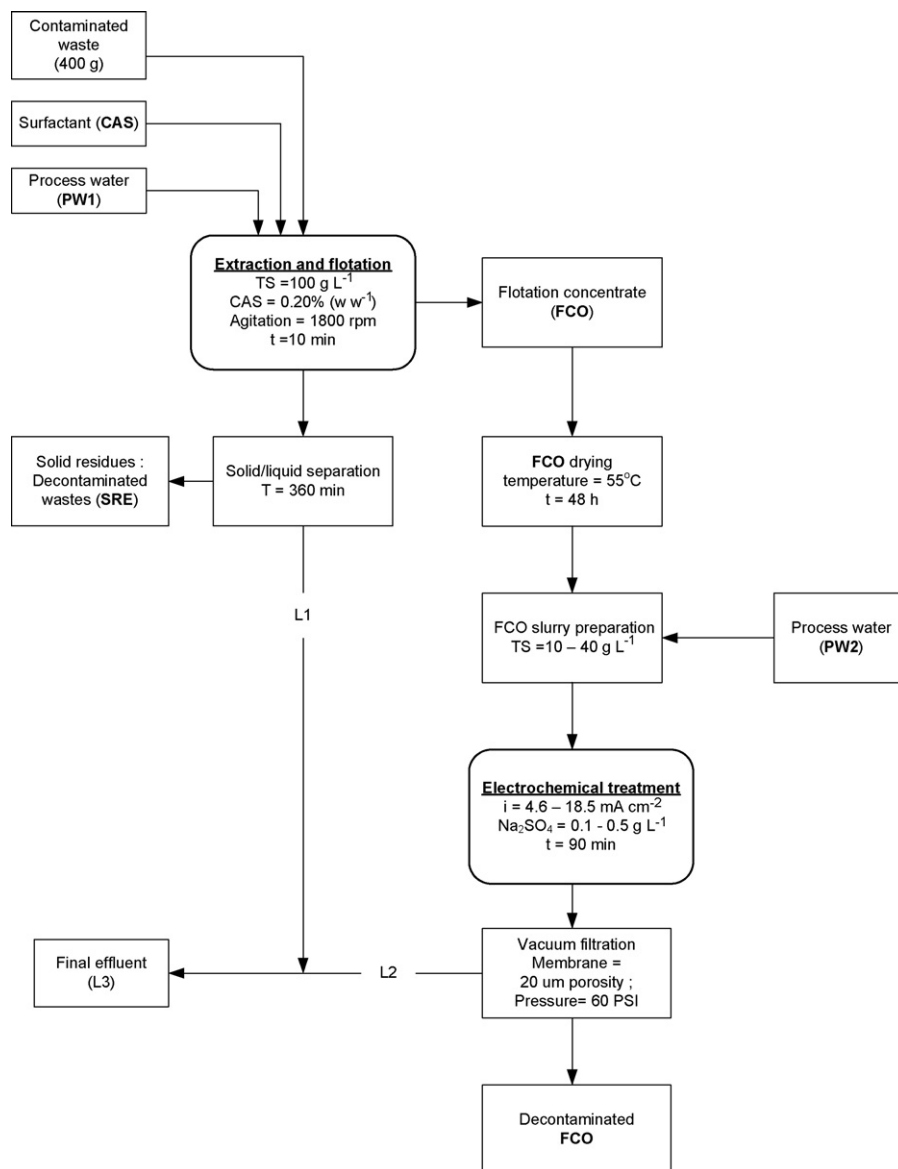


Fig. 1. Flowsheet of the PAH decontamination process of contaminated hazardous wastes.

FCO, was recovered by overflow in a container. FCO was dried for 48 h at 55 °C, and weighed in order to determine the TS of the hazardous wastes. Quantities of 1–2 g of FCO were isolated from the Soxhlet extraction step for PAH analysis. At the end of flotation, the non-floating material, named as solid residues (SRE) was subjected to sedimentation in a 4 L Pyrex cylinder. After 6 h of sedimentation, the supernatant (L1) was carefully withdrawn from the cylinder and SRE were recovered for the analysis of residual PAH.

2.4. Preparation of FCO suspensions for electrochemical treatment

The FCO suspensions were prepared in 500 mL Erlenmeyer flasks with stainless cap containing 1.5–6.0 g of dry FCO, in which 300 mL of tap water was added. The Erlenmeyer flasks were maintained in orbital shaker (Lab-Line Instruments Inc., model 3520) at 250 rpm and at room temperature for a period of 24 h. The resulting slurries were transferred into an electrolytic cell containing 1.2 L of tap water (process water, PW2). The mixtures were then agitated for a period of 30 min before the current intensity was imposed for electrochemical treatment of the FCO.

2.5. Electrochemical oxidation of FCO suspension

Electrochemical degradation of PAH in FCO slurry was carried out in a batch electrolytic cell made of acrylic material with a dimension of 12 cm (width) × 12 cm (length) × 19 cm (depth). The electrode sets (anode and cathode) consisted of ten parallel pieces of metal 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 the FCO suspensions. The anodes were made of expanded titanium (Ti) covered with ruthenium oxide (RuO₂), each one having a solid surface area of 65 cm² and a void area of 45 cm². The cathodes were made of plate of stainless steel (SS, 316 L) having a surface area of 110 cm² (10 cm width × 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. The mass transport coefficient (k_m) of the electrolytic cell ranged from $0.8 \times 10^{-5} \text{ m s}^{-1}$ to $1.2 \times 10^{-5} \text{ m s}^{-1}$. For all tests, a working volume of 1.5 L of FCO suspension 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. Between two tests, electrolytic cell (including the electrodes) were cleaned with 5% (v/v) nitric acid solution for at least 30 min and then and then rubbed with a sponge and rinsed with tap water. At the end of the electrochemical treatment, FCO slurry underwent vacuum filtration on Whatman membrane no. 4 (20 μm pore size). The solid residue obtained after filtration constituted the decontaminated FCO residues. Liquid fraction, L2 was mixed together with the liquid L1 and the mixture constituted the final effluent as shown in Fig. 1.

It is worth noting that, the first set of electrodegradation experiments consisted to test different operating parameters such as, current densities (4.06–18.46 mA cm^{-2}), electrolyte concentration (6.25–25 $\text{kg Na}_2\text{SO}_4 \text{ t}^{-1}$ of dry waste), pulp density (1.0–4.0% TS) in order to determine the optimal conditions (reduce cost and increase effectiveness) for treating FCO slurry from AIW. Sodium sulfate was selected as supporting electrolyte (rather than sodium chloride) in order to avoid organochlorinated compound formation during electrolysis. Sodium sulfate was analytical grade reagent and supplied by Fisher Scientific. During these assays, 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. The best conditions determined while treating FCO slurry from AIW were then applied for decontaminated of FCO slurry from soils.

2.6. Analytical techniques

The pH was determined using a pH-meter (Fisher Acumet model 915) equipped with a double-junction Cole–Palmer electrode with Ag/AgCl reference cell. A conductivity meter (Oakton Model 510) was used to determine the ionic conductivity of the effluent. The temperature of treated-effluent was monitored using a thermo-meter (Cole–Palmer model Thermo Scientific Ertco). Moisture content was determined according to the method 2540B [28]. Total carbon (C), total nitrogen (N) and sulfur (S) were analyzed by a CHNS Leco analyser. Granulometry was analyzed using five sieves sizes as follows: 2–1–0.5–0.25–0.125–0.0053 mm as described in Mercier et al. [29]. Calcium (Ca), potassium (K), and sodium (Na) were analyzed by ICP-AES as described in Djedidi et al. [30].

Analyses of PAH were carried out after Soxhlet extraction [31]. Dichloromethane was used as extraction solvent of PAH. The solid sample was Soxhlet extracted for 24 h using 300 mL of dichloromethane (MA. 400-PAH 1.1, 2003). After the extraction was complete, the extraction solution was concentrated to approximately 5 mL using a rotary evaporator (Büchi Rotavapor-R, Rico Instrument Co.) under reduced pressure in a water bath at lower than 26 °C.

PAH were quantified using a PerkinElmer, model Clarus 500 gas chromatograph coupled mass spectrometer (GC-MS) on a VF-5MS-CFS column (0.25 mm diameter, 30 m long and 0.25 μm film thickness) 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 PAH at a concentration of 1000 mg L^{-1} in dichloromethane–benzene (3:1) (Supelco, Canada) was used as a standard for PAH.

2.7. Economic aspect

The economic study included chemical and energy consumption. The energy consumed was estimated at a cost of 0.06 USD $\text{\$ kWh}^{-1}$, which corresponded to the cost in the province of Québec (Canada). The energy consumption, E_C (kWh), calculated by multiplying the current applied I (A) to the cell voltage, U_C (V), and taking into account the treatment time t (h) can be expressed as follows:

$$E_C(\text{kWh}) = \frac{U_C I t}{1000} \quad (1)$$

The specific energy consumption, E_S (kWh t^{-1} of dry waste) can be expressed as follows:

$$E_S(\text{kWh/t}) = 1000 \frac{U_C I t}{TS V_S} \quad (2)$$

where TS (g L^{-1}) represents the total solid concentration in foam concentrate suspensions (FCO) and V_S (L) represents the total volume of the suspension.

The electrolyte (Na_2SO_4 industrial grade) provided by Laboratory Mat (Beauport, Canada) was estimated at a cost of 0.30 USD $\text{\$ kg}^{-1}$. The total cost was evaluated in terms of U.S. dollars spent per metric ton of soils or aluminum industry wastes (USD $\text{\$ t}^{-1}$).

3. Results and discussion

3.1. PAH extraction from aluminum industry waste (AIW)

The PAH extraction performance from AIW was evaluated according to the extraction procedure previously described by Bongo et al. [26] and Mouton et al. [27]. The results are summarized in Table 2. 16 PAH were investigated in the AIW samples and were comprised of different number of aromatic rings (2-, 3-, 4-, 5- and 6-ring PAH). With the exception of BJK, the concentrations in untreated-AIW samples were not above the maximum PAH limits

Table 2
PAH concentration (mg kg^{-1}) in aluminum industry wastes (AIW).

PAH	Untreated-AIW	Treated-AIW	Foam concentrate (FCO-AIW)
2-ring PAH			
NAP	0.5 \pm 0.0	0.3 \pm 0.0	3.3 \pm 0.0
MEN	0.4 \pm 0.0	0.2 \pm 0.0	4.8 \pm 0.1
Sum	0.9	0.4	8.0
3-ring PAH			
ACN	0.4 \pm 0.0	0.1 \pm 0.0	4.0 \pm 0.3
ACA	0.4 \pm 0.0	0.2 \pm 0.0	3.7 \pm 0.1
FLU	–	Nd	Nd
PHE	42.3 \pm 0.3	24.4 \pm 0.6	389 \pm 17
ANT	5.3 \pm 0.3	3.1 \pm 0.2	26.6 \pm 1.3
Sum	48.4	27.8	423
4-ring PAH			
FLE	242 \pm 3	140 \pm 3	1137 \pm 23
PYR	260 \pm 10	97.2 \pm 4.2	1807 \pm 13
BAA	259 \pm 13	155 \pm 11	1697 \pm 27
CHR	747 \pm 6	420 \pm 15	5315 \pm 20
Sum	1507	812	9956
5-ring PAH			
BJK	1150 \pm 38	717 \pm 10	6857 \pm 13
BAP	165 \pm 3	87.2 \pm 2.2	1442 \pm 9
DAN	89.4 \pm 3.4	56.8 \pm 2.6	618 \pm 16
Sum	1404	861	8916
6-ring PAH			
INP	218 \pm 13	144 \pm 4	1418 \pm 18
BPR	233 \pm 12	127 \pm 6	1657 \pm 13
Sum	451	271	3075
Σ PAH (mg kg^{-1})	3424 \pm 3	1972 \pm 59	22,380 \pm 171

prescribed by the Government of Québec [32] for disposal of wastes in landfills.

From Table 2 it can be seen that 4-ring PAH (FLE, PYR, BAA and CHR) were present in the highest concentration (initial PAH content: 1507 mg kg^{-1}) with a percentage of extraction of 46%, followed by 5-ring PAH (BJK, BAP and DAN) (initial concentration of 1404 mg kg^{-1}) with a yield of extraction of 38% and 6-ring PAH (INP and BPR) with a sum of 451 mg kg^{-1} and 40% removal. The lowest concentrations of PAH in the untreated-AIW were recorded for 2-ring PAH (NAP and MEN) and for 3-ring PAH (ACN, ACA, FLU, PHE, and ANT). Finally, a total PAH concentration of 1972 mg kg^{-1} was measured in the treated-AIW sample, in comparison to 3424 mg kg^{-1} recorded in the untreated-AIW sample, which corresponds to 42% of PAH removal. It should be noted that after treatment, BJK presented lower concentration than 1000 mg kg^{-1} (the limiting value recommended by MENV) and the treated-AIW can be considered as non-hazardous material.

The PAH removal from AIW was quite similar to that obtained by Bongo et al. [26] while studying different surfactants for AIW decontamination. This study revealed that the use of the CAS in flotation was more efficient than other surfactants like Tween 80 for PAH removal from AIW. In fact, the authors concluded that the foaming properties of the CAS during flotation improve the phenomena of air–liquid transfer of the hydrophobic compounds. However, the first stage of the AIW treatment involved the production of FCO with higher concentration of PAH. An amount of 18.5 g FCO-AIW was recovered by overflow in a container and analyzed in term of PAH content. An average concentration of total PAH recorded in FCO-AIW was $22,380 \pm 171 \text{ mg kg}^{-1}$, which was 6.5 times higher than

that measured (3424 mg kg^{-1}) in the untreated-AIW samples. With the exception of FLE, the concentrations of each PAH comprised of 4, 5 and 6 rings were above the limits fixed by the Government of Québec [32] and contributed to the classification of FCO-AIW as hazardous residual matter for the environment. FCO-AIW needed to be treated to reduce disposal cost. Thus, a suspension of FCO-AIW was prepared using different TS concentrations and subjected to electrochemical oxidation.

3.2. Electrochemical treatment of FCO-AIW suspension

3.2.1. Influence of applied current density

One of the main factors affecting the electrochemical oxidation efficiency is the current density. The performance of the electrolytic cell in treating FCO-AIW suspension was evaluated at various current densities ranging from $4.6\text{--}18.5 \text{ mA cm}^{-2}$ without supporting electrolyte addition at a TS concentration of 10 g L^{-1} and at a retention time of 90 min (see Table 3, assays A-1, A-2 and A-3). The residual PAH concentrations recorded at the end of the treatment varied from $18,440$ to 7709 mg kg^{-1} compared to $22,380 \text{ mg kg}^{-1}$ initially measured in the FCO-AIW suspension. PAH degradation increased with current density in the range of $4.6\text{--}18.5 \text{ mA cm}^{-2}$. Similar results have been recorded by Yavuz and Kaporal [33] while studying electrochemical oxidation of phenol by using ruthenium mixed metal oxide electrode. 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} . The decomposition of the pollutants occurs due to electrophilic attack of oxidizing species, e.g. hydroxyl radicals (OH^\bullet), which are generated electrochemically.

Table 3
Electrochemical treatment of foam concentrate suspensions from aluminum industry wastes (FCO-AIW).

Parameters	Assays								
	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9
Electrochemical treatment procedure									
Current density (mA cm^{-2})	4.6	9.2	18.5	9.2	9.2	9.2	9.2	9.2	9.2
Power consumption (kWh t^{-1})	1680	3720	9360	3180	3000	2880	3000	1470	735
Electrolyte (Na_2SO_4) (kg t^{-1})	0	0	0	10	25	50	25	12.5	6.25
Foam TS (%)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	2.0	4.0
Conductivity ($\mu\text{S cm}^{-2}$)	763	763	763	1450	1780	2180	2180	2180	2180
Final temperature ($^\circ\text{C}$)	27	35	55	34	32	30	32	30	30
Final pH	6.4	6.5	6.6	7.2	7.2	7.1	7.1	7.1	7.2
Residual PAH concentration in foam suspension (mg kg^{-1})									
2-ring PAH									
NAP	2.3	1.1	0.8	1.2	1.3	1.4	1.3	1.3	2.6
MEN	3.1	2.3	1.1	1.5	1.7	1.7	1.7	1.7	3.0
3-ring PAH									
ACN	3.4	1.8	1.1	1.1	1.2	1.2	1.2	1.3	2.5
ACA	3.0	1.6	1.0	1.5	1.4	1.5	1.4	1.4	2.5
PHE	360	271	192	240	241	257	241	244	296
ANT	18.7	16.2	12.5	12.5	12.7	13.0	12.7	13.4	18.9
4-ring PAH									
FLE	965	469	316	513	538	510	538	620	706
PYR	1301	804	581	764	780	785	780	823	978
BAA	1338	805	562	813	932	933	932	987	1170
CHR	4760	2079	1528	2035	2291	2589	2291	2379	2949
5-ring PAH									
BJK	5797	3752	2781	3811	3940	4610	3940	4094	5755
BAP	1117	750	608	803	938	986	938	941	1236
DAN	479	321	207	265	321	351	321	344	415
6-ring PAH									
INP	1060	731	432	745	717	799	717	772	915
BPR	1234	839	486	753	863	913	863	896	1272
ΣPAH (mg kg^{-1})	18,440	10,843	7709	10,758	11,578	12,750	11,578	12,119	15,722
Degradation (%)	21.3	51.0	67.0	55.2	52.2	49.2	52.2	49.9	30.6
Treatment cost ($\text{USD } \$ \text{ t}^{-1}$)	101	223	562	194	188	188	188	92	46
Cost ($\text{USD } \$ \text{ kg}^{-1}$ of PAH removed)	25.58	19.36	38.28	16.67	17.36	19.50	17.36	8.96	6.90

It is well known that those generated species react favorably with electron-rich compounds [34]. In fact, hydroxyl radicals react with the double bonds $-C=C-$ and attack the aromatic nucleus, which are the major component of refractory PAH. The real mechanism cannot be investigated in such multi-component system. Further investigation with model systems (using synthetic solutions) should be undertaken to elucidate the mechanism. The largest PAH oxidation (67% of PAH decay) was observed at 18.5 mA cm^{-2} . By comparison, for current densities of 4.6 and 9.2 mA cm^{-2} , the total PAH decays were 21.3% and 51%, respectively. Power consumption increased from 1680 to 9360 kWh t^{-1} as the current density increased from 4.6 to 18.5 mA cm^{-2} . At an energy cost of $0.06 \text{ USD } \$ \text{ kWh}^{-1}$, the electro-oxidation process involved a treatment cost of 101 , 223 and $562 \text{ USD } \$ \text{ t}^{-1}$ of treated FCO-AIW while imposing 4.6 , 9.2 and 18.5 mA cm^{-2} , respectively. Although at the higher current density of 18.5 mA cm^{-2} , higher degradation was obtained, the treatment cost ($562 \text{ USD } \$ \text{ t}^{-1}$) was high compared to the cost of approximately $300 \text{ USD } \$ \text{ t}^{-1}$ often required for the management of such residues. In order to validate and reinforce the choice of 9.2 mA cm^{-2} as optimal current, the costs in $\text{USD } \$ \text{ kg}^{-1}$ of PHA removed have been calculated (Table 3). As expected, a relatively low cost of $19.35 \text{ USD } \$ \text{ kg}^{-1}$ of PAH removed was recorded while imposing 9.2 mA cm^{-2} . By comparison, 25.38 and $38.28 \text{ USD } \$ \text{ kg}^{-1}$ of PAH removed were recorded while imposing 4.6 mA cm^{-2} and 18.5 mA cm^{-2} , respectively. Consequently, the assay A-2 using 9.2 mA cm^{-2} of current density and involving an energy cost of $223 \text{ USD } \$ \text{ t}^{-1}$ was selected for the next step of the study.

3.2.2. Influence of supporting electrolyte

In order to further reduce the energy consumption, sodium sulfate (Na_2SO_4) was used as supporting electrolyte since it modifies the conductivity of the effluent and facilitates the passage of the electrical current. Thus, various concentrations of Na_2SO_4 were added to the system and change in PAH reduction rate was noted. The current density of 9.23 mA cm^{-2} was held constant over the retention time of 90 min. A TS concentration of 1.0% of FCO-AIW was imposed during these assays. Table 3 (assays A-4, A-5 and A-6) presents the yields of PAH degradation while imposing different concentrations of Na_2SO_4 . The yields of PAH degradation (49–55%) were quite similar regardless of supporting electrolyte concentration imposed. There was not a significant effect of electrolyte concentration on the electrochemical oxidation efficiency in the investigated range of 10 – $50 \text{ kg Na}_2\text{SO}_4 \text{ t}^{-1}$. This is consistent with the results of Chen and Chen [35] while oxidizing orange II dye synthetic solution. The same trend has also been recorded by Fernandes et al. [36]. However, as expected, the energy consumed (2880 to 3180 kWh t^{-1}) was low compared to 3720 kWh t^{-1} recorded without any addition of supporting electrolyte while imposing a current density of 9.2 mA cm^{-2} (assay A-2). It is interesting to add a certain quantity of electrolyte in order to reduce the power consumption and consequently, to reduce the cost related to the electrochemical treatment. For instance, for the same oxidation efficiency around 51–52% recorded, the treatment cost (including only, energy and electrolyte costs) was estimated to $188 \text{ USD } \$ \text{ t}^{-1}$ while adding $25 \text{ kg Na}_2\text{SO}_4 \text{ t}^{-1}$ in FCO-AIW suspension (assay A-5), compared to $223 \text{ USD } \$ \text{ t}^{-1}$ recorded without any addition of supporting electrolyte (assay A-2) for the same current density imposed.

3.2.3. Influence of total solids concentration

The effects of TS concentration on electrochemical oxidation of FCO-AIW suspension are shown in Table 3 (assays A7, A8 and A9). TS concentration varied from 1.0% to 4.0% at the conditions of 9.2 mA cm^{-2} of current density and 90 min of retention time. The yield of PAH degradation decreased with the TS concentration. The PAH degradation yields were 52%, 50% and 31%, while the TS concentration of 1.0%, 2.0% and 4.0% were respectively imposed. For

1.0% and 2.0%, the yields of PAH decomposition were quite similar. However, when the TS concentration increased to 4.0%, the performance of the electrolytic cell decreased drastically with only 31% of PAH removal. This can be attributed to the fact that the reactions at the electrode were probably limited by mass transfer while imposing 4.0%. Indeed, in the presence of a high concentration of TS, the FCO-AIW suspension was not mixed well so that the reaction towards the electrode was limited. Consequently, a TS concentration of 2.0% was retained (assay A-8) since 50% of PA was removed and the treatment cost ($92 \text{ USD } \$ \text{ t}^{-1}$) was two times less high than that recorded ($188 \text{ USD } \$ \text{ t}^{-1}$) while imposing 10 g L^{-1} of TS concentration.

According to the results mentioned above, the electrolytic cell operated at current density of 9.2 mA cm^{-2} , TS concentration of 2.0%, Na_2SO_4 concentration of 12.5 kg t^{-1} and a retention time of 90 min gave the best performance of electro-oxidation of FCO-AIW suspension. It was then important to determine whether the results of these tests are reproducible or not. For that, the best assay (determined in terms of effectiveness and cost) was repeated in triplicate to verify the effectiveness and reproducibility of electro-oxidation performance in treating FCO-AIW suspension. An average value of total PAH concentration of $22,380 \pm 171 \text{ mg kg}^{-1}$ was measured in untreated FCO-AIW suspension. It was found that BJK ($6857 \pm 13 \text{ mg kg}^{-1}$), CHR ($53,157 \pm 20 \text{ mg kg}^{-1}$), PYR ($18,077 \pm 13 \text{ mg kg}^{-1}$), BAA ($1697 \pm 27 \text{ mg kg}^{-1}$) and BPR ($1657 \pm 15 \text{ mg kg}^{-1}$) were present in the highest concentrations (4- to 6-ring PAH). In contrast, the compounds having 2- and 3-ring PAH were represented in the lowest concentrations: PHE ($389 \pm 17 \text{ mg kg}^{-1}$), ANT ($26.6 \pm 1.3 \text{ mg kg}^{-1}$) and MEN ($4.8 \pm 0.1 \text{ mg kg}^{-1}$). By comparison, the application of electrochemical treatment reduced the total PAH concentration to an average value of $12,091 \pm 302 \text{ mg kg}^{-1}$. The PAH removal had a mean value of $49 \pm 1\%$. The compounds initially represented in the highest concentrations in untreated-suspension were removed with a percentage of degradation varying from 43% to 56%. The residual concentrations of these PAH were as follows: BJK ($3995 \pm 120 \text{ mg kg}^{-1}$), CHR ($2340 \pm 53 \text{ mg kg}^{-1}$), PYR ($837 \pm 14 \text{ mg kg}^{-1}$), BAA ($984 \pm 5 \text{ mg kg}^{-1}$) and BPR ($938 \pm 90 \text{ mg kg}^{-1}$). However, the residual BJK and CHR concentrations remained higher than the limit fixed by the Government of Québec, which contributed to the classification of FCO-AIW as hazardous residual matter for the environment.

3.3. PAH extraction from soils

The extraction procedure used for soil treatment was identical to that employed while treating AIW. The results are indicated in Table 4. It can be seen that Soil-3 was the most contaminated soil with a total initial PAH concentration of $4160 \pm 11 \text{ mg kg}^{-1}$, followed by Soil-1 (initial PAH concentration: $3569 \pm 46 \text{ mg kg}^{-1}$) and Soil-2 (initial PAH concentration: $1758 \pm 19 \text{ mg kg}^{-1}$). In these soil samples, 4-ring PAH (FLE, PYR, BAA and CHR) were present in the highest concentration with a percentage of PAH extraction varying from 43% to 57%, followed by 5-ring PAH (BJK, BAP and DAN) with a yield of PAH extraction ranging between 39% and 61% and 3-ring PAH (CAN, ACA, FLU, PHE and ANT) with a PAH removal varying from 48% to 66%. The lowest concentration of PAH in the untreated soils samples were recorded for 2-ring PAH (NAP and MEN) with a percentage of extraction varying from 56% to 59%. During the extraction procedure, an amount of 20–24 g dry FCO-Soil was recovered by overflow.

Analyses of PAH carried out on FCO-Soil samples revealed that these samples were very concentrated in PAH and the total concentrations recorded in FCO-Soil-1, FCO-Soil-2 and FCO-Soil-3 samples were $22,886 \pm 395 \text{ mg kg}^{-1}$, $11,212 \pm 446 \text{ mg kg}^{-1}$ and $29,516 \pm 332 \text{ mg kg}^{-1}$, respectively (see Table 5). These con-

Table 4
PAH concentration (mg kg^{-1}) in polluted soils.

PAH	Soil-1		Soil-2		Soil-3	
	Untreated	Treated	Untreated	Treated	Untreated	Treated
2-ring PAH						
NAP	102 ± 5	52.0 ± 3.1	7.8 ± 0.2	2.8 ± 0.1	2.6 ± 0.2	1.3 ± 0.2
MEN	76.5 ± 4.3	35.9 ± 2.0	4.2 ± 0.7	2.4 ± 0.4	22.6 ± 1.1	9.0 ± 1.4
Sum	178	87.9	12.0	5.3	25.2	10.3
3-ring PAH						
ACN	218 ± 2	92.4 ± 7.7	3.3 ± 0.2	1.8 ± 0.2	4.8 ± 0.8	2.5 ± 0.2
ACA	6.4 ± 0.2	3.3 ± 0.2	17.3 ± 0.6	7.2 ± 0.3	61.2 ± 0.5	30.2 ± 2.0
FLU	25.6 ± 1.6	14.3 ± 0.9	20.8 ± 0.6	8.7 ± 0.6	115 ± 1	54.5 ± 3.3
PHE	253 ± 2	146 ± 9	162 ± 4	48.2 ± 2.3	450 ± 12	243 ± 3
ANT	56.5 ± 0.1	32.9 ± 3.8	52.3 ± 2.3	20.7 ± 1.9	190 ± 0	96.3 ± 5.2
Sum	558	289	256	86.6	830	426
4-ring PAH						
FLE	422 ± 13	234 ± 8	324 ± 8	144 ± 5	602 ± 6	319 ± 9
PYR	598 ± 5	279 ± 12	221 ± 9	96.1 ± 4.3	474 ± 8	244 ± 5
BAA	301 ± 3	206 ± 10	5.5 ± 0.2	2.8 ± 0.1	10.2 ± 0.4	5.1 ± 0.1
CHR	337 ± 6	218 ± 3	140 ± 2	56.5 ± 5.5	366 ± 1	194 ± 7
Sum	1658	938	691	299	1452	762
5-ring PAH						
BJK	422 ± 10	275 ± 9	296 ± 10	119 ± 8	648 ± 14	332 ± 5
BAP	175 ± 2	98.9 ± 6.5	188 ± 9	70.2 ± 2.6	441 ± 10	208 ± 8
DAN	115 ± 7	56.0 ± 5.1	21.3 ± 2.5	9.8 ± 1.2	88.7 ± 5.5	40.3 ± 2.6
Sum	711	430	505	199	1178	580
6-ring PAH						
INP	234 ± 9	114 ± 6	166 ± 2	65.4 ± 4.3	366 ± 5	164 ± 6
BPR	230 ± 11	154 ± 6	131 ± 5	54.8 ± 3.3	308 ± 12	139 ± 8
Sum	463	268	297	120	674	303
ΣPAH (mg kg^{-1})	3569 ± 46	2009 ± 76	1758 ± 19	710 ± 32	4160 ± 11	2082 ± 66

centrations were 6–7 times higher than that measured in the untreated-soil samples. Considering the compounds for which the standard values are set, it can be seen that several compounds (e.g. PYR, BAA, CHR, BJK, BAP or INP) had residual concentrations above the limiting values recommended by the Government of Québec

concerning hazardous waste legislation [32]. Consequently, those residues were considered as hazardous material for the environment and needed to be decontaminated before being buried or disposed off in a site for domestic wastes. Suspensions of FCO-Soil were prepared and subjected to electrochemical oxidation. The best conditions of electrochemical treatment determined while treating FCO-AIW suspensions were applied.

Table 5
PAH concentration (mg kg^{-1}) in foam concentrates from soils (FCO-Soil).

PAH	FCO		
	Soil-1	Soil-2	Soil-3
2-ring PAH			
NAP	514 ± 8	68.5 ± 2.3	14.3 ± 0.8
MEN	382 ± 8	26.7 ± 1.0	180 ± 5
Sum	896	95	194
3-ring PAH			
ACN	1236 ± 26	22.7 ± 0.8	38.3 ± 1.6
ACA	48.6 ± 1.7	124 ± 2	416 ± 11
FLU	183 ± 5	177 ± 7	786 ± 18
PHE	1670 ± 11	1420 ± 21	2720 ± 27
ANT	390 ± 6	417 ± 11	1620 ± 23
Sum	3528	2160	5580
4-ring PAH			
FLE	2980 ± 13	1883 ± 41	3790 ± 37
PYR	4480 ± 17	1186 ± 39	2980 ± 18
BAA	1615 ± 17	35.7 ± 1.1	81.2 ± 3.6
CHR	2020 ± 13	775 ± 8	2620 ± 23
Sum	1,095	3880	9471
5-ring PAH			
BJK	2210 ± 18	1907 ± 45	5400 ± 45
BAP	1240 ± 17	1193 ± 177	3140 ± 27
DAN	760 ± 47	147 ± 8	760 ± 11
Sum	4210	3246	9300
6-ring PAH			
INP	1877 ± 185	1083 ± 70	2690 ± 37
BPR	1280 ± 18	746.7 ± 11.7	2280 ± 45
Sum	3157	1830	4970
ΣPAH (mg kg^{-1})	22,886 ± 395	11,212 ± 446	29,516 ± 332

3.4. Electrochemical treatment of FCO-Soil suspension

The effectiveness of the electrolytic cell in treating FCO-Soil suspensions were evaluated at a current density of 9.2 mA cm^{-2} in the presence of $12.5 \text{ kg NaCl t}^{-1}$, at a TS concentration of 2.0% and a retention time of 90 min. Table 6 indicates the residual PAH concentrations in FCO-Soil sample after electrochemical treatment. The application of electrochemical treatment removed the total PAH concentration to average values of $14,675 \pm 90 \text{ mg kg}^{-1}$, $4924 \pm 144 \text{ mg kg}^{-1}$ and $15,214 \pm 5 \text{ mg kg}^{-1}$ for FCO-Soil-1, FCO-Soil-2 and FCO-Soil-3, respectively. The PAH removal yields respectively had a mean value of $44 \pm 2\%$, $54 \pm 1\%$ and $53 \pm 1\%$. It is worth noting that for FCO-Soil-1 suspension, the electrochemical treatment resulted in residual BAA, BAP and DAN concentrations below the maximum prescribed limits by the Government of Québec, but not with PYR, BJK, INP and CHR. With the exception of BJK compound, the residual PAH concentrations in FCO-Soil-2 were not above the maximum limiting values recommended for hazardous residual matter for the environment. Considering now FCO-Soil-3, the most contaminated-soil sample, the electrochemical treatment did not allow reaching residual concentrations below the limiting value for PYR, CHR, BJK, BAP and INP.

In three cases, BJK was not reduced below the acceptable value recommended in spite of its relatively low initial content. Likewise, during the treatment of FCO-AIW suspensions, BJK was not also oxidized below the limiting value recommended (1000 mg kg^{-1}). Thus, in our experimental conditions, BJK remained one of the compounds difficult to oxidize. Increasing current density or treatment

Table 6
Electrochemical treatment of foam concentrate suspensions from soils (FCO-Soil).

Parameters	FCO		
	Soil-1	Soil-2	Soil-3
Electrochemical treatment procedure			
Current density (mA cm^{-2})	9.2	9.2	9.2
Power consumption (kWh t^{-1})	1582	2415	2505
Electrolyte (Na_2SO_4) (kg t^{-1})	12.5	12.5	12.5
Form total solids (%)	2.0	2.0	2.0
Conductivity ($\mu\text{S cm}^{-2}$)	1696 ± 28	566 ± 25	395 ± 22
Final temperature	27 ± 1	36 ± 1	38 ± 1
Final pH	2.3 ± 0.1	7.4 ± 0.1	8.6 ± 0.2
Residual PAH concentration in foam suspension (mg kg^{-1})			
2-ring PAH			
NAP	197 ± 16	19.2 ± 4.2	3.1 ± 0.4
MEN	116 ± 19	16.9 ± 2.7	67.0 ± 4.1
3-ring PAH			
ACN	771 ± 27	12.2 ± 0.8	16.3 ± 2.9
ACA	22.8 ± 1.3	55.2 ± 3.6	199 ± 5
FLU	89.6 ± 10.4	89.5 ± 5.5	210 ± 6
PHE	845 ± 41	618 ± 27	1690 ± 12
ANT	170 ± 11	243 ± 24	526 ± 13
4-ring PAH			
FLE	1960 ± 39	598 ± 25	2447 ± 30
PYR	3703 ± 29	451 ± 22	1869 ± 25
BAA	803 ± 37	13.9 ± 3.5	48.7 ± 4.1
CHR	1730 ± 17	304 ± 24	1060 ± 15
5-ring PAH			
BJK	1024 ± 45	1118 ± 36	2291 ± 14
BAP	583 ± 24	613 ± 24	1760 ± 30
DAN	408 ± 18	91.4 ± 0.2	399 ± 7
6-ring PAH			
INP	1454 ± 30	397 ± 1	1480 ± 16
BPR	825 ± 13	284 ± 24	1147 ± 25
Σ PAH (mg kg^{-1})	$14,675 \pm 90$	4924 ± 144	$15,214 \pm 5$
Total degradation (%)	44.1 ± 1.8	53.7 ± 0.7	52.8 ± 1.0
Treatment cost ($\text{USD } \\$ \text{ t}^{-1}$)			
Energy	95	144	150
Na_2SO_4	4	4	4
Total cost	99	148	154

time could allow enhance the oxidation of such a compound, but the treatment cost will increase. Another alternative could be the use of an electrolytic cell comprising of electrode having more catalytic effect, such as Ti/BDD (titanium coated with boron doped diamond). In fact, on such electrodes (used as anode), refractory organic pollutants can be subjected to two effects: direct anodic oxidation, where the organics can be destroyed at the electrode surface, and indirect oxidation where a mediator is electrochemically generated to carry out the oxidation [37–39]. A peculiarity of Ti/BDD electrode results from its capacity to produce $\text{H}_2\text{S}_2\text{O}_8$, a powerful oxidant capable of oxidizing and modify the structure of organic molecules [40–41] and leading to more oxidized and less toxic compounds. $\text{H}_2\text{S}_2\text{O}_8$ will be obtained by anodic oxidation of sulfate.

4. Conclusion

In this work a two-stage process combining PAH extraction using surfactant and electrochemical degradation of PAH in foam concentrates suspensions for the remediation of polluted wastes (including soils and aluminum industry wastes) has been developed and evaluated at a laboratory scale. The extraction procedure allowed recovering a foam concentrate (FCO) strongly loaded with PAHs ($11,212\text{--}29,516 \text{ mg kg}^{-1}$). The subsequent electrochemical treatment of FCO suspension (1.0–2.0% TS) was carried out in a parallelepipedic electrolytic cell comprising of Ti/RuO₂ (anode) and stainless steel (cathode). The best performance for PAH degrada-

tion in FCO suspension was obtained while the electrolytic cell was operated at a current density of 9.2 mA cm^{-2} , a TS concentration of 2.0% during 90 min of treatment in the presence $12.5 \text{ kg Na}_2\text{SO}_4 \text{ t}^{-1}$. Finally, the application of the process on aluminum industry wastes (AIW) (initial content $3424 \text{ mg PAH kg}^{-1}$) allowed extracting 42% of PAH, whereas 50% of PAH was degraded in the resulting FCO-AIW suspension by electrochemical oxidation. By comparison, 44–60% of PAH was extracted from contaminated soils (initial content of $1758\text{--}4160 \text{ mg PAH kg}^{-1}$) and 21% to 55% of PAH were oxidized in FCO-Soil suspensions. Electrochemical treatment costs of FCO suspension (including only electrolyte and energy consumption) recorded in the best experimental condition varied from 99 to 188 $\text{USD } \$ \text{ t}^{-1}$ compared to 300–600 $\text{USD } \$ \text{ t}^{-1}$ most often required for the disposal of such residues in specialised sites.

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