

Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate

Nathalie Meunier^a, Patrick Drogui^b, Camille Montané^{c,1}, Robert Hausler^{a,2},
Guy Mercier^b, Jean-François Blais^{b,*}

^a Station expérimentale des procédés pilotes en environnement, École de technologie supérieure,
1100, rue Notre-Dame Ouest, Montréal, Que., Canada H3C 1K3

^b Institut national de la recherche scientifique (INRS-Eau Terre et Environnement), Université du Québec,
490 rue de la Couronne, Québec, Que., Canada G1K 9A9

^c École nationale supérieure de chimie de Rennes (ENSCR), Avenue du Général Leclerc, 37500 Rennes, France

Received 1 December 2005; received in revised form 24 February 2006; accepted 27 February 2006

Available online 5 April 2006

Abstract

This paper provides a quantitative comparison between electrocoagulation and chemical precipitation based on heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) removal from acidic soil leachate (ASL) at the laboratory pilot scale. Chemical precipitation was evaluated using either calcium hydroxide or sodium hydroxide, whereas electrocoagulation was evaluated via an electrolytic cell using mild steel electrodes. Chemical precipitation was as effective as electrocoagulation in removing metals from ASL having low contamination levels (30 mg Pb l⁻¹ and 18 mg Zn l⁻¹). For ASL enriched with different metals (each concentration of metals was initially adjusted to 100 mg l⁻¹), the residual Cr, Cu, Pb and Zn concentrations at the end of the experiments were below the acceptable level recommended for discharge in sewage urban works (more than 99.8% of metal was removed) using either electrocoagulation or chemical precipitation. Cd was more effectively removed by electrochemical treatment, whereas Ni was easily removed by chemical treatment. The cost for energy, chemicals and disposal of metallic residue of electrocoagulation process ranged from US\$ 8.83 to 13.95 tds⁻¹, which was up to five times lower than that recorded using chemical precipitation. Highly effective electrocoagulation was observed as the ASL was specifically enriched with high concentration of Pb (250–2000 mg Pb l⁻¹). More than 99.5% of Pb was removed regardless of the initial Pb concentration imposed in ASL and, in all cases, the residual Pb concentrations (0.0–1.44 mg l⁻¹) were below the limiting value (2.0 mg l⁻¹) for effluent discharge in sewage works.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Metal; Soil; Leaching; Electrocoagulation; Decontamination; Effluent; Removal; Solubilization

1. Introduction

The increasing amount of heavy metal-contaminated soil is a consequence of technological and industrial processes and creates a societal health risk [1,2]. Prior to 1987, landfilling was commonly used for the final disposal of contaminated soils [3]. Nowadays, soil washing is one of the most common methods used for soil remediation [4]. Different options have been investigated over the years for metal solubilization from soil,

including inorganic acids leaching (H₂SO₄, HCl, HNO₃, etc.) [5,6], organic acids leaching (citric acid, acetic acid, etc.) [7], bioleaching [8], use of chelating agents (EDTA, ADA, DTPA and NTA) [9], surfactants [10] and biosurfactants [11].

On the other hand, leached-metals have to be removed from soil leachates. Many methods have been developed to remove heavy metals from industrial effluents [12,13], including precipitation, co-precipitation, electrodeposition, electrocoagulation, cementation, membrane separation, solvent extraction, ion-exchange, adsorption and biosorption [14,15]. In spite of good extraction of metals achieved in chemical treatment (using either Ca(OH)₂ or NaOH as precipitating agent), the large consumption of chemicals implies relatively high operating cost [14,15]. Likewise, the precipitates formed are voluminous and sometimes induce high sludge production [16].

* Corresponding author. Tel.: +1 418 654 2541; fax: +1 418 654 2600.

E-mail addresses: camille.montane@eleves.ensc-rennes.fr (C. Montané), robert.hausler@etsmtl.ca (R. Hausler), blaisjf@ete.inrs.ca (J.-F. Blais).

¹ Tel.: +33 2 23 23 80 00; fax: +33 2 23 23 81 99.

² Tel.: +1 514 396 8499; fax: +1 514 396 8584.

Nomenclature

ASL	acid soil leachate solution
pH_{th}	theoretical pH of precipitation of metal ion in form of hydroxide
PAL	pointe-aux-lièbres
t	metric ton
tds	metric ton of dry soil
$v v^{-1}$	volume volume ⁻¹
$w v^{-1}$	weight volume ⁻¹

Heavy metals in soil leachate can be also removed using electrocoagulation. This method is widely used for heavy metals recovery from municipal and industrial effluents (mining, metallurgy) [12,17]. A renewed interest in electrocoagulation has been spurred by the search for reliable, cost-effective water treatment processes. This technology delivers the coagulant in situ by anodic dissolution and produces subsequently, iron (or aluminium) hydroxides having a considerable sorption capacity, while the simultaneous cathodic reaction allows for pollutant removal either by deposition on cathode electrode or by flotation (evolution of hydrogen at the cathode) [18]. By comparison, conventional chemical precipitation typically adds a basic salt, which forms insoluble compounds with dissolved impurities and, with settling providing the primary pollutant removal path. Likewise, during electrocoagulation process, liquid is not enriched with anions and salts content does not increase, compared to chemical metal precipitation [19]. This contributes in producing metallic sludges which are compact using electrocoagulation compared to those generated by chemical precipitation [20]. Electrolytic treatment is characterized by simple equipment, brief retention time and easy operation, which would also contribute to reduce the operating cost in large scale application [21,22].

Recently, researchers from INRS-ETE have developed a hybrid process (chemical and electrochemical processes combined) called successive saline leaching and electrochemical Pb recovery (SSLELR) process for soil decontamination [23]. The process consists in treating soil by means of a saline leaching procedure using high concentration of chloride ions at pH 3.0, followed by Pb recovery via an electrolytic cell using mild steel electrodes and operated at current intensity of 3.0 A. Leaching and electrochemical treatment have successively carried out in a closed loop. Electrochemical treatment is able to reduce Pb content in soil leachate from 650 to 0.15 mg l⁻¹ and this, without production of metallic sludge residue or with a small amount of residue sludge. This process has been only tested for Pb recovery from soil leachate. However, the most important heavy metals often encountered in contaminated-soil include Pb, Cr, Cu, Zn, As, Ni and Cd [3,10,24].

As it is also important to prevent heavy metals pollution of groundwaters, rivers and lakes in the surrounding areas [25,26], it should be interesting to verify that, the electrolytic cell conceived by Djedidi et al. [23] is effective in treating acidic soil leachate strongly loaded with several heavy metals.

Indeed, this study represents one of the stages of a complete process developed for the PAL-soil decontamination including, metal leaching and metal recovery from leachate. The objective in this paper is to quantitatively compare electrocoagulation and chemical precipitation (using either Ca(OH)₂ or NaOH) to determine the most effective process (in term of cost-effective) in treating acidic soil leachate weakly or strongly loaded with heavy metals (Cd, Cr, Cu, Ni, Pb and Zn). The two approaches were evaluated by measuring weight of residue sludge produced, chemicals consumed, energy consumed and reduction in metal content.

2. Materials and methods

2.1. Soil

Soil used in this work came from the Pointe-aux-Lièbres (PAL) site (Quebec, Canada) and contained 73% sand, 21% silt and 6% clay. Some physical pre-treatments (Grizzly, Tyler Sweco sieves, Reichert spiral and hydrocyclone) have been applied to this soil to obtain granulometric fractions having different levels of metal contamination. As the fraction of soil less than 20 µm has already been studied [23], the fraction of soil larger than 20 µm (but less than 2 mm) has been used for this work. The metal concentrations in this fraction of soil were as follows: 0.65 ± 0.12 mg Cd kg⁻¹, 178 ± 5 mg Cr kg⁻¹, 186 ± 4 mg Cu kg⁻¹, 80 ± 2 mg Ni kg⁻¹, 813 ± 16 mg Pb kg⁻¹ and 538 ± 7 mg Zn kg⁻¹. Cu, Pb and Zn concentrations are above the criteria B set by the Environment Ministry of Quebec [27], which are respectively 100, 500 and 500 mg kg⁻¹. Due to this level of contamination, this soil cannot be used for agricultural, residential or recreational purposes without a proper decontamination.

2.2. Acidic soil leachate production

Acid soil leachate solution (ASL) was prepared according to Meunier et al. [28] by suspending in a 30 l polypropylene tank reactor 2 kg of the selected soil with 20 l tap water (pulp density of 10% w v⁻¹–100 g l⁻¹). The suspension was agitated at 500 rpm using a 7.62 cm diameter three blade axial impeller (Stainless steel SS-316L, Labcor Technical Sales, Montreal, Canada) to a Caframo RZR50 rotor (Labcor Technical Sales, Montreal, Canada) and acidified to pH 2.0 ± 0.2 with 4N HCl (Fisher Scientific, ACS reagent). After 2 h of mixing (leaching), a proper amount of E-10 (Ciba Specialty Chemicals Water Treatments, Inc.) anionic polymer solution (1 g E-10 l⁻¹ of water) was added to the mixture and the leachate was separated from the soil by settling. The supernatant was also filtered through a Whatman No. 4 membrane (Whatman International Ltd., Maidstone, England) to eliminate any trace of soil particles. ASL was then kept at room temperature until metals recovery assays were performed. It is to be noted that, even if the contaminated-soil (PAL-soil) used to produce the acidic leachate was the same with that used by Djedidi et al. [23], the way of producing the soil leachate was different. Indeed, the PAL-soil leachate studied by Djedidi et al. [23], was obtained by the addition of 5.5 mol NaCl l⁻¹

in a 25% of PAL-soil pulp density maintained at pH 3.0 using sulfuric acid (H_2SO_4). These different procedures of metals solubilization from PAL-soil allowed to work with leachates having different chemical characteristics (in term of initial pH, metal content, chloride content, sulfate content), which are capable of influencing the subsequent process used to recovery metals from leachate.

2.3. Adjustment of metal concentrations before ASL treatment

In order to simulate various levels of metals contamination and test both processes (electrocoagulation and chemical precipitation) under different conditions, ASL was simultaneously or individually enriched with the selected heavy metals (Cd, Cr, Cu, Ni, Pb and Zn). The metals were added in ASL in form of chloride salts ($\text{CdCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, PbCl_2 and ZnCl_2 , Fisher Scientific, ACS reagent). For the individual enrichment of ASL, only one metal was selected and its concentration was initially adjusted to around 100 mg l^{-1} before treatment. In particular, for Pb, ASL was specifically enriched with Pb at concentrations ranging from 100 to 2000 mg l^{-1} . For the simultaneous doping of ASL, each concentration of metal was initially adjusted to around 100 mg l^{-1} before treatment. A 10 min period of mixing was allowed in order to insure the complete dissolution of metals prior to the chemical or electrochemical treatment. It worth noting that the adjustment of metal took into account the initial concentration of the selected metal in ASL.

2.4. Electrolytic cell

The electrolytic cell was made of acrylic material with a dimension of 12 cm (width) \times 12 cm (length) \times 19 cm (depth). The electrodes sets (anode and cathode) consisted of eight parallel pieces of mild steel plates each, having a surface area of 220 cm^2 , situated 1.5 cm apart and submerged in the soil leachate [29]. The electrodes were installed on a perforated acrylic plate placed at 2 cm from the bottom of the cell. The eight electrodes were all individually connected to the dc power supply Xantrex XFR40-70 (Aca Tmetrix Inc., Ont., Canada); four anodes and four cathodes alternated in the electrode pack [29]. The four electrodes connected to the positive outlet of power supply were consumed during the experiments while the four cathodes were insoluble (non-consumable electrodes). In fact, the cathodic polarization protected the mild steel electrodes from corrosion. Mixing in the cell was achieved by a Teflon-covered stirring bar installed between the perforated plate and the bottom of the cell. A working volume of 1.8 l of leachate was used for all experiments. Samples of 10 ml were drawn at 10 min intervals and monitored for pH and residual metals concentration. Between two assays, electrolytic cell (including the electrodes) was cleaned with 5% (v v^{-1}) hydrochloric acid solution and then rubbed with a sponge and rinsed with tap water. Current was adjusted to 3.0 A and held constant for each run with a retention time of 90 min in order to produce a final effluent having a pH close

to the neutral value and suitable for discharge in sanitary sewer [23].

2.5. Chemical treatment of ASL

In order to compare the electrochemical techniques used for metals recovery with the traditional chemical precipitation, ASL was also treated using either calcium hydroxide or sodium hydroxide solutions. The hydroxide solutions were, respectively, prepared with 20 g of hydrated lime ($\text{Ca}(\text{OH})_2$) (USadian Liquid Air Ltd., Montreal, Canada) and 50 g of NaOH (97% ACS reagent, ACP Chemical, Montreal, Canada) by liter of water. Metals precipitation was carried out in a 2 l tank (pyrex glass) containing 1 l of ASL mixed with an impeller coupled to a mixer. The hydroxide solutions were gradually added to the ASL until the pH of the mixture was stabilised around 8.0. This pH value was imposed in order to produce an effluent having a pH close to the neutral value and suitable discharge in sewer. Then, the mixture was subjected to settling for 24 h before filtration using a Whatman No. 4 membrane under vacuum.

2.6. Sampling and analysis

The pH was determined using a pH-meter (Fisher Acumet model 915) equipped with a double-junction Cole-Palmer electrodes with Ag/AgCl reference cell. Total solids were measured according to the method 2540B [30]. To determine metal concentrations, the samples were first filtered on Whatman 934-AH membrane (Whatman International Ltd., Maidstone, England) under vacuum, then filtrates were acidified with concentrated HCl (5% v v^{-1}) and kept at 4°C until analysed. The digestion method of the soil was executed by digesting 0.5 g dry samples in presence of HNO_3 , HF and HClO_4 , in a final solution of 5% HCl (method 3031 I; [30]). The Buffalo River Sediment (Standard reference material 2704, National Office of Standard, Washington, DC, USA, 20340) was also digested in parallel. The metal concentrations were determined by plasma emission spectroscopy with a simultaneous ICP-AES (Inductively Coupled Plasma, Varian company, Vista model). Cd, Cr, Cu, Ni, Pb and Zn were analysed over two (three for Pb) wavelengths and a ratio of those results was kept as the final value for each metal. Quality controls were performed with certified liquid samples (multi-elements standard, catalogue number 900-Q30-100 and 900-Q30-101, SCP Science, Lasalle, Canada) to insure the conformity of the measurement apparatus.

2.7. Economic evaluation

The economic study included only chemicals consumption, metallic sludge disposal and energy consumption. The chemicals costs were determined by using a lime ($\text{Ca}(\text{OH})_2$) cost of $\text{US\$ } 140 \text{ t}^{-1}$ and a caustic soda (NaOH) cost of $\text{US\$ } 600 \text{ t}^{-1}$ which in both cases correspond to an industrial grade quality. The disposal cost for the metallic sludge including transportation and charges for hazardous waste disposal, was evaluated at $\text{US\$ } 300 \text{ t}^{-1}$ (per ton of dry residue). However, it is important to underscore that the disposal cost for metallic sludge does

Table 1
Comparison between electrochemical and chemical treatment of ASL

Parameters	Initial ASL composition	Electrocoagulation treatment	Chemical precipitation		Permissive levels ^a
			Ca(OH) ₂ treatment	NaOH treatment	
Final pH	1.9 ± 0.1	7.1 ± 0.3	8.1 ± 0.1	8.3 ± 0.2	–
Chemical consumption (kg tds ⁻¹)	–	–	88.7 ± 2.3	65.0 ± 0.0	–
Energy consumption (kWh tds ⁻¹)	–	41.7 ± 11.5	–	–	–
Metallic sludge prod. (kg tds ⁻¹)	–	25.7 ± 0.6	4.7 ± 0.1	2.1 ± 0.8	–
Cd (mg l ⁻¹)	0.4 ± 0.4	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	2.0
Cr (mg l ⁻¹)	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	5.0
Cu (mg l ⁻¹)	3.2 ± 0.5	0.0 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	5.0
Ni (mg l ⁻¹)	0.2 ± 0.0	0.2 ± 0.1	0.1 ± 0.0	0.1 ± 0.1	5.0
Pb (mg l ⁻¹)	29.7 ± 0.7	0.3 ± 0.1	0.3 ± 0.0	0.5 ± 0.5	2.0
Zn (mg l ⁻¹)	18.0 ± 0.8	0.0 ± 0.0	0.2 ± 0.0	0.5 ± 0.3	10.0
Neutralization cost (US\$ tds ⁻¹)	–	–	12.41 ± 0.32	39.00 ± 0.00	–
Energy cost (US\$ tds ⁻¹)	–	2.50 ± 0.69	–	–	–
Disposal cost (US\$ tds ⁻¹)	–	7.72 ± 0.19	1.40 ± 0.03	0.62 ± 0.23	–
Total cost ^b (US\$ tds ⁻¹)	0.0	10.22 ± 0.81	13.81 ± 0.29	39.62 ± 0.23	–

^a Quebec City recommendations for effluent discharge in sewer [31].

^b The total cost excluded the leaching cost, which has not been considered in this presentation.

not include the cost related to the drying of this residue. The energy consumed was estimated at a cost of US\$ 0.06 kWh⁻¹. The total cost for each process tested was evaluated in term of money spent per ton of dry soil treated (US\$ tds⁻¹).

3. Results and discussion

3.1. Heavy metals removal from ASL

Table 1 indicates the initial metal concentrations in the ASL. The comparison of these values with the guideline from Quebec City (for effluent discharge in the sewage urban works) [31] shows that, with the exception of Pb and Zn, the initial concentration of heavy metals (Cr, Cu, Cd and Ni) in ASL did not exceed the maximum values permitted. Table 1 also presents the results obtained by electrocoagulation and by chemical precipitation using either Ca(OH)₂ or NaOH. Effectiveness of the treatments was measured in terms of weight of residue sludge produced, chemical consumption, energy consumed and reduction in metal concentration.

Considering the residual Pb and Zn concentrations, the two processes (electrocoagulation and chemical precipitation) were effective in reducing metals concentration below the limiting values (5.0 and 10 mg l⁻¹, respectively) recommended by Québec City. However, the amount of metallic sludge measured during electrocoagulation treatment (25.7 ± 0.6 kg tds⁻¹) was 7–10 times higher than that recorded during chemical precipitation using either Ca(OH)₂ (4.7 ± 0.1 kg tds⁻¹) or NaOH (2.1 ± 0.8 kg tds⁻¹). The amount of Ca(OH)₂ and NaOH consumed were 88.7 ± 2.3 and 65.0 ± 0.0 kg tds⁻¹, respectively, whereas 41.7 ± 11.5 kWh tds⁻¹ were consumed during electrochemical treatment. The chemical precipitation using NaOH required low concentration of reagent compared to the treatment using Ca(OH)₂. This difference can be explained by the fact that sodium sulfate is highly soluble at pH 8.3 while calcium sulfate is not. So at least half of the residue is composed of calcium

sulfate when we use lime. Other authors concluded the same in the past [15,32]. Moreover, the electrolytic cell was capable of producing enough hydroxyl ions (the product of electrolysis of water at the cathode electrodes) to compensate the acid-buffer and make the soil leachates alkaline. It is the reason for which the pH increase from 2.0 to around 7.0 during electrochemical treatment.

It could also be interesting to compare the total cost (including only chemical consumption, energy consumption and metallic sludge disposal) required for metal removal from ASL using electrocoagulation versus chemical precipitation. A total cost of US\$ 10.22 ± 0.81 tds⁻¹ was linked to the electrocoagulation treatment of ASL, compared to US\$ 13.81 ± 0.81 and 39.62 ± 0.81 tds⁻¹ recorded during chemical treatment. The relatively high total cost of US\$ 39.62 tds⁻¹ recorded during the treatment using NaOH was mainly attributed to its high cost of chemical product (US\$ 600 per metric ton of NaOH compared to US\$ 140 per metric ton for Ca(OH)₂). Likewise, this cost difference between chemical and electrochemical processes can be explained by the fact that, the total cost of electrochemical treatment did not include the cost of the consumable anode electrode.

The weight of each iron electrode used was 73 g and theoretically according to Faraday's law, 35 h of operating time is needed for complete anodic dissolution. It worth noting that, the electrode cannot be used to its last millimeter of thickness owing to corrosion and deposition of the heavy metals. Consequently, the maximum lifetime of sacrificial anode electrode might be equal approximately to 80% of 2100 min (i.e. 1680 min). Thus, considering the theoretical lifetime of 1680 min versus 90 min of retention time, only 5.4% of mild steel was consumed during electrolysis. Since the remaining anode electrodes were used to treat other ASL produced during the period of the assays, the total operating cost did not here include the electrode costs. In fact, this laboratory study allowed estimating the lifetime of sacrificial anode electrode, which must be considered in large scale

Table 2

Comparison between chemical and electrochemical treatment of ASL initially and simultaneously enriched with heavy metals (Cd, Cr, Cu, Ni, Pb and Zn)

Parameters	Initial ASL composition	Control ^a	Electrocoagulation treatment	Chemical precipitation	
				Ca(OH) ₂ treatment	NaOH treatment
Final pH	2.0 ± 0.1	2.1	6.8 ± 0.2	8.2 ± 0.1	8.2 ± 0.1
Chemical consumption (kg tds ⁻¹)	–	–	–	152.0 ± 4.0	114.3 ± 3.1
Energy consumption (kWh tds ⁻¹)	–	–	38.3 ± 8.0	–	–
Metallic sludge prod. (kg tds ⁻¹)	–	–	32.6 ± 3.8	14.1 ± 0.5	10.5 ± 0.6
Cd (mg l ⁻¹)	106.6 ± 7.0	110.9	6.1 ± 0.2	24.7 ± 3.3	40.0 ± 6.4
Cr (mg l ⁻¹)	95.6 ± 5.1	89.1	0.0 ± 0.0	0.6 ± 0.1	0.1 ± 0.0
Cu (mg l ⁻¹)	105.5 ± 19.0	108.7	0.0 ± 0.0	0.6 ± 0.0	0.1 ± 0.1
Ni (mg l ⁻¹)	109.5 ± 2.9	113.2	10.6 ± 0.4	5.1 ± 2.3	3.7 ± 1.2
Pb (mg l ⁻¹)	99.6 ± 12.3	93.7	0.0 ± 0.0	0.6 ± 0.1	0.3 ± 0.3
Zn (mg l ⁻¹)	93.9 ± 6.8	91.2	0.2 ± 0.0	0.7 ± 0.2	0.2 ± 0.1
Neutralization cost (US\$ tds ⁻¹)	–	–	–	21.28 ± 0.56	68.60 ± 1.8
Energy cost (US\$ tds ⁻¹)	–	–	2.30 ± 0.48	–	–
Disposal cost (US\$ tds ⁻¹)	–	–	9.78 ± 1.13	4.24 ± 0.15	3.16 ± 0.2
Total cost ^b (US\$ tds ⁻¹)	0.0	0.0	12.08 ± 1.30	25.52 ± 0.71	71.76 ± 2.0

Each concentration of metal was initially adjusted to around 100 mg l⁻¹.

^a The total cost excluded the leaching cost, which has not been considered in this presentation.

^b Soil leachate contained in a separate tank was subjected to settling for a period of 24 h and used as control.

application. Indeed, in full-scale application, the total investment costs required for ASL treatment by electrocoagulation must include the electrode costs.

3.2. Treatment of ASL initially enriched with several heavy metals

In order to evaluate the performances of electrocoagulation and chemical precipitation in removing metals from acidic soil leachate strongly loaded with heavy metals, the soil leachate was initially and simultaneously enriched with different metals (Cd, Cr, Cu, Ni, Pb and Zn) before treatment. Each concentration of metal was initially adjusted to around 100 mg l⁻¹ by adding metallic salts in ASL. The initial composition of ASL enriched with metals is given in Table 2. The residual Cr, Cu, Pb and Zn concentrations became undetectable at the end of electrocoagulation. However, for Cd and Ni, the residual concentration of 6.1 and 10.6 mg l⁻¹ were respectively recorded, which were above the limiting values (2.0 mg l⁻¹ for Cd and 5.0 mg l⁻¹ for Ni) recommended by Quebec City. According to Hayes [33], the theoretical pHs of metal precipitation (in form of metal hydroxides) required to reach a metal residual concentration of 10⁻⁵ M in solution are as follows: Cd (pH_{th} 9.4), Cr (pH_{th} 5.7), Cu (pH_{th} 6.6), Ni (pH_{th} 8.9), Pb (pH_{th} 6.5) and Zn (pH_{th} 8.5). By comparison, during electrocoagulation, the final pH recorded was around 7.0. This can be one of the reasons for which, the residual Cr, Cu, Pb and Zn concentrations became undetectable at the end of treatment, whereas the residual Ni and Cd concentrations were above the limiting values recommended by Quebec City. An increase of the pH over 9.0 by prolonging the treatment time is required for the removal of Cd and Ni under the permissive levels. However, a prolonged treatment would increase the amount of metallic sludge and energy consumption, resulting in an increase in operating costs. Others studies have shown that at pH 8.0, the molar concentrations

of soluble Cd(II) and Ni(II) (controlled by hydroxides) is much higher than for Cr(III), Cu(II), Pb(II) and Zn(II) [16,33]. By comparison, both chemical treatments using NaOH and Ca(OH)₂ allowed to reach residual metal concentrations below the acceptable level recommended but not for Cd. Considering only the two metals (Cd and Ni) for which the residual concentrations were above the limiting values, it can be seen that, electrochemical treatment was more effective in removing Cd than chemical treatment, whereas Ni was easily removed by chemical treatment. As seen from Fig. 1, Cu, Pb and Zn were the easiest metals removed by electrochemical treatment, followed by Cr. Indeed, it took 40 min for the electrolytic cell to reach residual Cu, Cr and Pb concentrations below the limiting values recommended, whereas 50 min was required for Zn. In fact, Cd and Ni remained the most difficult metals to remove from ASL using either electrochemical and chemical precipitation. One of the possible explanation for this is that the relatively higher energy

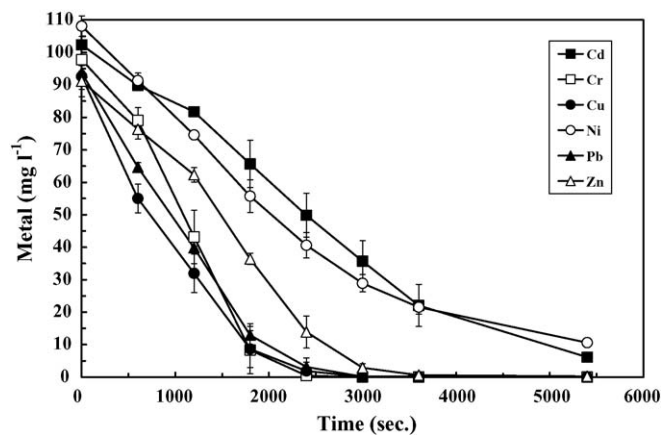


Fig. 1. Variation of metal concentrations during electrocoagulation treatment of ASL enriched with heavy metals (Cd, Cr, Cu, Ni, Pb and Zn); each metal concentration was initially adjusted to around 100 mg l⁻¹.

Table 3
Electrochemical treatment of ASL initially enriched with only one metal (Cd, Cr, Cu, Ni, Pb or Zn)

Parameters	Mono-metallic doped solutions											
	Cd		Cr		Cu		Ni		Pb		Zn	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
pH	2.0	7.3	2.0	7.1	2.2	7.5	2.0	7.1	2.1	7.5	2.1	7.2
Energy cons. (kWh tds ⁻¹)	–	52.5	–	50.0	–	47.5	–	50.0	–	52.5	–	47.5
Metallic sludge (kg tds ⁻¹)	–	32.2	–	19.4	–	31.1	–	21.7	–	20.6	–	28.9
Cd (mg l ⁻¹)	103	2.0	0.9	0.0	1.0	0.0	0.9	0.0	0.9	0.0	0.9	0.0
Cr (mg l ⁻¹)	0.1	0.0	99.1	0.0	0.2	0.0	0.1	0.0	0.2	0.0	0.1	0.0
Cu (mg l ⁻¹)	3.5	0.0	3.5	0.0	87.2	0.0	3.6	0.0	3.5	0.1	3.4	0.0
Ni (mg l ⁻¹)	0.2	0.2	0.2	0.2	0.2	0.2	109	3.2	0.21	0.15	0.2	0.1
Pb (mg l ⁻¹)	29.1	0.0	30.3	0.0	33.6	0.0	30.2	0.5	94.7	0.25	28.6	0.0
Zn (mg l ⁻¹)	18.6	0.1	17.1	0.0	18.5	0.0	17.9	0.0	17.8	0.0	92.2	0.0
Energy cost (US\$ tds ⁻¹)	–	3.15	–	3.00	–	2.85	–	3.00	–	3.15	–	2.85
Disposal cost (US\$ tds ⁻¹)	–	9.67	–	5.83	–	9.33	–	6.50	–	6.17	–	8.67
Total cost (US\$ tds ⁻¹)	–	12.82	–	8.83	–	12.18	–	9.50	–	9.32	–	11.52

required (22.6 and 22.9 kcal mol⁻¹, respectively) for solid phase formation of Cd(OH)₂ and Ni(OH)₂ could not favorably compete with the other metallic precipitates (Cu(OH)₂, Pb(OH)₂, Cr(OH)₃ and Zn(OH)₂) which require only an energy varying from 7.1 to 14.0 kcal mol⁻¹ in aqueous phase at 20 °C [34,35].

An amount of 152.0 ± 4.0 kg Ca(OH)₂ tds⁻¹ and 114.3 ± 3.1 kg NaOH tds⁻¹ were, respectively, required for chemical precipitation, whereas 38.3 ± 8.0 kWh tds⁻¹ of energy were consumed during electrocoagulation. It is to be noted that, an increase of 41.6 and 43.1% of amount of chemicals were, respectively, recorded using Ca(OH)₂ and NaOH, compared to the amount of chemicals required during the treatment of ASL weakly loaded with metals (Table 1). In fact, during the chemical treatment of ASL strongly loaded with metal, high amounts of chemical products were required to reach the critical saturation point to initiate nucleation process (germination process) and subsequent solid formation allowing an effective metal removal by precipitation. Considering electrocoagulation, a decrease of 8.2% of energy consumed was recorded owing to the increase of the electrical conductivity induced by adding metallic salts in ASL. The high consumption of chemicals during the treatment of ASL loaded with metals induced an increase of metallic sludge. An increase of 66.7 and 80.0% of amount of residue sludge produced were recorded using Ca(OH)₂ and NaOH, respectively, whereas an increase of only 21.2% was measured during electrocoagulation, by comparison with the amount of metallic sludge produced during the treatment of ASL weakly loaded with metals (Table 1). However, the amount of metallic sludge produced during electrocoagulation was two to three times higher than that recorded using chemical precipitation.

Finally, under these experimental conditions (ASL strongly loaded with metals), a total cost of US\$ 12.08 ± 1.30 tds⁻¹ was required using electrocoagulation, while US\$ 25.52 ± 0.17 and 71.75 ± 2.0 tds⁻¹ were required using Ca(OH)₂ and NaOH, respectively. It worth noting that, the total cost of electrocoagulation was quite similar to that recorded during the treatment of ASL weakly loaded with metals (US\$ 10.81 ± 0.81 tds⁻¹). By comparison, treatment of ASL strongly loaded with heavy met-

als using chemical precipitation induced an increase of 45–46% of total cost. This was mainly attributed to the high amounts of chemical products required to reach a pH around 8.0 while treating ASL strongly loaded with metal. The treatment of ASL strongly loaded with metals using electrocoagulation was two to five times less expensive than the chemical precipitation. Consequently, in large scale application it would be advantageous to apply electrocoagulation process.

3.3. Electrochemical treatment of ASL enriched with only one toxic metal

In order to evaluate the performance of electrocoagulation process in the case of ASL containing a high concentration of only one toxic metals (Cd, Cr, Cu, Ni, Pb or Zn), additional experiments were conducted by adjusting each concentration of the selected metal to around 100 mg/l before treatment. These experiments are interesting to compare the results with those obtained previously using ASL strongly loaded with several heavy metals. For that, six individual assays were carried out. The results are summarized in Table 3. Interestingly, the residual concentrations of Cd (2.0 mg l⁻¹) and Ni (3.2 mg l⁻¹) recorded, respectively, were equal or below the acceptable level recommended by Quebec City, contrarily to the results obtained using ASL strongly loaded with heavy metals (see Table 2). Indeed, when ASL contained high concentrations of different metals, several competitive reactions occurred simultaneously either at the cathode (metals deposition on the cathode electrodes) or in solution (precipitation and co-precipitation of metals with ferrous hydroxides), leading to insufficient yields of Cd and Ni removal. There was probably a good affinity between the others metals (Cr, Cu, Pb, and Zn) and ferrous hydroxides compared to this occurring between Cd or Ni and Fe(OH)₂. Likewise, considering cathodic reduction, there was also a good affinity between the metals (Cr, Cu, Pb, and Zn) and the cathode electrodes by comparison with this occurring between Cd or Ni and the cathode electrodes. It is to be noted that, metals were mainly removed by co-precipitation and deposition using this configuration of

electrolytic cell [17]. In fact, at the start of the experiment, an amount of metals was removed by cathodic reduction (metal was formed and deposited on the cathodes electrodes) according to the reaction (1):



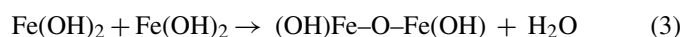
where Me is the metal (Cd, Cr, Cu, Ni, Pb, or Zn) and z the valence of the metal. A thin layer of metals was visually seen to be deposited on cathode electrodes. Several metals can be simultaneously or successively reduced on cathode electrodes.

According to the electrochemical motive force (EMF) series the order of metals deposition should be as follows: $\text{Cu} > \text{Pb} > \text{Ni} > \text{Cd} > \text{Cr} > \text{Zn}$. However, numerous parameters, such as the pollutant concentration, redox potential of the pollutant, and the affinity existing between the pollutant and cathode electrodes, can considerably influence cathodic reduction [17,20].

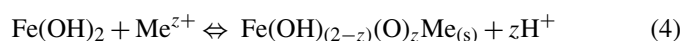
In the same time, ferrous ions were produced by anodic dissolution (reaction (2)), which reacted with hydroxide ions in solution to produce $\text{Fe}(\text{OH})_2$:



Ferrous hydroxide particles were produced up to a sufficient concentration to initiate polymerization or condensation reactions illustrated by reaction (3) [36]:



The appearance of polymeric complexes $[\text{Fe}_2(\text{O})(\text{OH})_2]$ allowed removing metallic pollutant from ASL, mainly by adsorption mechanism. The hydroxide polymeric complexes have a considerable sorption capacity [19]. Likewise, the monomer $\text{Fe}(\text{OH})_2$, can directly react with metallic pollutant by surface complexation or co-precipitation (as described by reaction (4)) [21,37]:



Eq. (4) is quite similar to that proposed by [38], while describing the mechanism of pollutant removal from solution during electrocoagulation. These authors reported that, during electrocoagulation, the dissolved pollutant can be removed by surface complexation or electrostatic attraction. Eq. (5) illustrates the

surface complexation in which the pollutant can act as a ligand (L) to bind a hydrous iron moiety:



Indeed, it took about 20 min for the cell to produce enough hydroxyl ions and induce a green precipitate. At the end of the electrochemical treatment, the greenish precipitate occurring during electrolysis was rapidly (less than 1 h) transformed to a red precipitate owing to ferrous ion oxidation to ferric ion in the presence of dissolved oxygen.

Thus, during electrochemical treatment of ASL strongly loaded with different metals, Cr, Cu, Pb and Zn were easily removed compared to Cd and Ni. However, in the case of the treatment of ASL containing only one metal represented in high concentration, for each metal tested, electrocoagulation was effective to reach the limiting value recommended (Table 3). Although the residual concentration of both Cd and Ni were equal or below the acceptable level, Cd and Ni were the two metals having the highest concentrations in the ASL at the end of the experiment, showing that Cd and Ni remained the most difficult metals to remove from ASL.

The amount of metallic sludge produced ($19.4\text{--}32.2 \text{ kg tds}^{-1}$) was quite similar to that recorded ($32.6 \pm 3.8 \text{ kg tds}^{-1}$) using ASL strongly loaded with different heavy metals. This demonstrates that, metallic sludge production did not depend on the amount of contaminants in ASL. It results from anodic dissolution and, more importantly from the amount of ferrous hydroxides particles, which precipitate with the pollutants (Cd, Cr, Cu, Ni, Pb, or Zn). The energy consumed ranged from 47.5 to $52.5 \text{ kWh tds}^{-1}$, whereas an average of $38.3 \pm 8.0 \text{ kWh tds}^{-1}$ was recorded in the case of the treatment of ASL strongly loaded with different metals. This difference can be explained by the increase of the electrical conductivity when ASL contains several metals represented in high concentrations. It is well-known that, during electrochemical treatment, for a given current intensity, as the conductivity of electrolyte increases, the energy consumption decreases. Finally, a total cost varying from US\$ 8.83 to 12.82 tds^{-1} was required during the assays with the mono-metallic doped solutions (Table 3). By comparison, a total cost of $12.08 \pm 1.30 \text{ tds}^{-1}$ was recorded during the treatment of ASL strongly loaded with different heavy metals. The total costs were quite similar regardless of the initial concentrations

Table 4
Electrochemical treatment of ASL initially enriched with lead

Parameters	Initial concentration of Pb (mg l^{-1}) added in ASL ^a					Control ^b
	250	500	1000	1500	2000	
Final pH	6.2	6.6	6.0	6.0	5.8	2.1
Energy consumpt. (kWh tds^{-1})	35.0	35.0	35.0	32.5	32.5	–
Metallic sludge prod. (kg tds^{-1})	31.1	35.0	35.0	40.0	39.4	0.0
Residual [Pb] (mg l^{-1})	0.84	0.71	1.36	1.44	0.00	1960
Metal removal (%)	99.6	99.7	99.9	99.9	100.0	2.0
Energy cost ($\text{US\$ tds}^{-1}$)	2.10	2.10	2.10	1.95	1.95	–
Disposal cost ($\text{US\$ tds}^{-1}$)	9.33	9.50	10.50	12.00	11.83	0.00
Total cost ($\text{US\$ tds}^{-1}$)	11.43	11.60	12.60	13.95	13.78	0.00

^a The total cost excluded the leaching cost, which has not been considered in this presentation.

^b Soil leachate contained in a separate tank was subjected to settling for a period of 24 h and used as control.

of pollutants (Cd, Cr, Cu, Ni, Pb, or Zn) in ASL. This demonstrates that, during electrocoagulation, the total operating cost is not linked to metal content in ASL but depends on the power consumption required to increase the pH from 2.0 to 7.0.

3.4. Electrochemical treatment of ASL specifically enriched with Pb

Among the pollutants often encountered in contaminated soils, Pb is the most important inorganic contaminant recorded [39,40]. Pb concentrations can reach thousand to hundred of thousand of mg of Pb per kg of soil [40]. In order to evaluate the effectiveness of electrocoagulation process in the presence of ASL strongly loaded with Pb only, additional experiments were carried out by imposing high concentrations of Pb (250, 500, 1000, 1500 and 2000 mg l⁻¹) in ASL. Initial Pb concentrations in ASL were adjusted by addition of PbCl₂. The results obtained are summarized in Table 4. More than 99% of Pb was removed regardless of the initial concentration imposed in ASL. Interestingly, in all cases, the residual Pb concentrations (0.0–1.44 mg l⁻¹) were below the limiting value (2.0 mg l⁻¹) recommended by Québec City. The results are also presented in Fig. 2. The residual Pb concentration became below the acceptable level at the treatment time of 60 min for the initial Pb concentrations imposed of 500, 1000, 1500 and 2000 mg l⁻¹, whereas 40 min was required using an initial concentration of Pb of 250 mg l⁻¹ in ASL. The changes in Pb concentration of ASL shows that the maximum decrease in Pb concentration was recorded after the first 20 min of the experiment followed by a slight decrease until the end of experiment. Indeed, in the first 20 min, Pb was mainly removed by cathodic reduction as described by reaction (1); a thin layer of Pb was visually seen to be deposited on cathode electrodes. The slight decrease occurring between 20 and 60 min was mainly attributed to coprecipitation or precipitation. As indicated above, at the start of the experiment, ferrous ions were produced by anodic dissolution (reaction (2)). Then, hydroxide ferrous was produced in solution up to a sufficient concentration to initiate polymeriza-

tion reactions, inducing the formation of green precipitate. The formation of the polymeric complexes was favored in the presence of high amount of OH⁻ ions to compensate the buffer and make the solution alkaline. Hydroxide ions (OH⁻) were generated at the cathodes owing to water an oxygen reduction:



Indeed, it took 20 min for the cell to produce enough OH⁻, and Fe(OH)₂ and initiate the polymerization reaction. The subsequent formation of polymeric complexes contributed in removing the residual amount of Pb recorded after 20 min. It is to be noted that, the polymeric complexes formed did not remain in solution during a long period of time. They were immediately separated from the solution and stayed on the surface of the liquid owing to the gas bubbles (H₂) produced at the cathode electrodes (reaction (4)). In fact, the bubbles attached to the flocs formed, and the solids were found to be moving up to the surface with bubbles.

The energy consumed was quite similar (32.5–35.0 kWh tds⁻¹), whereas the amount of metallic sludge could be different (Table 4). For example, 35.0 kg tds⁻¹ of metallic sludge was produced during the treatment of ASL containing 500 or 1000 mg Pb l⁻¹, compared to 40 kg tds⁻¹ produced by imposing 1500 or 2000 mg Pb l⁻¹ in ASL. By comparison, for an initial concentration of 250 mg Pb l⁻¹, an amount of 31.1 kg tds⁻¹ of metallic sludge was recorded. Finally, the total cost of the treatment ranged from US\$ 11.43 to 13.95 tds⁻¹, which range was quite similar to that recorded during electrochemical treatment of ASL strongly loaded with different heavy metals (Cd, Cr, Cu, Ni, Pb or Zn) (Table 2) or during the treatment of ASL containing only one metal in high concentration (Table 3). This confirms that, the total operating cost of the electrochemical treatment of ASL was mainly attributed to the power consumption required to increase the pH from 2.0 to 7.0, which energy depended on the retention time and current intensity imposed.

4. Conclusion

This study has shown the possibility to use electrochemical technique to remove efficiently and economically heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) from acidic soil leachate (ASL) compared to traditional metal precipitation using either lime or sodium hydroxide. The comparison of electrocoagulation and chemical precipitation processes used for ASL treatment (in the presence of ASL weakly loaded with metals), demonstrated the practical advantage of electrochemical treatment in terms of cost and effectiveness.

For ASL strongly loaded with metals (each concentration of the metals was initially maintained at 100 mg l⁻¹), at the end of both processes (electrocoagulation and chemical precipitation), the residual metals (Cr, Cu, Pb and Zn) concentrations were below the acceptable level recommended by Québec City for effluent discharge in the sewage urban works but not for Ni and Cd. These two metals were difficult to remove owing to several competitive reactions occurring simultaneously during

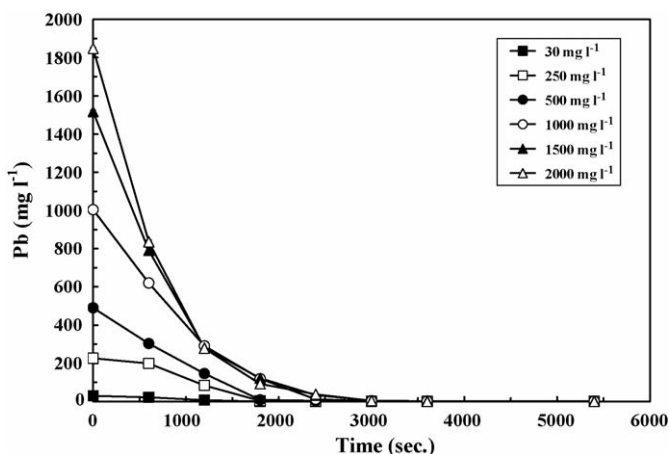


Fig. 2. Variation of metal concentrations during electrocoagulation treatment of ASL specifically enriched with lead at different concentrations (30, 250, 500, 1000 and 2000 mg l⁻¹).

precipitation, co-precipitation or metal deposition at the cathode electrodes. However, additional electrochemical experiments carried out by adjusting individually each concentration of the selected metal (Cd, Cr, Cu, Ni, Pb or Zn) to around 100 mg l⁻¹ in ASL, showed that Ni and Cd could be removed up to a residual concentration equal or below the limiting value recommended. Likewise, the performance of electrocoagulation process for metal removal was emphasized as the ASL was specifically enriched with high concentrations of Pb (250–2000 mg l⁻¹). More than 99.5% of Pb was removed regardless of the initial Pb concentration imposed in ASL and, in all cases, the residual Pb concentrations (0.0–1.44 mg l⁻¹) were below the limiting value (2.0 mg l⁻¹) recommended by Québec City. Electrochemical treatment involved a total cost varying from US\$ 8.83 to 13.95 tds⁻¹, which was up to five times less expensive than that recorded using chemical precipitation. The total cost included only, energy consumption, chemicals consumption, and metallic sludge disposal. Finally, electrocoagulation technique could form the basis of an economical process capable of efficiently removing heavy metals from many acidic leachates (soil, sludge, and ash leachates).

However, an economical study should be carried out to critically and sharply demonstrate the economical advantage of electrocoagulation application (including energy costs, metallic residues disposal costs and the costs required to build and operate the electrochemical reactor) compared to chemical precipitation. Finally, electrocoagulation process should be tested at the pre-industrial pilot scale for designing treatment facilities.

Acknowledgments

Sincere thanks are due to NSERC and Canada Research Chair program for their financial support. Thanks are also due to NSERC (post-doctoral fellowship program) for providing financial assistance to one of the authors (NM). The authors are very grateful to Myriam Chartier for her technical assistance.

References

- [1] J.O. Nriagu, J.M. Pacyna, Quantitative assessment of world-wide contamination of air, water, and soils by trace metals, *Nature* 333 (1988) 134–139.
- [2] J.O. Nriagu, A history of global metal pollution, *Science* 272 (1996) 22–24.
- [3] USEPA, Clean up the Nation's Waste Sites: Markets and Technology Trends, EPA/542/R/96/005, US Environmental Protection Agency, Washington, DC, 1997.
- [4] G. Mercier, J. Duchesne, D. Blackburn, Prediction of metal removal efficiency from contaminated soils by physical methods, *J. Environ. Eng. Div. ASCE* 127 (2001) 348–358.
- [5] P.H. Masscheleyn, F.M. Tack, M.G. Verloo, A model for evaluating the feasibility of an extraction procedure for heavy metal removal from contaminated soils, *Water Air Soil Pollut.* 113 (1999) 63–76.
- [6] G. Mercier, J. Duchesne, D. Blackburn, Mineral processing technology followed by chemical leaching to remove mobile metals from contaminated soils, *Water Air Soil Pollut.* 135 (2002) 105–130.
- [7] R. Bassi, S.O. Prasher, B.K. Simpson, Extraction of metals from a contaminated sandy soil using citric acid, *Environ. Prog.* 19 (2000) 275–282.
- [8] C. White, A.K. Sharman, G.M. Gadd, An integrated microbial process for the bioremediation of soil contaminated with toxic metals, *Nat. Biotechnol.* 16 (1998) 572–575.
- [9] R.W. Peters, Chelant extraction of heavy metals from contaminated soils, *J. Hazard. Mater.* 66 (1999) 151–210.
- [10] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Surfactant-enhanced remediation of contaminated soil: a review, *Eng. Geol.* 60 (2001) 371–380.
- [11] C.N. Mulligan, R.N. Yong, B.F. Gibbs, S. James, H.P.J. Bennett, Metal removal from contaminated soil and sediments by the biosurfactant surfactin, *Environ. Sci. Technol.* 33 (1999) 3812–3820.
- [12] C.S. Brooks, *Metal Recovery from Industrial Wastes*, Lewis Publishers Inc., Chelsea, MI, 1991.
- [13] A.P. Chmielewski, T.S. Urbanski, W. Migdal, Separation technologies for metals recovery from industrial wastes, *Hydrometallurgy* 45 (1997) 333–344.
- [14] J.W. Patterson, Industrial wastes reduction, *Environ. Sci. Technol.* 23 (1989) 1032–1038.
- [15] J.F. Blais, S. Dufresne, G. Mercier, État du développement technologique en matière d'enlèvement des métaux des effluents industriels, *Rev. Sci. Eau* 12 (1999) 689–713.
- [16] D. Couillard, G. Mercier, Précipitations sélectives des métaux solubilisés biologiquement de boues aérobies d'épuration, *U.S. J. Chem. Eng.* 70 (1992) 1021–1029.
- [17] N. Meunier, P. Drogui, C. Gourvenec, G. Mercier, R. Hausler, J.F. Blais, Removal of metals in leachate from sewage sludge using electrochemical technology, *Environ. Technol.* 25 (2004) 235–245.
- [18] G. Chen, Electrochemical technologies in wastewater treatment, *Sep. Purif. Technol.* 38 (2004) 11–41.
- [19] V.E. Cenk, A.N. Belevtsev, Electrochemical treatment of industrial waste water, *Effluent Water Treat. J.* (1985) 243–247.
- [20] F. Persin, M. Rumeau, Le traitement électrochimique des eaux et des effluents, *Tribune de l'Eau* 42 (1989) 45–56.
- [21] K. Rajeshwar, J. Ibanez, *Environmental Electrochemistry—Fundamentals and Applications in Pollution Abatement*, Academic Press, San Diego, CA, 1997, 776 p.
- [22] H. Wendt, G. Kreysa, *Génie Electrochimique—Principes et Procédés*, Dunod, Paris, France, 2001, 386 p.
- [23] Z. Djedidi, P. Drogui, R. BenCheikh, G. Mercier, J.F. Blais, Laboratory study of successive soil saline leaching and electrochemical lead recovery, *J. Environ. Eng. Div. ASCE* 131 (2) (2005) 305–314.
- [24] C.R. Evenko, D.A. Dzombak, *Remediation of Metals-contaminated Soils and Groundwater, Ground-water Remediation Technologies Analysis Center, Technology Evaluation Report TE-97-01*, Pittsburgh, Pennsylvania, 1997, 53 p.
- [25] E. Baath, Effects of heavy metals in soil on microbial processes and populations (a review), *Water Air Soil Pollut.* 47 (1989) 335–379.
- [26] M.J. McLaughlin, B.A. Zarcinas, D.P. Stevens, N. Cook, Soil testing for heavy metals, *Commun. Soil Sci. Plant Anal.* 31 (2000) 1661–1700.
- [27] Ministère de l'Environnement du Québec, Grille des critères génériques sur les sols, 2002, website: <http://www.menv.gouv.qc.ca/indexA.htm>.
- [28] N. Meunier, J. Laroulandie, J.F. Blais, R.D. Tyagi, Lead removal from acidic solutions by sorption on cocoa shells: effect of some parameters, *J. Environ. Eng. Div. ASCE* 129 (8) (2003) 693–698.
- [29] I. Beauchesne, N. Meunier, P. Drogui, R. Hausler, G. Mercier, J.F. Blais, Electrolytic recovery of lead in used lime leachate from municipal waste incinerator, *J. Hazard. Mater.* 120 (2005) 201–211.
- [30] APHA, AWWA, WPCF, *Standards Methods for Examination of Water and Wastewaters*, 20th ed., American Public Health Association, American Water Works Association and Water Pollution Control Federation, Washington, DC, 1999.
- [31] Ville de Québec, Règlement sur les rejets dans le réseau d'égout sanitaire ou unitaire, Ville de Québec, Canada, 2001, 15 p.
- [32] K.A. Baltpurvins, R.C. Burns, G.A. Lawrence, A.D. Stuart, Effect of electrolyte composition on zinc hydroxide precipitation by lime, *Water Res.* 31 (1997) 973–980.
- [33] P.C. Hayes, *Process Selection in Extractive Metallurgy*, Hayes Publishing Co., Brisbane, Australia, 1985, 406 p.

- [34] J.D. Allison, D.S. Brown, K.J. Novo-Gradac, MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual, EPA/600/3-91/021, United States Environmental Protection Agency, Office of Research and Development, Washington, DC, 1991.
- [35] NIST, Critical Stability Constants of Metal Complexes Database (Standard Reference Database 46) Version 4.0, National Institute of Standards and Technology, 1997.
- [36] J.P. Jolivet, De la solution à l'oxyde, Condensation des cations en solution aqueuse, Chimie des surfaces des oxydes, Inter Édition, Paris, France, 1994 (in French).
- [37] S.K. Lee, Electrochemical contaminant removal from aqueous media, US Patent 3,926,754 (1989).
- [38] J.G. Ibanez, M.M. Singh, Z. Szafran, Laboratory experiments on electrochemical remediation of the environment. Part 4. Color removal of simulated wastewater by electrocoagulation–electroflotation, *J. Chem. Educ.* 75 (8) (1998) 1040–1041.
- [39] C. Xintaras, Analysis Paper: Impact of Lead Contaminated Soil on Public Health, US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta, GA, 1992.
- [40] T. Nedwed, D.A. Clifford, A survey of lead battery recycling sites and soil remediation processes, *Waste Manage.* 17 (1997) 257–269.