



## Study of organic matter during coagulation and electrocoagulation processes: Application to a stabilized landfill leachate

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### ABSTRACT

Organic matter contained in leachates appears to be a relevant indicator of waste evolution. Among the physico-chemical treatments applied to stabilize leachates, coagulation–flocculation is considered a classical process and electrocoagulation can be developed. Electrocoagulation tests were carried out in a laboratory pilot using aluminium plates and compared to classical coagulation–flocculation with aluminium ions and to electrolysis alone. The leachate used in this study came from the landfill of Crezin (Limoges, France) and it presented low biodegradability and high concentration of macromolecules. To assess the efficiency of the chemical and electrochemical processes, we specifically studied Organic Matter (OM) by using two protocols: adsorption on XAD resins and fractionation by ultrafiltration. Biodegradable Dissolved Organic Carbon (BDOC) measurements were applied to the fractions extracted by XAD resins and were also used as an indicator of the efficiency of the treatments. Residual organic matter concentration was the same for the two processes but its composition appeared different after electrocoagulation: a higher percentage of small hydrophilic organic molecules which seemed to be less biodegradable than the initial organic matter was observed.

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### 1. Introduction

Landfilling is currently upgraded in order to reduce environmental impacts to the minimum. Indeed, while sanitary landfills are common economically and environmentally acceptable methods to dispose solid wastes, the leachates generated during their operation represent a threat to the environment as they may carry toxic contaminants to groundwater supplies [1] and to the surrounding soil. Their composition must thus be controlled and it must not pose a threat to the environment after treatment. The natural waste biodegradation is very slow, so landfills present a potential environmental threat for many years. Treatment of leachate is thus required for a long time, even after the closure of the sites, involving high costs. For these environmental and economical reasons, studies are now being conducted to enhance leachate treatment processes to minimise potential long-term environmental impacts.

Leachate is particularly difficult to treat because of its variable composition and high proportion of refractory materials.

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Good performances towards BOD, COD and humic material removal have been obtained with biological methods when treating fresh and easily biodegradable leachates. Physico-chemical treatment rather than biological treatment must be applied for older ones and a physico-chemical process commonly called coagulation–flocculation is usually used. An alternative technique to coagulation–flocculation has also appeared to be efficient: electrocoagulation. This process consists in generating, in the effluent to be treated, metallic ions by using the principle of soluble anodes (iron or aluminium). However, this process presents limits now well known. First, the conductivity of the effluent must be high enough to limit the solution temperature variations (Joule effect) sometimes responsible for kinetic modifications [2]. In addition, electrode dissolution is controlled by the concentration of chloride ions in the effluent as they increase the conductivity and consequently decrease the energy consumption. EC must thus be well adapted for treatment of leachates because of their high conductivity and chloride content.

Many studies [3,4] have been conducted to determine the major categories of compounds found in landfill leachate (including organic matter, inorganic ions, anthropogenic micropollutants such as heavy metals and xenobiotic organic chemicals). The organic content of municipal solid waste landfill leachate may vary extensively according to different influencing parameters from one site to another, but Organic Matter (OM) is always ubiquitous. Indeed, Humic Substances (HS) represent the major organic con-

**Table 1**  
Physico-chemical and chemical characteristics of leachate depending on the age of the landfill [10,11].

	Young leachate	Intermediate leachate	Stabilized leachate	
				Crezin leachate
Age of the landfill	<5 years	5–10 years	>10 years	30 years
pH	<7	=7	>7	7.2
COD (g O <sub>2</sub> L <sup>-1</sup> )	>20	3–15	<2	0.38
Biodegradability (BOD <sub>5</sub> /COD)	Medium >0.3	Low 0.1–0.3	Very low <0.1	0.18
Concentration in organic acids	High >80% of DOC	Medium 20–30% of DOC	None	None
Organic load	Mainly fatty acids	Reduction of fatty acids and organic compounds with apparent molecular weight <0.5 Da	Mainly organic compounds with apparent molecular weight >0.5 kDa	70% of DOC were organic compounds with apparent molecular weight >0.5 kDa

stituent of a landfill leachate. They play a dual but very important role both in the biogeochemistry of the medium and the pollutant chemistry, by providing an energy source for microorganisms and also immobilising or enhancing the solubility of micropollutants. Their main characteristics are their complexity and heterogeneity. The knowledge about HS can be improved by separating its different fractions to determine fundamental chemical information about their biogenesis and environmental roles. Generally OM is roughly classified into three fractions [5–7]:

- Simple compounds identifiable by specific analyses, easily biodegradable and with low molecular weight: hydrocarbons, organic acids (mainly fatty acids in leachate), amino acids and alcohols.
- Humic acid-like fraction characteristic of a humification stage and composed of highly aromatic and compounds with high molecular weight and a cellulosic origins.
- Fulvic acid-like compounds with medium to high molecular weight and relatively rich in carboxylic and hydroxylic groups.

Nevertheless such a classification does not take into account the fraction of the dissolved organic carbon that belongs neither to the humic nor to the fulvic acids. This fraction, usually called the hydrophilic fraction, is expected to constitute a substantial fraction of the DOC content [7]. More competent extraction protocols such as adsorption on both ion exchange resins and non-ionic macroporous resins were thus developed and successfully employed to study organic matter from natural media (aquatic or soils) as well as leachates [8,9].

In order to evaluate the efficiency of leachate treatments and more specifically to study the removal of organic matter, residual organic matter must be characterised and quantified to consider all the phenomena that occur during treatment. Leachate collection provides another useful application in that waste quality depends on its state of decomposition. Therefore, if leachate is collected after leaving the landfill, it can be used as a “mirror”, reflecting how far waste decomposition has already progressed. However, the investigated landfills normally contain waste of different ages, so decomposition states differ. That is why collected leachate contains typical final and intermediate products of every waste degradation state existing within the landfill (Table 1). In order to develop more appropriate ways of treating this effluent and also to have a better understanding of the chemical processes, effluent needs to be precisely characterised. Leachate was thus characterised using both conventional methods and the Biodegradable Dissolved Organic Carbon (BDOC) method in order to investigate refractory OM considered as humic-like substances (HS<sup>\*</sup>). This method was tested to assess the long-term biodegradability because conventional methods seem insufficient as they only take easily biodegradable OM into account and as degradation proceeds the OM gets increasingly stable towards biodegradation.

That is why the protocol of Servais et al. [12] that was originally designed for surface water was modified in order to adapt it for leachates analysis.

This work was thus aimed at studying the feasibility of the electrocoagulation process to treat leachates. The efficiency was evaluated by comparing it with the conventional treatment called coagulation–flocculation and to an electrolyse step using non-soluble electrodes. The leachate characteristics and more specifically its significant chloride ion content was well in agreement with the requirements of the electrocoagulation treatment. Particular attention was paid to the behaviour of organic matter in the leachate during treatment by considering its composition of hardly and slowly biodegradable organic molecules.

## 2. Material and methods

### 2.1. Leachate origins and sampling

The leachate was sampled from the landfill of Crézin (near Limoges, France), opened in 1974. Municipal solid wastes and non-hazardous industrial wastes were dumped there until the landfill was closed in 1997. As the waste reached the maturation stage, macromolecules represented a large part of the organic carbon [7,13,14]. The leachate was periodically pumped into a drain box at the bottom of the landfill. It was collected by using the existing leachate collection system and stored in the dark at 4 °C. In order to remove stagnant water, leachate was pumped for 15 min (about 200 L) before sampling.

### 2.2. coagulation–flocculation experiments

Al<sup>3+</sup> and Fe<sup>3+</sup> ions can both be used as coagulant to treat leachate. In this study, electrocoagulation was conducted using aluminium plates, and therefore coagulation was carried out using aluminium sulphate salts (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> 14H<sub>2</sub>O, Prolabo, VWR International, Fontenay sous Bois, France). All experiments were carried out using the Jar Test method. The Numeric Flocculator 10409 (Fischer Bioblock Scientific) was equipped with stainless steel paddles (7.5 cm × 2.5 cm) and allowed to work simultaneously with six 1 L tall-form cylindrical beakers. Appropriate contact times consisted in 5 min of rapid mixing at 150 rpm for coagulation, 15 min of slow mixing at 30 rpm for flocculation and 30 min of settling followed by sand filtration. The sand filtration step was performed in a column (diameter = 3 cm) filled with sand coming from Fontainebleau (Prolabo, VWR International, Fontenay sous Bois, France) to have a 15 cm height. The pH was adjusted to 6.0 using acid (HCl, Prolabo, VWR International, Fontenay sous Bois, France) or basic (NaOH, Prolabo, VWR International, Fontenay sous Bois, France) solutions. All the experiments were carried out at ambient temperature (20 ± 1 °C). pH, turbidity, BOD<sub>5</sub>, COD, DOC were systematically measured by adapted analytical methods after filtration on a sand filter (see Section 2.4).

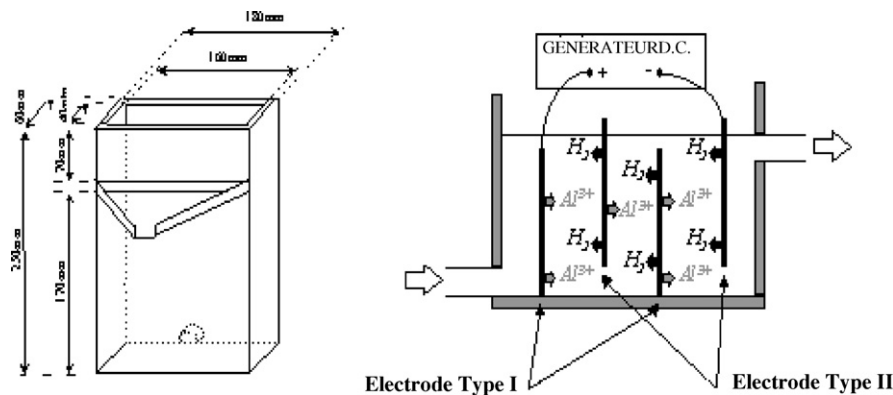


Fig. 1. Electrocoagulation reactor scheme and presentation of disposal electrodes (allowing a sinusoidal movement of water).

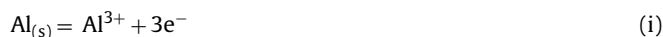
### 2.3. Electrocoagulation experiments

The electrocoagulation process consists of generating, in the effluent to be treated, some metallic ions by using the principle of soluble anodes (aluminium). Experiments were conducted in a Plexiglas electrolysis cell with a total volume of 1.25 L (Fig. 1). From two to ten aluminium electrodes could be placed in parallel in the electrocoagulation pilot but only two electrodes (bipolar mode) were connected to a DC generator supplying 10 A under 65 V. These electrodes were made of aluminium alloy (1050A, Duralinox) containing manganese (0.5–0.8%), silicon (0.15–0.35%), phosphorus (0.03%) and sulphur (0.035%) with aluminium constituting the remainder. Two different types of planes, separated by an inter-electrode distance varying between 2 mm and 1 cm, were used: type 1 (active area  $S = 241 \text{ cm}^2$ ) and type 2 ( $S = 255 \text{ cm}^2$ ) to permit a sinusoidal circulation of the effluent.

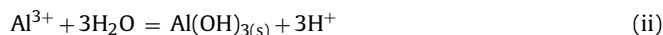
The following experimental protocol was used for electrocoagulation treatment: the leachate passed through the pilot (flow of 187 L/h) where increasing current intensities (from 1 to 10 A) were imposed. These design and operation conditions fixed the residence time within the electrocoagulation reactor to 20 s. After electrocoagulation, the flocculation step was carried out by using the same Jar Test method in the same conditions as after coagulation. Treated leachate was thus mixed during 15 min at 30 rpm and then settled during 30 min before the sand filtration step. Electrocoagulation was compared to coagulation–flocculation by studying the same parameters.

The main reactions likely to take place with aluminium electrodes are described hereafter:

- at the anode, aluminium is oxidised:



The metallic  $\text{Al}^{3+}$  ions formed can then react with water to form aluminium hydroxides:



- at the cathode, water is reduced:



The formed flocs can then be removed by settling [15] or flotation [16].

As observed in coagulation, several monomeric species  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_4^-$ , and polymeric species  $\text{Al}_2(\text{OH})_2^+$ ,  $\text{Al}_6(\text{OH})_{15}^{3+}$ ,  $\text{Al}_7(\text{OH})_{17}^{4+}$ ,  $\text{Al}_8(\text{OH})_{20}^{4+}$ ,  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ ,  $\text{Al}_{13}(\text{OH})_{34}^{5+}$  formed until transformation into  $\text{Al}(\text{OH})_{3(s)}$  according to the complex kinetics of precipitation [17,18].

Using Faraday's second law, the experimental amount of aluminium dissolved at the anode was compared to the theoretical amount calculated. If the effluent to be treated does not contain species that can be oxidised at the anode, the current efficiency for the reaction (i) can be supposed to be near 100%. If the current yield is higher than 100%, it can be explained by the superposition of a chemical and an electrochemical reaction. Authors studying electrocoagulation processes with aluminium electrodes usually obtained current yield higher than 100% because of dissolution at the cathode. This result cannot be explained by the electrochemical process in which only the anodes should be dissolved. Picard et al. [19] showed that there was probably a chemical attack on the aluminium cathode by hydroxyl ions generated during water reduction (iii). In this work, this phenomenon was observed and all the values were corrected by calculation according to Picard et al. [19]. The results thus considered the real quantity of aluminium dissolved.

RAMAN measurements applied on flocs did not clearly differentiate floc structure obtained by coagulation and electrocoagulation. This result confirmed that the species involved in the formation of the floc was the same ( $\text{Al}^{3+}$ ) in both cases.

Ge et al. [20] considered that the anodic oxidation can lead to the production of hypochlorite ions ( $\text{HClO}/\text{ClO}^-$ ). Several authors [21,22] showed that an indirect reaction of oxidation of a municipal solid waste leachate by chlorine helped to decrease ammonia concentrations and chemical oxygen demand. Tsai et al. [23] and Shao et al. [24] underlined a modification of functional groups of organic matter during electrochemical treatment. However this OM oxidation was effective only if the quantity of chloride and the increase of current density were large enough.

The electrolysis tests were carried out with the same pilot as those for electrocoagulation but by using insoluble stainless steel electrodes (type 316). All the conditions of contact time and mixing remained the same as for the electrocoagulation experiments.

### 2.4. Analytical methods

Sample pH was measured under magnetic stirring with a CyberScan 510 pHmeter from Eutech Instruments equipped with a combined  $\text{Ag}/\text{AgCl}/\text{KCl}$  4M glass electrode and with a platinum temperature probe, turbidity with a turbidimeter from HACH and conductivity with a LF 538 conductimeter from WTW equipped with a Tetracon 325 measuring cell. The temperature was systematically measured to correct conductivity (reference temperature:  $\pm 25^\circ\text{C}$ ). In the temperature range from  $-10$  to  $+55^\circ\text{C}$ , the maximal error on measurement was  $\pm 0.5\%$ .

Dissolved Organic Carbon (DOC) concentrations were measured by a TOC analyser (OI analytical 1010) and UV absorbance measurements at  $\lambda = 254 \text{ nm}$  by using a double-beam spectrophotometer

mC<sup>2</sup> Safas. The measurement accuracy was  $\pm 0.005$  U of absorbance between 220 and 700 nm. These parameters allow calculating the SUVA index, defined as the ratio of the absorbance at 254 nm to the DOC content. It gives information about the hydrophobic and aromatic characters of organic molecules in a given sample. The higher the SUVA index, the more aromatic (and more hydrophobic) the molecules.

Anion and cation concentrations were determined by ionic chromatography (Dionex 100) and Chemical Oxygen Demand (COD) were measured by using standard method (AFNOR, Chemical Oxygen Demand, NF T90-101, 1997).

## 2.5. Characterisation of organic matter

### 2.5.1. Fractionation of organic matter by ultrafiltration

Leachate OM was fractionated before and after treatment by ultrafiltration using membrane cut-offs of 0.5, 3 and 30 kDa. The membrane used (YM type, Amicon) were composed of regenerated cellulose. They are considered to be non-ionic and are often used to fractionate humic substances [25].

The membranes were rinsed and put in a millipore cell to ultrafiltrate organic matter. Ionic strength and pH were respectively fixed at 0.04 M (by NaNO<sub>3</sub>) and 7.2 (which corresponded to the leachate pH). A constant stirring at the membrane surface was maintained to prevent polarization effects.

Each time that 50 mL of filtrate was recovered, 50 mL of milliQ water at pH 7.2 and ionic strength 0.04 M was introduced (diafiltration procedure). With this method, the concentration of organic carbon was avoided at the membrane surface, thus preventing larger molecules from passing through the membranes [26].

### 2.5.2. Fractionation of organic matter according to the hydrophobic character of molecules

Leachate samples before and after treatment were filtered through a 0.45  $\mu\text{m}$  membrane to remove humins insoluble at any pH. Humic-like acids (HA\*) were then separated by precipitation after acidification with HCl (37%) at pH 2. After removal of humic-like acids by filtration through a 0.45  $\mu\text{m}$  membrane, leachate at pH 2 was fractionated according to the hydrophobic character of its molecules by using the protocol of Malcolm and Mac Carty [9] depending on the solubility of the organic compounds. The protocol allowed the separation of organic matter in three different fractions, each fraction gathering molecules presenting the same physico-chemical properties.

The fractionation of the dissolved organic matter was carried out using non-ionic resins in series (DAX-8, acrylic nature, slightly polar and XAD-4, styrene-divinylbenzene type, non-polar). This protocol allowed the determination of hydrophobic-like substances (HPO\*) adsorbed on DAX-8 resin and transphilic-like substances (TPH\*) adsorbed on XAD-4 resin. The hydrophilic-like substances (HPI\*) were not adsorbed on these resins. These different fractions of organic matter represent families of molecules for which the structure is not well defined. The volumes of resin and sample used were respectively 5 mL and 156 mL and the percolation flow was fixed at 50 mL/h. The relative percentage of each fraction was determined by measuring DOC.

## 2.6. Biodegradable dissolved organic carbon (BDOC)

To evaluate BDOC, DOC containing samples were incubated in the dark at 20 °C and agitated during 28 days at 50 rpm with microorganisms that consumed BDOC. The method of Servais et al. [12] was developed for natural surface waters with initial carbon concentration ranging from 1 to 5 mg/L. Leachate contains higher DOC content and potentially toxic components. Furthermore, leachate derives from an anaerobic medium, while Servais'

method refers to aerobic conditions. This method was thus modified for application on leachate. Labanowski and Feuillade [27] already used BDOC for OM fractions extracted from leachate, their instructions were thus followed. The most important modifications done for a direct application on our leachate were:

- Dilution of the samples to reach a DOC concentration of 10 mg C L<sup>-1</sup>.
- Dilution with a nutritive solution prepared according to the protocol of Reuschenbach et al. [28] to compensate for leachates salt dilution and support the growth. The nutrient solution used corresponds to the solution recommended in the normalized biodegradability tests of organic substances (OECD 301 and ISO 14593 tests). For 1 L of nutritive solution: 170.0 mg L<sup>-1</sup> KH<sub>2</sub>PO<sub>4</sub>, 435 mg L<sup>-1</sup> K<sub>2</sub>HPO<sub>4</sub>, 668 mg L<sup>-1</sup> Na<sub>2</sub>HPO<sub>4</sub> 2H<sub>2</sub>O, 10.00 mg L<sup>-1</sup> NH<sub>4</sub>Cl, 55 mg L<sup>-1</sup> CaCl<sub>2</sub> 2H<sub>2</sub>O, 45 mg L<sup>-1</sup> MgSO<sub>4</sub> 7H<sub>2</sub>O and 50  $\mu\text{L}$  of FeCl<sub>3</sub> solution ([FeCl<sub>3</sub>] = 3.52 g L<sup>-1</sup>). The pH was fixed at 7 to ensure the solubility of all the fractions.
- Sterilisation of leachate samples by filtration after 0.2  $\mu\text{m}$  filters in order to avoid the precipitation of organic macromolecules in the autoclave.
- Use of isolated aerobic bacteria instead of an autochthonous microbial inoculum because autochthonous bacteria would have been anaerobic, therefore not cultivable with Servais' method. Modification into anaerobic conditions was impractical with regard to instrumental complexity. Also, leachate pollution potential after leaving the landfill was of interest, i.e. its behaviour in sewage purification plants, surface water bodies, soil and groundwater, most of them being aerobic environments. The use of *B. subtilis* as a single strain is useful to facilitate reproducibility and comparability. It was isolated from aerated waste samples by Labanowski and Feuillade [27] who showed that it was obviously able to adapt to leachate conditions. The leachate samples were sprinkled with 1 mL of inoculum (about 10<sup>5</sup>–10<sup>6</sup> bacteria mL<sup>-1</sup>).

The BDOC concentration was determined by the difference between the initial and the minimal DOC content observed during the incubation time. The results were expressed as percentages of the DOC of the samples.

After coagulation and electrocoagulation treatments, the residual organic matter quantity and volume were not sufficient enough to test the biodegradability of extracted organic compounds.

## 3. Results and discussion

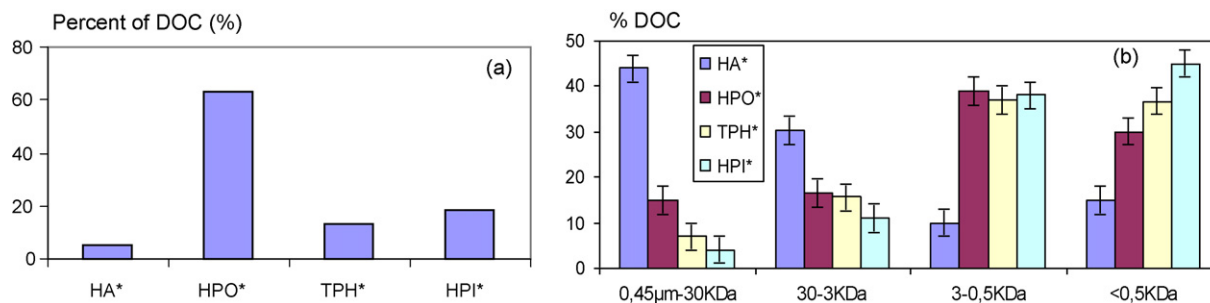
### 3.1. Leachate characterisation

The main physico-chemical characteristics of the leachate of Crezin are given in Table 2. According to [29,30] and Table 1, these characteristics were indicators of a stabilized leachate (pH > 7 and low conductivity) with a low organic content (DOC, COD and UV Absorbance). The BOD<sub>5</sub>/COD ratio represents the proportion of biodegradable organics in the leachate. Leachate from a young landfill usually has a higher BOD<sub>5</sub>/COD (>0.5) ratio compared to the one of a leachate from an older or stable landfill (<0.2). For the leachate of Crezin, BOD<sub>5</sub>/COD = 0.18 underlining a low biodegradability of the organic matter content.

The fractionation of this stabilized leachate by the protocol of Thurman and Malcom [6] showed that it was mainly constituted of hydrophobic-like substances (HPO\*) rather than humic-like acids (HA\*), transphilic-like substances (TPH\*) or hydrophilic-like substances (HPI\*) (Fig. 2a). The most important part of the humic-like acids corresponded to the most important values of apparent molecular weight (>3 kDa) (Fig. 2b) while more than 80% of the apparent molecular weight of the hydrophilic-like substances

**Table 2**  
Main physico-chemical parameters of Crezin leachate. (Detection limit of analytical methods are expressed in parentheses).

pH	Conductivity	COD	DOC	UV absorbance	BOD <sub>5</sub>	Ratio BOD <sub>5</sub> /COD
Standard NFT 90-008 (±0.1)	WTW LF 538 (mS cm <sup>-1</sup> ) (±0.02)	Standard NFT 90-101 (mg O <sub>2</sub> L <sup>-1</sup> ) (±0.2)	Carbon Analyzer Dohrmann Phoenix 8000 (mg C L <sup>-1</sup> ) (±0.2)	Spectrometer Agilent (cm <sup>-1</sup> ) (±0.002)	Standard NFT 90-110 (mg O <sub>2</sub> L <sup>-1</sup> ) (±0.2)	–
7.2	3.2	380	104	0.602 × 5	70	0.18



**Fig. 2.** (a) Repartition of humic-like substances in the leachate and (b) apparent molecular weight distribution of the humic-like substances in the leachate.

were lower than 3 kDa. The major part of hydrophobic-like substances and transphilic-like substances were between 0.5 and 3 kDa (Fig. 2b).

The BDOC content was around 10% of the initial DOC content corresponding to a low biodegradability. BODC contents of HA\*, HPO\*, TPH\* and HPI\* were respectively 6, 14, 5 and 2% of the initial DOC content; the HPI\* fraction was thus the least biodegradable fraction. On the contrary, the HPO\* fraction was the most biodegradable fraction.

### 3.2. Leachate treatment by coagulation and electrocoagulation

The reduction of UV absorbance, COD and DOC after treatment of the leachate of Crezin by coagulation and electrocoagulation for  $0 \leq [Al] \text{ (g/L)} \leq 1.5$  and pH 6.2 is presented in Fig. 3. Both treatments were equally effective in removing UV absorbance, COD and DOC. UV absorbance was more effectively removed when compared to COD or DOC (respectively 60, 45 and 38%) suggesting preferential removal of aromatics compounds. The SUVA index decreased from 30 to 20 L/cm/gC confirming a decrease of the aromatic and hydrophobic character of the organic compounds after treatment. Both treatments were thus selective and a better removal of HA\* and HPO\* compounds was observed.

Lefévre and Legube [31] worked on the removal of organic compounds in natural waters by coagulation and showed that fulvic acids were usually more easily removed than humic acids of the same origin.

Although the efficiency of coagulation and electrocoagulation were similar, the residual organic compounds were not necessar-

ily the same. An electrolytic process could have altered organic molecules during electrocoagulation.

### 3.3. Evaluation of the refractory organic matter

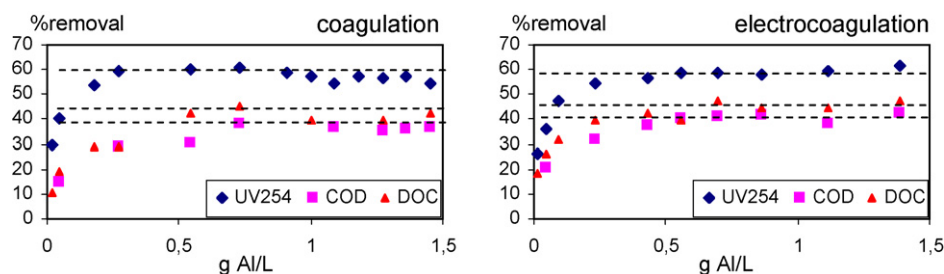
Coagulation and electrocoagulation never eliminate all the organic matter of a leachate. A residual fraction is always observed, but the residual concentrations themselves do not allow identifying if this fraction is exactly the same for both processes.

Further study of the residual organic matter was thus realised after each of the previous treatments and after a new treatment: electrolysis. The dissolved organic carbon was characterized by fractionation according to hydrophobic character and apparent molecular weight.

#### 3.3.1. Fractionation of organic matter according to the hydrophobic character after treatment

Fig. 4 shows how the different fractions of organic matter were affected by coagulation, electrolysis and electrocoagulation treatments.

More than half of the HA\* compounds were removed by coagulation and electrocoagulation. Similar results were previously reported in literature [32]. Both processes led to the same order of removal: HA\* > HPO\* > TPH\* > HPI\*. Hydrophobic molecules could be adsorbed or entrapped more easily at the surface of the flocs and compounds presenting a higher apparent molecular weight and thus a weaker charge density could be more easily neutralised by coagulation and electrocoagulation. The less hydrophobic the molecules were, the lower their reactivity was, as observed for



**Fig. 3.** Percentages of reduction of UV absorbance, DOC and COD of leachate obtained after coagulation and electrocoagulation according to the aluminium concentration (pH 6.2).

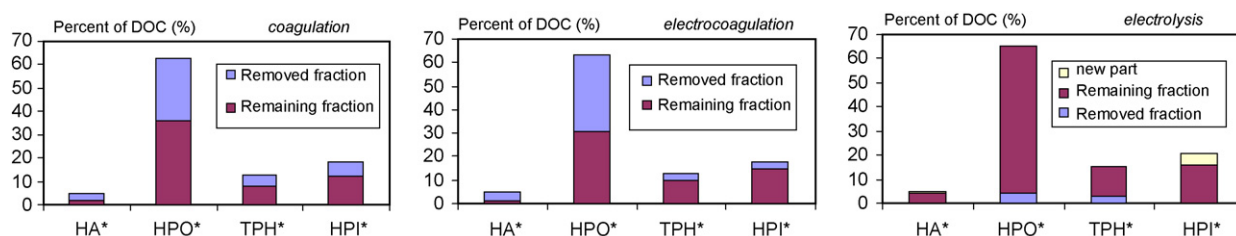


Fig. 4. Distribution of the eliminated and remaining part of DOC in each fraction of the leachate treated by coagulation, electrocoagulation and electrolysis.

the HPI\* fraction. HPO\* was the predominant fraction of the DOC content in the leachate. Even if it was more efficiently removed, it remained predominant after treatment, followed by HPI\* and TPH\* compounds. After electrocoagulation, the residual organic matter contained (in proportion) less hydrophobic compounds (HPO\*) and more hydrophilic compounds (TPH\* and HPI\*) than after coagulation.

Electrolysis experiments were carried out in the same conditions of current density as during electrocoagulation tests in order to evaluate its impact on the molecules. A small part of HPO\* and TPH\* compounds were transformed into HPI\* compounds during the electrolytic process (Fig. 4). This could explain the differences observed in the residual organic compounds between coagulation and electrocoagulation. Chloride ions' concentrations were evaluated before and after treatment to check that this modification could not be attributed to the formation of chlorine and then to the oxidation of the molecules by the newly formed chlorine. No consumption of chloride ions was observed as was expected because the experimental conditions should not allow the production of chlorine in the solution.

### 3.3.2. Fractionation of the organic matter by ultrafiltration after treatments

Fig. 5 shows the distribution of the apparent molecular weight of organic molecules in the leachate before and after treatment by coagulation, electrocoagulation and electrolysis. The results are expressed in percentage of the initial dissolved organic carbon content of the leachate. The 0.45  $\mu\text{m}$  to 30 kDa fraction appeared to be the most efficiently removed by both coagulation and electrocoagulation processes. These results confirmed what was previously observed in literature [33] that is to say a better removal of high molecular weight compounds by coagulation. Brizard [34] observed a better removal of OM coming from surface water (more than 85%) by coagulation, electrocoagulation and electrolysis. The initial organic matter load was however much lower than those of leachates and the composition was different. 30–3 kDa and 3–0.5 kDa fractions seemed well removed by coagulation (around 6 and 21% respectively) and even better by electrocoagulation (around 11 and 31% respectively) but more refractory to electrolysis (only 2 and 5% respectively).

Organic compounds lower than 0.5 kDa were poorly removed by coagulation (only 6%) and even less by electrocoagulation (only 1%). According to Tsai et al. [23], the small molecules can be removed by coagulation and sometimes by electrocoagulation. Electrolysis increased the quantity of organic compounds lower than 0.5 kDa which could be explained by the transformation of larger molecules (mainly HPI\* newly formed fractions). The same effect could occur during electrocoagulation, leading to the formation of new, smaller molecules trapped or adsorbed at the surface of the flocs. After treatment of leachates by aluminium electrodes, Tsai et al. [23] observed a decrease of organic molecules higher than 10 kDa and an increase of organic molecules between 1 and 10 kDa.

Ultrafiltration results correlated to those of hydrophobic fractionation. High apparent molecular weight molecules (mainly hydrophobic compounds) were removed during coagulation and electrocoagulation treatments. Low apparent molecular weight molecules (mainly hydrophilic compounds) were better removed by coagulation as electrocoagulation could produce new more hydrophilic compounds.

### 3.3.3. Evaluation of the biodegradability (BDOC) after treatment

BDOC content was around 10% of the initial DOC content in Crezin leachate. BDOC of treated leachate was evaluated after coagulation, electrocoagulation and electrolysis.  $30 \pm 5\%$  of the initial BDOC content was removed by both coagulation and electrocoagulation. No removal was observed during electrolysis. The organic molecule structure change during electrolysis did not yield to biodegradable compounds. This could be explained why the percentages of BDOC removal for coagulation and electrocoagulation were the same while these two processes did not lead to the same composition of organic matter (hydrophobicity and apparent molecular weight) after treatment.

The percentage of BDOC removal observed after coagulation treatment was close to those reported by Croué [35] and Volk et al. [36,37] when studying humic substances of surface water. The evolution of BDOC of organic matter coming from leachate was similar to those of natural origin.

The biodegradability of HA\*, HPO\*, TPH\* and HPI\* of the Crezin leachate were studied before treatment. BDOC represented respectively 6, 10, 5 and 3% of the DOC. The HPO\* fraction, which was the

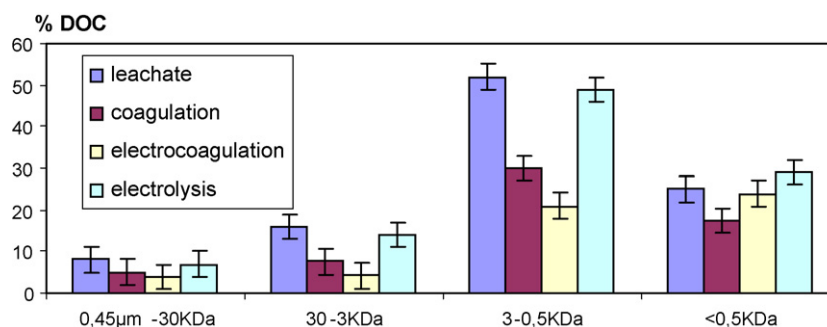


Fig. 5. Distribution of the apparent molecular weight of organic molecules of the leachate before and after treatment by coagulation, electrocoagulation and electrolysis.

predominant organic part of the leachate, was also more biodegradable and thus mainly responsible for the biodegradability of the leachate and for the decrease of biodegradability after treatment (30% reduction). The HPI\* fraction, which was the smallest organic part of the leachate, was also the least biodegradable. Even if the quantity of HPI\* increased after electrolysis, it could not induce a better biodegradability of the leachate.

Labonowski and Feuillade [27] compared organic fractions extracted from natural water and leachate. They observed that the fractions extracted from natural water were always higher in concentration than the ones extracted from leachate (excepted for HPO\*). HPI fraction appeared to be the most biodegradable fraction extracted from the water.

#### 4. Conclusion

The coagulation and electrocoagulation treatment of the organic matter extracted from a municipal solid waste landfill leachate led to the same removal of the organic load. The most hydrophobic compounds were the predominant compounds in the leachate and also the most biodegradable. However, the biodegradability remained weak compared to that of organic molecules of a natural origin. Coagulation and electrocoagulation treatment mainly affected hydrophobic molecules and after treatment 30% of the initial BDOC quantity was removed. Electrolysis (and as a consequence electrocoagulation) increased the amount of hydrophilic organic compounds of lower apparent molecular weight. Because these molecules were also the least biodegradable neither coagulation nor electrocoagulation could improve their biodegradability. Thus, an additional biological treatment after electrocoagulation in order to increase the removal of organic molecules is not justified.

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