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# Implementation of electrochemical advanced oxidation processes for the treatment of soil washing solutions from polycyclic aromatic hydrocarbon contaminated soils

Clément Trellu

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Institute for Water Education

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**Implementation of electrochemical advanced oxidation processes for the treatment of soil washing solutions from polycyclic aromatic hydrocarbon contaminated soils**

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Erasmus Joint doctorate programme in Environmental Technology for Contaminated Solids, Soils and Sediments (ETeCoS<sup>3</sup>)



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## ABSTRACT

Remediation of soil contaminated by polycyclic aromatic hydrocarbons (PAHs) is an important societal, environmental, economical and technological challenge, due to the high number of sites contaminated by these persistent and toxic compounds. Environmental engineering companies using conventional bioremediation processes often fails to reach sufficient PAH removal rates from historically contaminated soils. Therefore, there is a real need for the development of innovative solutions.

In the present work, the characterization of 6 historically tar oil-contaminated soils showed that 42 to 86% of PAH are located in the sand fraction, either adsorbed on various coal/coke/wood particles or integrated in resinified and weathered tar oil particles. Thus, either selective separation of the most contaminated fraction or surfactant-enhanced soil washing (SW) appears to be promising alternatives to bioremediation, according to the level of sequestration of PAHs. Further investigations were performed on the surfactant-enhanced SW process, which is based on the transfer of PAHs from the soil-sorbed fraction to the washing solution. This process generates SW solutions containing a large amount of surfactant and pollutant. They have to be treated in order to avoid environmental contamination and ensure the cost-effectiveness of the whole process.

Anodic oxidation (AO) was identified as a suitable and promising process for the treatment of SW solutions containing PAHs and Tween® 80 as extracting agent. The detailed understanding of mechanisms involved in the removal of organic compounds from SW solutions during AO allowed the implementation of two different treatment strategies:

- First, it was emphasized that the use of AO at low current intensity during long treatment times (23 h) allows the selective degradation of target pollutants (PAHs) and the reuse of the SW solution for additional SW steps. Thus, the large amount of Tween® 80 saved strongly improves the cost-effectiveness and ecological footprint of SW processes, particularly when the high sequestration of pollutants requires several SW steps using high surfactant concentrations.

- In contrast, high removal rates of organic compounds and production of more biodegradable by-products was observed during short treatment times (3 h) by AO at high current intensity. Thus, synergistic effects were obtained for the combination of AO with a biological post-treatment. High removal rates with optimized operating costs can be achieved. Moreover, AO can also be used as a post-treatment (polishing step) for the removal of hardly-biodegradable compounds. This treatment strategy aims at avoiding environmental contamination by SW solutions.

Both treatment strategies have to be considered for a suitable management of SW solutions. In view of promising results obtained, scientific challenges related to the scale-up of this process were discussed.

## RÉSUMÉ

La dépollution des sols contaminés par des hydrocarbures aromatiques polycycliques (HAPs) est un enjeu important de société, à la fois environnemental, économique et technologique, du fait du grand nombre de sites contaminés par ces composés toxiques et persistants. Les entreprises d'ingénierie de l'environnement utilisant des procédés conventionnels de bioremédiation font souvent face à des rendements trop faibles d'élimination des HAPs dans les sols historiquement contaminés. Il y a donc un besoin réel de développer des solutions innovantes.

Dans cette étude, 6 sols historiquement contaminés par des huiles de goudron ont notamment été caractérisés par la présence de 42 à 86% des HAPs dans la fraction sableuse, adsorbés sur diverses particules de charbon/coke/bois ou intégrés à l'intérieur de particules d'huile de goudron résinifiées et altérées. Ainsi, en fonction du niveau de séquestration des HAPs, la séparation sélective de la fraction la plus contaminée ou l'utilisation de procédés de lavage de sol (LS) utilisant des surfactants apparaissent comme des alternatives prometteuses aux procédés de bioremédiation. Une attention particulière a ensuite été portée sur le procédé de LS utilisant des surfactants, qui est basé sur l'optimisation du transfert des HAPs du sol vers la solution de lavage. Ce procédé génère des solutions de LS contenant de grandes quantités de surfactants et de polluants. Celles-ci doivent être traitées dans le but d'éviter la contamination de l'environnement et d'améliorer le rapport coût-efficacité du procédé.

L'oxydation anodique (OA) a été identifiée comme un procédé adéquat et prometteur pour le traitement de solutions de lavage de sol contenant des HAPs et du Tween® 80 comme agent d'extraction. La compréhension détaillée des mécanismes impliqués dans l'élimination des composés organiques présents dans les solutions de LS a permis de mettre en place deux stratégies de traitement différentes :

- Tout d'abord, il a été mis en évidence que l'utilisation de l'OA à des courants faibles et pendant des temps de traitement longs (23 h) permet la dégradation sélective des polluants ciblés (les HAPs) et la réutilisation de la solution de LS pour des étapes supplémentaires de LS. La grande quantité de Tween® 80 ainsi économisée améliore fortement le rapport coût-efficacité et l'empreinte

écologique des procédés de LS, en particulier lorsque la séquestration des polluants dans le sol requiert plusieurs étapes de LS et l'utilisation de fortes concentrations en surfactant.

- En revanche, des rendements élevés d'élimination des composés organiques et la production de sous-produits plus biodégradables a été observée lors de l'utilisation de l'OA à forte intensité et pendant des temps de traitement courts (3 h). Ainsi, des effets synergétiques ont été obtenus lors de la combinaison de l'OA avec un post-traitement biologique. D'importants rendements d'élimination avec des coûts opératoires optimisés peuvent être atteints. De plus, l'OA peut aussi être utilisée comme post-traitement pour l'élimination des composés faiblement biodégradables. Cette stratégie de traitement a pour but d'éviter toute contamination environnementale par les solutions de LS.

Ces deux stratégies de traitement doivent être prises en considération pour une gestion optimale et appropriée des solutions de LS. Au vu des résultats prometteurs obtenus, les défis scientifiques reliés au changement d'échelle de ce procédé ont été discutés.

## SINTESI

La bonifica dei suoli contaminati da idrocarburi policiclici aromatici (IPA) è considerata una sfida sociale, ambientale e tecnologica di fondamentale importanza a causa dell'elevato numero di siti inquinati dai suddetti composti caratterizzati da elevata tossicità e persistenza nell'ambiente. Ad oggi, l'impegno di tecniche di bonifica convenzionali a mezzo di processi biologici, da parte di aziende operanti nel campo dell'ingegneria ambientale, hanno riscontrato risultati poco soddisfacenti in termini di efficienze di rimozione degli IPA da siti storicamente contaminati. Tutto ciò ha comportato, di conseguenza, il necessario sviluppo di soluzioni innovative.

Nel presente lavoro, la caratterizzazione di sei siti storicamente contaminati da olio di catrame ha rivelato una percentuale di IPA, variabile dal 42 al 86%, presente all'interno della frazione sabbiosa dei suoli, sia adsorbiti su varie particelle di carbone/coke/legno, sia integrato all'interno di particelle di catrame d'olio resinose ed alterate da agenti atmosferici. Pertanto, l'impiego di tecniche quali la separazione selettiva delle frazioni di suolo maggiormente contaminate o il soil washing (SW) a mezzo di agenti surfattanti sono state ritenute, tenendo conto dei possibili livelli di rimozione degli IPA raggiungibili, valide alternative alle tecniche di bonifica a mezzo di processi biologici. A tal scopo, ulteriori indagini sono state effettuate sul processo di SW a mezzo di agenti surfattanti. Quest'ultimo processo risulta essere basato sul fenomeno di solubilizzazione, all'interno della soluzione di lavaggio, degli IPA adsorbiti alle particelle di suolo comportando, di contro, la conseguente formazione di soluzioni, derivanti dal processo di SW, ad elevata concentrazione di tensioattivi e contaminanti. Questo aspetto rende, quindi, necessario un trattamento delle soluzioni stesse ai fini di evitare possibili contaminazioni ambientali e garantire la convenienza economica dell'intero processo.

A tal riguardo, l'ossidazione anodica (AO) è stata identificata come opportuna e promettente tecnica per il trattamento delle soluzioni dalla fase di SW contenenti IPA e Tween® 80; quest'ultimo impiegato come agente estraente nel processo di SW. La comprensione dettagliata del fenomeno alla base della rimozione dei contaminanti organici dalla soluzione del processo di SW, durante la fase di AO, ha permesso l'attuazione di due differenti strategie di trattamento:

- In primo luogo, è stato enfatizzato che l'impiego del processo di AO con bassi valori di densità di corrente ed elevati tempi di trattamento (23 h) consente la degradazione selettiva dei contaminanti d'interesse (IPA) e il riutilizzo delle soluzioni di lavaggio in ulteriori step del processo di SW. In tal modo, il recupero di elevate quantità di surfattante può fortemente migliorare la convenienza economica e l'impronta ecologica dei processi di SW, specialmente in riferimento ai casi in cui è necessario l'impiego di numerosi cicli di lavaggio ai fini della rimozione dei contaminanti.
- Di contro, sono state osservate elevate efficienze di rimozione dei contaminanti organici e l'incremento di sotto-prodotti maggiormente biodegradabili durante fasi di AO condotti con minori tempi di trattamento (3 h) ed elevati valori di densità di corrente. Da tale strategia è stato possibile osservare effetti sinergici dovuti alla combinazione del processo di AO e post-trattamenti di natura biologica con la possibilità di ottenere elevate efficienze di rimozione contestualmente all'ottimizzazione dei costi operativi. Inoltre, considerando che il processo di AO può essere impiegato come post-trattamento (fase di affinamento) per la rimozione di composti lentamente biodegradabili, è stato possibile assumere l'idoneità applicativa di tale strategia nella prevenzione dei fenomeni di contaminazione ambientale da parte delle soluzioni provenienti dalla fase di SW.

Da tali osservazioni, quindi, è stato osservato che entrambe le suddette strategie devono essere prese in considerazione ai fini di una gestione ottimale concernente le soluzioni derivanti dalla fase di SW. Inoltre, alla luce dei promettenti risultati ottenuti durante il presente lavoro, è stato possibile discutere l'interessante aspetto della sfida scientifica mirata alla possibilità di scale-up del processo.

## SAMENVATTING

De ontvervuiling van de besmetten gronden door geurig algemeenecclus koolwaterstof (GAK) is een belangrijk inzet voor de maatschappij, voor het milieu, de economie en de technologie door het feit dat een heel groot aantal besmetten landschappen door deze giftige en aanhoudende samengestelden.

De engineeringen bedrijven van het milieu gebruikende conventionele procedés van bioremediëring lijden vaak aan zwakke opbrengsten van de eliminatie van de GAK in de historische besmetten gronden. Er is toch een echt nood om vernieuwende oplossingen te ontwikkelen.

In dit onderzoek , 6 historische besmetten gronden door teerolie zijn gekarakteriseerd door de aanwezigheid van 42 tot 86 % van de GAK in het zandig deel, geabsorbeerde op verschillende deeltjes van kool/coke/hout of anders zich geïntegreerd binnen deeltjes van verharsten en aangetasten teerolie. Zo, in functie van het niveau van de opsluiting van de GAK, de selectieve scheiding van de meest besmetten deel of het gebruik van het procedé van het wassen van de grond (GW) gebruikend oppervlakken die als veelbelovende alternatieven aan bioremediëring procedés verschijnen. Een bijzonder aandacht heeft dan op het procedé van GW gesteund, gebruikend oppervlakken die gebaseerd is op de optimalisering van de overdracht van de gronde GAK naar de wasoplossing. Deze procedé genereert oplossingen van GW bevattende groot hoeveelheden van oppervlakken en verontreinigende stoffen. Deze moeten behandeld worden in het doel van de besmetting van het milieu te vermijden en het verband kosten-doeltreffendheid te verbeteren.

De anode oxidatie (AO) werd geïdentificeerd als een adequaat en veelbelovend procedé voor de behandeling van de oplossingen van grond wassen GW bevattende GAK en Tween® 80 als extractiemiddel. De uitvoerig bevattingsvermogen van de betrokken werkwijzen in de verwijdering van de organische samenstellingen aanwezig in de GW oplossingen geholpen om twee verschillende behandelingsstrategieën te zetten :



- Eerst en vooral het is vanzelfsprekend dat het gebruik van AO met zwakke stromen en tijdens lange tijd van verwerking (23 uren) staat de selectieve degradatie van de bepaald verontreinigend GAK toe en het hergebruik van de GW oplossing voor de aanvullende stappen van GW. De groot kwantiteit van Tween® 80 zo gesparen verbeterd het verband kosten-doeltreffendheid en de ecologische voetafdruk van de GW procedé, vooral als de opsluiting van de verontreinigende stoffen in de grond vergt verschillende stappen van (GW) en het gebruik van oppervlakken concentratie.
- Daarentegen, hoge opbrengsten van verwijdering van organische samengestelde en de productie van bijproducten meer biologische afbreekbaar werd geobserveerd toen het gebruik van zwakke intensiteit AO en tijdens kort verwerking tijd (3 uren). Zo, de synergistisch effecten waren geobserveerd toen de verbinding van AO met een biologische postverwerking. Belangrijke uitschakeling opbrengsten met optimale operationele kosten kunnen bereiken worden. Meer, de AO kan ook als postverwerking voor de verwijdering van zwak biologisch afbreekbaar samengesteld gebruiken worden. Deze strategie van behandeling heeft als doel het milieu besmetting door de GW oplossingen te vermijden.

Beide strategieën van verwerking moeten rekening worden voor een optimale en geschikt beheer van de oplossingen van (GW) gehouden. Volgens de veelbelovende resultaten gekregen, de wetenschappelijke uitdagingen verbonden tot de schaalverandering van deze procedé waren over gepraat.

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## LIST OF ABBREVIATIONS

2,4-D	2,4-dichlorophenoxyacetic acid
ACY	Acenaphthylene
ACE	Acenaphthene
ANT	Anthracene
AO	Anodic oxidation
AOP	Advanced oxidation process
B30 – B35	Brij 30 – Brij 35
BaA	Benzo[a]anthracene
BaP	Benzo[a]pyrene
BbF	Benzo[b]fluoranthene
BC	Black carbon
BDD	Boron doped diamond
BghiP	Benzo[g,h,i]perylene
BkF	Benzo[k]fluoranthene
BOD	Biological oxygen demand
BOD <sub>5</sub>	Biological oxygen demand at 5 days
BOD <sub>u</sub>	Ultimate biological oxygen demand
BP	Black particle
BT	Biological treatment
CAS	Cocoamidopropyl hydroxysultaine
CD	Cyclodextrin
CHR	Chrysene
CMC	Critical micellar concentration
CMCD	Carboxymethyl- $\beta$ -CD
COD	Chemical oxygen demand
COD <sub>sol</sub>	COD in the solution
COD <sub>tot</sub>	Total COD
CS	Carbon sponge
DahA	Dibenzo[a,h]anthracene
DDE	Dichlorodipenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DSA	Dimensionally stable anode

EAOP	Electrochemical advanced oxidation process
EC	Energy consumption
EF	Electro-Fenton
FLU	Fluorene
FLUO	Fluoranthene
HA	Humic acid
HA <sub>ads</sub>	Adsorbed humic acids
HA <sub>hob</sub>	Low or non-degraded humic acids
HA <sub>hob_ads</sub>	Adsorbed low or non-degraded humic acids
HA <sub>tot</sub>	Total humic acids
HOC	Hydrophobic organic compound
HPCD	Hydroxypropyl- $\beta$ -CD
HTAB	Hexadecyltrimethylammonium bromide
IdF	Soil 'Ile de France'
IND	Indeno[1,2,3-cd]pyrene
IoA	Index of agreement
LAS	Linear alkylsulfonate
MCD	Methyl- $\beta$ -CD
ME	Model efficiency
NAP	Naphthalene
(D)NAPL	(Dense) Non-aqueous phase liquid
NoF	Soil 'North of France'
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorobiphenyl
PCP	Pentachlorophenol
PHE	Phenanthrene
PYR	Pyrene
RAMEB	Randomly methylated- $\beta$ -CD
RMSE	Root mean square error
RWTO	Resinified and weathered tar oil
SDS	Sodium dodecylsulfonate
SF	Soil flushing
SOM	Soil organic matter
SS	Stainless steel

SW	Soil washing
SWEP	Methyl(3,4-dichlorophenyl)carbamate
TNT	Trinitrotoluene
TOC	Total organic carbon
TOC <sub>ads</sub>	TOC adsorbed
TOC <sub>sol</sub>	TOC in the solution
TW80	Tween® 80
TX100	Triton X 100
VOC	Volatile organic compound
VS	Soil 'Veringstrasse'
VSS	Volatile suspended solid





## **INTRODUCTION**

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## **CONTEXT, ISSUE, OBJECTIVES AND STRUCTURE OF THE THESIS**

# **1. Contaminated soils**

## **1.1. Overview of contaminated soils in Europe**

Soil is a scarce, essential and very slowly renewable resource. Therefore, the strong increase of contaminated areas is more and more recognized as a worldwide issue and will represent a major challenge for European countries during the 21<sup>st</sup> century. The number of potentially contaminated sites in Europe is estimated between 2.5 and 3.5 million sites. 350,000 (14%) are estimated to require remediation; among them, 110,000 have been identified and only 50,000 have been remediated [1]. Table 1 reports the areas identified as contaminated or where potentially contaminating industries are currently located, according to the different member states of the European Union (EU). It is also worth to mention that the maximum area of potentially contaminated sites is often one order of magnitude higher than the area of identified contaminated sites. The most industrialized (for example, Germany) and the most urbanized (The Netherlands, Denmark) countries are the most affected by the issue of soil contamination.

**Table 1.** *Area of identified contaminated sites and estimated maximum area of current potentially contaminating industry (% of the total country area) in the different member states of European Union. Data from [2].*

	Total country area (km <sup>2</sup> )	Area (%) of identified contaminated sites		Estimated max area (%) of current potentially contaminating industry
		Min	Max	
Austria	83858		0.2	43
Belgium	30528		4.2	42
Bulgaria	110879		7.0	74
Cyprus	9250		-	-
Czech Rep	78870	1.1	12	30
Denmark	43100	6.5	69	40
Estonia	45227	0.1	1.4	30
Finland	338144	0.1	1.2	20
France	675417	0.1	1.4	15
Germany	357022	0.8	8.4	50
Greece	131960		-	30
Hungary	93028	0.2	1.7	30
Ireland	70273	0.0	0.5	60
Italy	301263		8.3	50
Latvia	64189	0.1	0.8	20
Lithuania	65300		7.2	20
Luxembourg	2600	7.7	81	60
Malta	316	<0.1	6.3	-
Netherlands	41543	5.3	56	120
Poland	312685		35	30
Portugal	92200		-	40
Romania	238291		15	30
Slovakia	49033	0.1	0.9	20
Slovenia	20255	<0.1	<0.1	30
Spain	505911	<0.1	0.1	30
Sweden	441369		<0.1	2
UK	242900	0.1	0.7	30

A large range of industrial activities are involved in the growing number of contaminated sites, including for example mining activities, oil industry, chemical industry, gas and coking plants, waste disposal, military activities etc. Contaminants include inorganic compounds (heavy metals) and organic compounds (hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls, dioxins, chlorinated and aromatic solvents etc.) with various toxic, carcinogenic, mutagenic or genotoxic effects to higher organisms. Mineral oil and heavy metals are the most widespread contaminants in Europe (present in 60% of contaminated sites) [1]. In France, hydrocarbons (16%), lead (8%), PAHs (7%), chromium (6%), halogenated solvents (6%), copper (6%) and arsenic (6%) are the most common pollutants [3]. Moreover, diffuse contamination of soils by pesticides from agricultural activities is also a worrying issue. Besides, contaminated soils represent an important long-term source of contamination for groundwater.

Therefore, there is an urgent need to both reduce soil contamination and implement cost-effective soil remediation processes in order to reach a sustainable management of soils in Europe. In the short terms, it is direct economic issues that encourage most of efforts for soil remediation. Particularly, contaminated soils can strongly inhibit urban development because they represent large areas of non-usable fields for human activities. Thus, soil remediation is a key issue in highly urbanized regions where there is a lack of space for further development. The European Environment Agency estimated in 2014 that the management of contaminated soils in Europe costs annually around 6 billion Euros [1]. Further development of the soil remediation market is still hindered by a lack of political determination. While EU established standard regulation for air and water, there is still none specific common regulation on contaminated soils. Therefore, each country is developing its own regulation context. Only some countries (Belgium, Denmark, Germany, The Netherlands, Spain, UK, Italy, Finland etc.) defined a specific soil regulation; soil regulation in others country (France, Austria, Greece, Poland, Portugal, Ireland, Czech Republic, Sweden etc.) still depends on general waste / industrial regulations, water and air regulations (indirectly) or other general environmental laws. Most of these regulations are based on a risk assessment instead of a threshold approach. Risk assessment studies depend on (i) the nature and level of the pollution,

(ii) possible pathways for direct and indirect contact between pollutants and people (bioavailability) [4] and (iii) presence of people exposed to this contamination [5].

The implementation of a common soil framework directive by the EU is an important political challenge for the following years.

## **1.2. A focus on polycyclic aromatic hydrocarbon contaminated soils**

PAHs are chemically stable hydrophobic organic compounds made of two or more condensed aromatic rings. There are some natural sources such as forest fires or volcanic eruptions since they are generated by pyrolysis or incomplete combustion of organic compounds [6,7]. However, their main origin is anthropogenic; they are common constituents of soot particles, coal tars, mineral oils, etc. [8]. The development of manufactured gas plant and the rise of tar oil use during the 19<sup>th</sup> and 20<sup>th</sup> centuries strongly increased anthropogenic emissions and contaminations by PAHs. Due to their toxic, mutagenic and carcinogenic properties [9,10], PAHs are now a critical environmental concern.

Here are the main physicochemical properties of PAHs that govern their environmental fate:

- They have a high octanol/water ( $K_{ow}$ ) and organic carbon ( $K_{oc}$ ) partition coefficient as well as a low solubility in water. Therefore, they are persistent in the environment and interact strongly with solid surfaces, soil organic matter and non-aqueous phase liquid (NAPL) [11].
- They are semi- or non-volatile compounds (low Henry constant values).
- They have a density higher than 1 (dense non aqueous phase liquid (DNAPL)).

However, these properties mainly depend on the molecular weight of PAHs. For example, only light PAHs (mainly those with 2 aromatic rings) have relatively higher solubility in water and are considered as semi-volatile compounds. Table 2 reports the main physicochemical properties of 16 PAHs, which are the most often considered for an

easy and relevant monitoring of contaminated sites (they have been listed by the United States Environmental Protection Agency (USEPA)) [12].

There is a strong heterogeneity of regulations about PAH-contaminated soils. Regulations depend on the future use of the soil and specific national laws. For example, in France, a threshold of 50 mg  $\Sigma$ PAH kg<sup>-1</sup> has been defined for landfill disposal of inert wastes [13]. In contrast, Denmark enforced a threshold value of 1.5 mg  $\Sigma$ PAH kg<sup>-1</sup> for sensitive land use. Some other countries also prefer to add or to consider only a threshold value for benzo(a)pyrene, which is one of the most toxic PAH [14].

**Table 2.** Some physicochemical properties of the 16 USEPA PAHs. Data from [15–17].

PAHs	Formula	MW (g mol <sup>-1</sup> )	Density	Water Solubility at 25°C (mg L <sup>-1</sup> )	Log K <sub>oc</sub>	Henry constant at 25°C (Pa m <sup>3</sup> mol <sup>-1</sup> )
Naphthalene	C <sub>10</sub> H <sub>8</sub>	128.2	1.162	32	3.2	49
Acenaphthylene	C <sub>12</sub> H <sub>8</sub>	152.2	1.194	3.9	3.4	-
Acenaphthene	C <sub>12</sub> H <sub>10</sub>	154.2	1.024	3.4	3.7	15
Fluorene	C <sub>13</sub> H <sub>10</sub>	166.2	1.203	1.9	3.9	9.2
Phenanthrene	C <sub>14</sub> H <sub>10</sub>	178.2	1.172	1.3	4.2	4.0
Anthracene	C <sub>14</sub> H <sub>10</sub>	178.2	1.240	7.0×10 <sup>-2</sup>	4.2	5.0
Fluoranthene	C <sub>16</sub> H <sub>10</sub>	202.3	1.236	2.6×10 <sup>-1</sup>	4.6	1.5
Pyrene	C <sub>16</sub> H <sub>10</sub>	202.3	1.271	1.4×10 <sup>-1</sup>	4.6	1.1×10 <sup>-3</sup>
Benzo[a]anthracene	C <sub>18</sub> H <sub>12</sub>	228.3	1.174	1.0×10 <sup>-2</sup>	5.3	2.0×10 <sup>-2</sup>
Chrysene	C <sub>18</sub> H <sub>12</sub>	228.3	1.274	2.0×10 <sup>-3</sup>	5.3	1.0×10 <sup>-2</sup>
Benzo[b]fluoranthene	C <sub>20</sub> H <sub>12</sub>	252.3	-	1.5×10 <sup>-3</sup>	5.7	5.0×10 <sup>-2</sup>
Benzo[k]fluoranthene	C <sub>20</sub> H <sub>12</sub>	252.3	-	8.0×10 <sup>-3</sup>	5.7	6.9×10 <sup>-2</sup>
Benzo[a]pyrene	C <sub>20</sub> H <sub>12</sub>	252.3	1.284	3.8×10 <sup>-3</sup>	6.7	5.0×10 <sup>-2</sup>
Indeno[1,2,3-cd]pyrene	C <sub>22</sub> H <sub>12</sub>	276.3	-	2.0×10 <sup>-4</sup>	6.2	2.9×10 <sup>-2</sup>
Dibenzo[a,h]anthracene	C <sub>22</sub> H <sub>14</sub>	278.3	1.252	5.0×10 <sup>-4</sup>	6.5	4.8×10 <sup>-3</sup>
Benzo[g,h,i]perylene	C <sub>22</sub> H <sub>12</sub>	276.3	1.329	3.0×10 <sup>-4</sup>	6.2	1.4×10 <sup>-2</sup>

### 1.3. Soil washing and other soil remediation processes

Soil remediation is an area of environmental engineering that did not yet reach maturity. Cost-effectiveness and robustness of most of processes currently used have still to be further improved. The diagnostic of a contaminated site is also a critical step. Particularly, the nature and the location of a contamination have to be carefully defined. Then, there are three main types of treatment, which have a direct influence on treatment costs: *in-situ* (without excavation), on-site (with excavation, 7 € t<sup>-1</sup>) and *ex-situ* (with excavation and transportation of contaminated soils to a treatment center, 0.2 € t<sup>-1</sup> km<sup>-1</sup>) [18]. It is also worth to mention that soil remediation processes usually follow the following order of effectiveness: *ex-situ* > on-site > *in-situ*.

Several different remediation processes are currently used. However, here is a rapid overview of the main drawbacks of the most widespread soil treatment processes [19,20]:

- All processes based on biodegradation (natural attenuation, bioaugmentation, biostimulation, aerobic/anaerobic biological treatment, composting, bioslurry) are strongly hindered by the presence of highly sequestered and poorly bioavailable pollutants in real historically polluted soils. Moreover, *in-situ* biodegradation processes require very long treatment times.
- Phytoremediation processes are not able to treat deep contaminations (such as DNAPL). Long treatment times are also required.
- *In-situ* chemical oxidation processes are very expensive, due to the presence in soils of a lot of scavengers for oxidant species. Moreover, they also affect the microbial activity in soils. Furthermore, rebound effects can be observed due to the decrease of the sequestration of pollutants during the process.
- Reactive barriers are not easy to operate. Moreover, the pollution source and poorly mobile pollutants are not treated.
- The pump and treat process is strongly hindered by the presence of highly sequestered hydrophobic organic compounds (HOCs). Moreover, the pumping



system has to be carefully managed in order to avoid the extension of the pollution source.

- Thermal treatments (thermal desorption, pyrolysis, incineration) are very costly processes. Moreover, they often strongly affect the soil structure and the microbial activity.
- Processes such as venting and air sparging can be only applied for the removal of volatile organic compounds (VOCs). Moreover, a post-treatment of the contaminated air must be implemented.
- Solidification and stabilization processes only lead to the reduction of the mobility of pollutants.

This thesis focuses on the use of extracting agent-enhanced soil washing (SW) processes. This can be performed on-site or *ex-situ*. SW is a soil remediation process based on the transfer of organic pollutants from the soil-sorbed fraction to the SW solution [21,22]. This allows the decontamination of soils but an additional treatment has to be implemented for pollutants transferred in the aqueous phase. The benefit of this method is that it is easier to remove organic pollutants from the aqueous matrix than from the very complex soil matrix.

The implementation of remediation measures should always depend on pollution characteristics. Critical parameters are the nature and the level of contamination and sequestration of pollutants, because of their direct influence on the (bio)availability of pollutants [23]. For example, bioremediation processes should be used in case of low sequestration and high (bio)availability of pollutants because they are more cost-effective processes than SW. However, the presence of aged contaminations or pure phase strongly reduces the efficiency of biodegradation [24]. In such case, surfactant-enhanced SW processes may appear as a more suitable treatment strategy in order to improve pollutant removal rates.

The choice of the soil remediation process also depends on the objectives to be reached in terms of pollutant removal and timeline. The implementation of remediation actions can also take into consideration that PAH sequestration also limit their bioaccumulation and uptake in higher organisms [25]. Thus, risk assessment based on the availability of

pollutants instead of total concentration in soils appears to be a potential compromise for the reduction of treatment costs. But this does not take into account that the currently non-available fraction may be then (partly) mobilized, either because a new equilibrium is established after the removal of the available fraction from the aqueous phase or because environmental conditions change and the equilibrium shifts towards a higher solubility of pollutants, thus leading to long-term contaminations. Thus, for reaching requirements based on the total concentration of pollutants within reasonable times in case of low (bio)availability of pollutants, surfactant-enhanced SW might be a more suitable process than bioremediation [26].

## **2. Issue: how to manage soil washing solutions?**

The sequestration of PAHs in soils usually lead to the use of large amounts of extracting agents in order to reach sufficient removal rates of organic pollutants from soils. Thus, SW processes generate effluents containing high concentrations of extracting agents and PAHs. Therefore, the development of SW processes tightly relies on the effective management of SW solutions.

In this thesis, Tween® 80 (non-ionic synthetic surfactant) was chosen as extracting agent for the SW process because previous studies had already recommended its use for the treatment of PAH-contaminated soils [15].

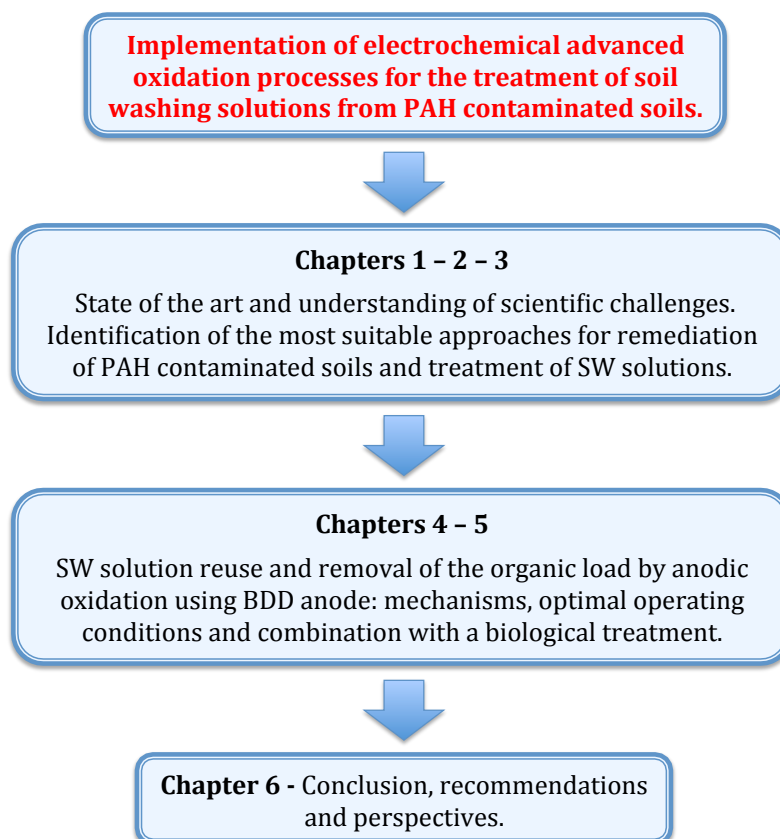
Electrochemical advanced oxidation processes (EAOPs) were selected for the study on the treatment of SW solutions because they are able to remove recalcitrant organic compounds [27–31]. This is ascribed to the generation of large amounts of hydroxyl radicals ( $\cdot\text{OH}$ ) as well as various highly oxidant species such as persulfate, active chlorine, ozone, according to operating conditions, nature of the effluent and choice of the supporting electrolyte. Hydroxyl radicals can be produced either in a homogeneous way in electrochemical cells by the electro-Fenton process or in a heterogeneous way (on the surface of the anode) by the anodic oxidation (AO) process [27–29].

### 3. Objectives and thesis structure

The objectives of the treatment of SW solutions are:

- to efficiently destroy PAHs present in SW solutions and to avoid environmental contamination from discharge of SW solutions;
- to reuse SW solutions for additional SW steps in order to improve SW effectiveness, reduce surfactant consumption and ensure the cost-effectiveness of the whole process.

This thesis is organized around 2 main parts, as described in Figure 1.



**Figure 1.** *Structure of the thesis.*

Here is a short description of the 6 chapters following this general introduction:

- Chapter 1 is a literature review on the treatment of SW solutions. A large range of processes are presented and compared as regards to the specific issue of SW solutions.
- Chapter 2 is a study performed during the mobility at the Helmholtz Center for Environmental Research (Leipzig, Germany). Characteristics of historically tar oil-contaminated soils are investigated and discussed. A new treatment strategy is proposed and tested for the most highly sequestered PAHs.
- Chapter 3 is dedicated to the comparison of several different EAOPs (AO and electro-Fenton, with various electrode materials) for the removal of humic acids (one of the main component of the soil organic matter). During electrolysis, both sorption and oxidation processes are observed, discussed and modeled.
- Chapter 4 is a study focused on the degradation mechanisms of Tween® 80 micelles and organic compounds entrapped inside micelles during AO. The optimal conditions for the selective degradation of target pollutants are identified. The reuse of a real SW solution is tested on a historically PAH-contaminated soil.
- Chapter 5 is a study partly performed during the mobility at the University of Cassino and Southern Lazio (Italy) and focused on the combination of AO with a pre- or post-biological treatment. It aims at the effective removal of the organic load of a synthetic SW solution in the most cost-effective way.
- Chapter 6 is a general conclusion on the main results obtained during this thesis. Recommendations are given for the treatment of SW solutions by AO. It is also discussed the scientific challenges and perspectives that still have to be faced for the scale-up of SW solution treatment by AO.

## **4. Novelty of the thesis**

PAH contaminated soils and treatment of SW solutions are very challenging issues for environmental engineering companies. The interest of the research project carried out during this thesis relied on the global consideration of these issues: from the characterization of contaminated soils to the identification of the most relevant treatment strategies and to the removal of target pollutants from SW solutions. All these aspects have to be considered at the same time in order to provide suitable and relevant improvements.

The following chapters report and discuss the new results and scientific challenges that have been faced during this thesis. All the conferences attended and papers (published, accepted or submitted) related to this thesis are listed in Appendix 1.

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# **CHAPTER 1**

## **LITERATURE REVIEW**

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### **TREATMENT OF SOIL WASHING / FLUSHING SOLUTIONS**

A part of this chapter has been published as a review article:

Trellu C., Mousset E., Pechaud Y., Huguenot D., van Hullebusch E.D., Esposito G., Oturan M.A., 2016. Removal of hydrophobic organic pollutants from soil washing/flushing solutions: A critical review. *Journal of Hazardous Materials*. 306, 149–174. doi:10.1016/j.jhazmat.2015.12.008

Another part of this chapter has been submitted for a book chapter:

Trellu C., van Hullebusch E.D., Huguenot D., Pechaud Y., Esposito G., Oturan M.A. Remediation of soil contaminated by HOCs: How to recover extracting agents from soil washing solutions? In *Contaminatd soils : from characterization to remediation*, Springer, Applied Environmental Science and Engineering for a Sustainable Future (submitted).

## Abstract

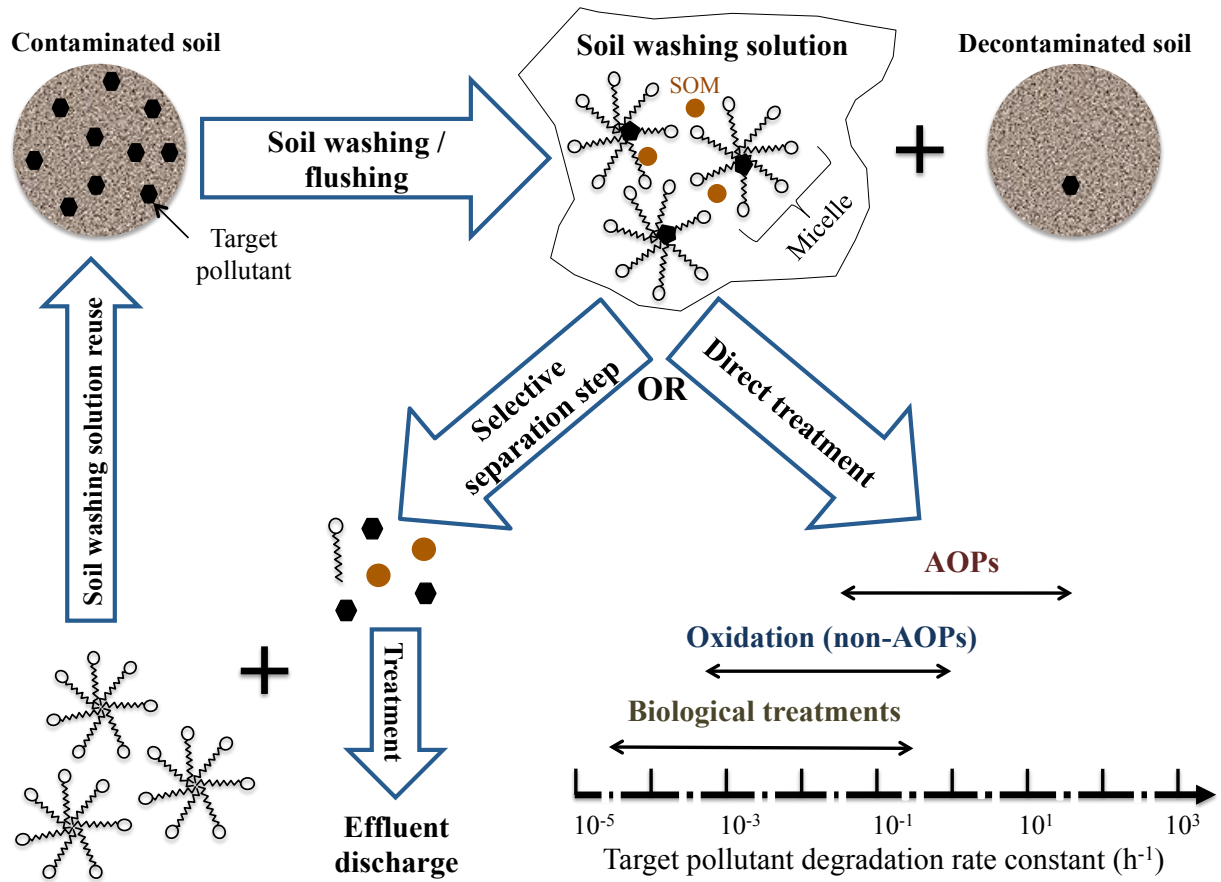
The release of hydrophobic organic pollutants results in long-term contamination of soils and groundwaters. This constitutes a common concern as these compounds have high potential toxicological impact. Therefore, development of cost-effective processes with high pollutant removal efficiency is a major challenge for researchers and soil remediation companies. Soil washing (SW) and soil flushing (SF) processes enhanced by the use of extracting agents (EAs) are conceivable and efficient approaches. However, this generates high strength effluents containing large amounts of EAs.

First, the treatment of SW/SF solutions aims at the removal of pollutants in order to avoid environmental contamination. Several degradation processes such as heterogeneous photocatalysis, technologies based on Fenton reaction chemistry (including homogeneous photocatalysis such as photo-Fenton), ozonation, electrochemical processes and biological treatments have been investigated. Main advantages and drawbacks as well as degradation mechanisms of organic compounds are reviewed and compared in this chapter.

EA recovery from SW/SF solutions prior further reuse for SW/SF is also a critical challenge in order to ensure the cost-effectiveness of SW/SF processes. Selective separation processes such as air stripping, solvent extraction, membrane and adsorption processes have been investigated. Large amounts of EAs can be recovered according to the physico-chemical characteristics of target pollutants and EAs. However, an additional step for the degradation of recovered pollutants is required. Besides, oxidation processes can also lead to partial recovery of EAs, according to operating conditions and reaction kinetics between organic compounds and oxidant species. Also, few studies in the literature reported on the reuse of biologically treated SW/SF solutions.

**Keywords:** Soil washing solution, Advanced Oxidation Processes, Biological treatment, Separation processes, Adsorption.

## Graphical abstract



## 1. Introduction

As a consequence of the continuous development of industrial and agricultural activities, environmental issues and considerations about a sustainable development are becoming increasingly important. Nowadays, these topics are considered for decision-making in industrial, economical and political areas. More stringent regulations about environmental pollution are introduced each year, mostly concerning wastes [1], ambient air [2], atmosphere [3] and water [4]. Recently, a greater attention has been paid to contamination of soils. However, the enforcement and the harmonization of new rules is still a crucial issue, mainly due to the high variability of the nature of contaminated soils and the high costs of immediate investments. These regulation levels are chosen by considering simultaneously health, economic, environmental and social factors. Thus, they have to be in agreement with two basic principles in the environmental field [5]:

- the reduction of exposure levels, to be as low as reasonably achievable;
- the prevention of conventional pollution via the best available techniques not entailing excessive costs.

Particularly, the treatment of polluted soils and sites using environmentally friendly and efficient remediation technologies is a major challenge. Soil quality is greatly affected by the release of hydrophobic pollutants from chemical, coke, wood and oil industries or by diffuse pollution from agricultural and transport activities [6]. The persistence of hydrophobic organic compounds (HOCs) in soils is a matter of significant public, scientific and regulatory concerns because of their potential toxicity, mutagenicity, carcinogenicity and ability to be bioaccumulated in the food chain [7]. Most of them are persistent in the natural environment, due to their slow degradation by natural attenuation or (photo) chemical/biological processes [8]. HOCs such as petroleum hydrocarbons, polychlorobiphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzodioxins and some pesticides are characterized by:

- a low solubility in water;
- a high octanol/water partition coefficient ( $K_{ow}$ );

- a high organic carbon/water partition coefficient ( $K_{oc}$ ), leading to their accumulation in soils by sorption mechanisms with the soil organic matter (SOM).

However, these physicochemical parameters vary according to each HOC and influence the mobility and the availability of HOCs in soils as well as their removal efficiency during the treatment. Moreover, their behavior is also influenced by their respective volatility.

Nowadays, all processes used for soil remediation have at least one important drawback such as heavy costs (thermal treatments), a high disturbance of soil texture and microbial activity (thermal treatments), a low efficiency and a long treatment time (biodegradation processes), or a selectivity towards target pollutants (volatile organic compounds (VOCs) for venting) [9]. This is why remediation companies are still looking for effective, less expensive and more environmentally friendly processes. Particularly, during the two last decades, soil washing / soil flushing (SW/SF) processes using EAs (EAs) (surfactants, biosurfactants, cyclodextrins (CDs), cosolvents) have shown promising results [10,11].

HOCs are mainly sorbed to the SOM [12] or present in non-aqueous phase liquids (NAPLs). EAs are used in order to enhance the solubility, desorption and biodegradation of soil pollutants [10]. These substances have shown promising results for the enhancement of techniques dealing with *in situ* chemical oxidation [13]. In fact, EAs improve the availability of hydrophobic soil pollutants for reactive oxygen species by transferring them into the aqueous phase. However, this process requires the use of large amounts of reagents [14] and leads to an important soil disturbance. This is why some authors have tried to develop an efficient method based on the removal of pollutants from the soil matrix by SW (*ex situ* process) or SF (*in situ* process), followed by a stage of treatment of the SW/SF solution [15–17]. This alternative combined process aims at disturbing as low as possible soil structure and biological activity, while removing and destroying efficiently pollutants with optimized operating costs.

However, it is widely recognized that the use of large amounts of costly EAs is one of the most important drawback of this treatment strategy [18]. The most direct approach for the reduction of EA consumption is the optimization of their use during SW/SF processes. Decontamination of polluted soils by SW/SF processes has already been



widely reviewed in the literature either with surfactants [10,11,19,20] or CDs [21] as EA. Interestingly, a suitable treatment of the SW solution can also lead to the recovery of large amounts of EA and strongly improve the cost efficiency of soil remediation.

This is why the main goals of this chapter are to answer the following issues:

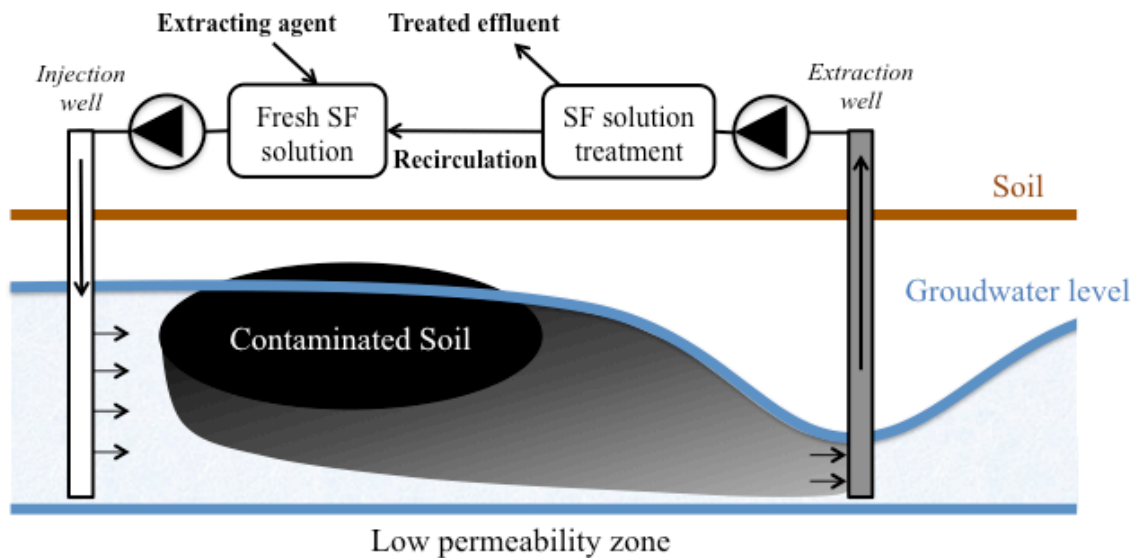
- How to remove pollutants from SW/SF solutions in order to avoid contamination of the environment? Heterogeneous photocatalysis, technologies based on Fenton reaction chemistry (including homogeneous photocatalysis such as photo-Fenton), ozonation, electrochemical processes, biological treatments and the combination of advanced oxidation processes (AOPs) with a biological treatment have been investigated.
- How to recover EAs during the treatment of SW/SF solutions in order to improve the cost-effectiveness of SW/SF processes? Selective degradation and selective separation processes such as liquid-liquid extraction, gas-liquid extraction, membranes and adsorption processes have been investigated.

## **2. Extraction of hydrophobic organic compounds from soil by soil washing and soil flushing processes**

Soil is a complex porous and solid matrix, which makes the treatment of contaminations more difficult. Particularly, HOCs have the ability to bind to SOM [12]. SOM originates from the contribution of fresh organic matter by living organisms or from the decomposition of this fresh organic matter by mostly biological processes called humification [22]. The integration of the organic matter with soil mineral particles forms the so-called clay-humus complex, which has an important influence on soil properties and sorption of HOCs [19]. In the following sub-sections, some extraction methods are presented, including SF and SW processes. The different EAs used are also explored.

### **2.1. Soil flushing process**

The SF process is an *in situ* process, where EAs are used in order to improve the mobility of NAPL by reducing interfacial tension between NAPL and groundwater [10]. Mobilized contaminants can then be recovered in extraction wells. However, SF is preferentially used for light NAPL remediation because pumping is easily managed from the surface of the underground water table. The efficiency of this process in real sites strongly depends on field characteristics (soil heterogeneity, contaminant nature, NAPL saturation, etc.) [23]. SF is characterized by the amount of solution used. It is normalized by comparing the volume of solution used to the pore volume of the soil. This ratio can range from 1 to more than 200 [21]. Figure 1.1 represents a schematic view of the SF process.



**Figure 1.1.** Scheme of a typical *in situ* soil flushing (SF) installation.

The electrokinetic surfactant-aided SF [24] can also be used. In the classical SF process, the driving force is the pressure gradient, while there is a voltage gradient in the electrokinetic surfactant-aided SF.

The SF process is appealing due to the absence of a preliminary excavation step, low environmental disruption, and reduction of worker exposure to hazardous materials [25]. However, this *in-situ* technique may lead to low effectiveness according to soil heterogeneities, permeability, porosity and type of contamination [23]. Moreover, displacement and extension of the contaminated zone is sometimes observed when the pumping system is not well managed [23].

## 2.2. Soil washing process

The SW process is an *ex situ* process, i.e., the soil has to be excavated before the treatment. It is operated at a certain solid/liquid ratio, in the range 1-100% [21] and most frequently between 5 and 40%. EAs are supplied to the system in order to improve the removal of contaminants sorbed to the soil [26]. The SW process enhances the contact between EAs and soil pollutants, thereby allowing a reduction of treatment

times as well as better treatment efficiency and treatment monitoring, compared to the SF process [21].

For reaching maximum removal rates and minimum costs related to EA consumption, the most important parameters to consider are (i) the extraction capacity of the EA chosen (ii) its cost (iii) its sorption to soil, which can lead to important loss of EA and adverse effects on the quality of soil (iv) the operating parameters, including concentration of EA, soil/liquid ratio, contact time, mixing conditions and number of successive washing steps [21]. Usually, preliminary tests and treatability studies allow the determination of the optimal parameters for the implementation of the SW process, which depend mainly on the nature and level of sequestration of pollutants. Besides, soil characteristics have also to be considered, for example, high organic matter and clay content could have strong adverse effects such as competitive solubilization of natural SOM, mobilization of hardly settling particles and high soil adsorption of EAs [20]. Last but not least, the horizontal and vertical location of the contaminated soil has also to be carefully studied before to excavate the soil fraction that will be treated. Excavation and treatment of non-polluted soil strongly decrease the cost-efficiency of the process.

## **2.3. Extracting agents**

Extracting aqueous solutions with or without additives are employed to mobilize HOCs from the soil to the SW/SF solution. Additives are used for increasing aqueous solubility of HOCs, since it is one of the main controlling mechanisms for SW efficiency. These EAs reduce the time necessary to treat a site compared to the use of water alone. Aside from their extracting and solubilizing capacities, they must be of low ecotoxicity for the soil and biodegradable [10]. Besides, they can also lead to the mobilization of heavy metals, as it has been recently reviewed by Mao et al. [11].

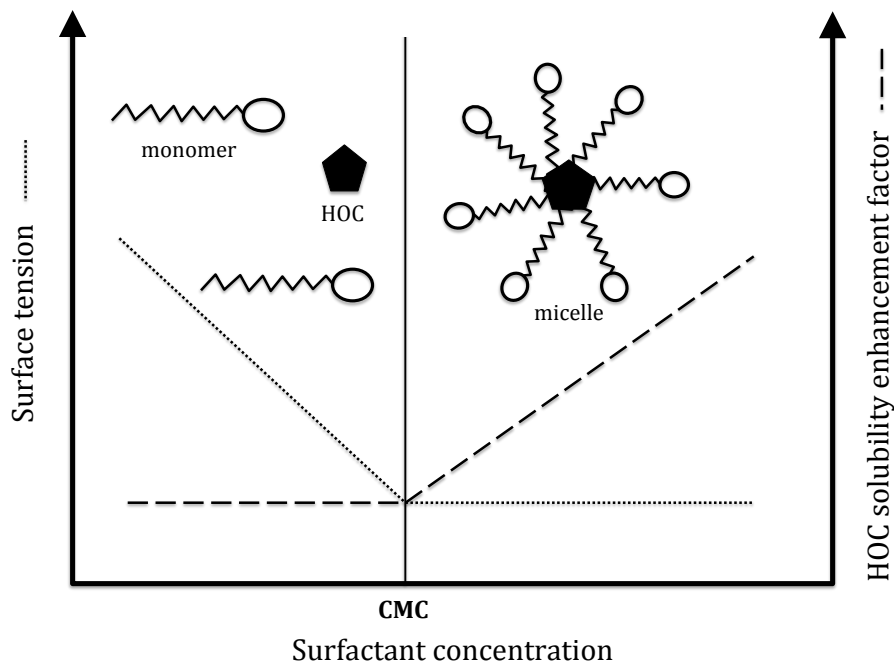
### **2.3.1. Synthetic surfactants**

Surfactants are amphiphilic molecules composed of two main components, the hydrophobic tail group and the hydrophilic head group. They are mainly characterized

by their chemical structure, hydrophilic-lipophilic balance and critical micellar concentration (CMC). CMC is the surfactant concentration above which micelles form and all additional surfactants added to the solution go to micelles. Below CMC, the surface tension changes strongly with the concentration of the surfactant. Above CMC, HOC solubility is strongly enhanced and the surface tension changes with a much lower slope (Figure 1.2) [10]. Different mechanisms are involved in surfactant-enhanced SW/SF, including the decrease of the interfacial tension, phase transfer of HOCs from the soil-sorbed to the micellar pseudo-aqueous phase and solubilization of HOCs inside the hydrophobic space formed by micelles [20]. HOC partitioning can be assessed by a mole fraction micellar phase / aqueous phase partition coefficient  $K_m$  (Eq. 1) [20].

$$K_m = \frac{X_m}{X_a} \quad (\text{Eq. 1})$$

whereby  $X_m$  and  $X_a$  are the ratio of the mole fraction of target pollutants in the micellar pseudo-phase and aqueous phase, respectively.



**Figure 1.2.** Surface tension and hydrophobic organic compounds (HOCs) solubility enhancement factor as a function of surfactant concentration.

Among EAs, synthetic surfactants have the best extraction effectiveness [10,27]. However, some of them are hardly biodegradable [28] and affected by precipitation or sorption onto soil, requiring larger amounts and possibly damaging soils [19,20]. Moreover, surfactants may also form emulsions with high viscosity that are difficult to manage and remove.

There are four major surfactant categories, which include anionics (such as sodium dodecylsulfate (SDS) or linear alkylbenzene sulfonate (LAS)), cationics (such as quaternary ammonium derivatives), amphoteric (such as cocoamidopropyl hydroxysultaine (CAS)) and nonionics (such as Brij 35 (B35), Tween 80 (TW80) or Triton X 100 (TX100)). Non-ionic surfactants are preferably used compared to ionic surfactants due to their lower soil sorption ability, higher solubilization capacity and higher cost-effectiveness [10].

### **2.3.2. Biosurfactants**

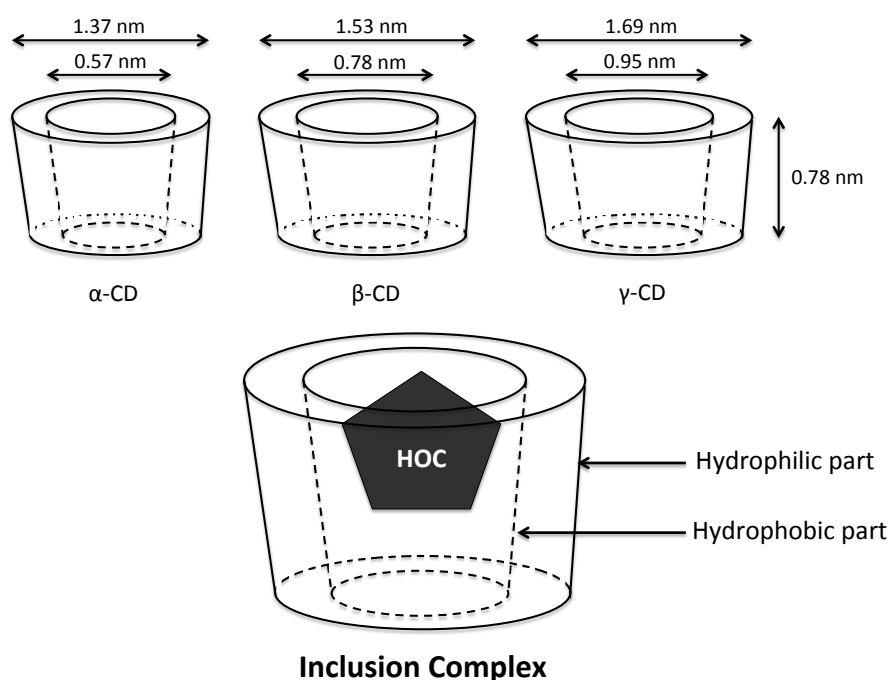
Biosurfactants are also amphiphilic compounds able to form micelles. They are of microbial origin and produced from renewable resources. Similarly to synthetic surfactants, biosurfactants have high extraction capacity [19,29]. For example, Lai et al. [30] observed that rhamnolipid (RHA) and saponin (biosurfactants) exhibited higher petroleum hydrocarbons removal efficiency from soil than TW80 and TX100 (synthetic surfactants). Other advantages of biosurfactants include higher biodegradability, ecological safety, lower toxicity and the possibility to be produced *in situ* [29,31]. However, the main issue that currently impairs their use in SW/SF processes is their economically reasonable production [29,32].

### **2.3.3. Cyclodextrins**

CDs have hydrophilic groups on the external side of their ring, which can dissolve in water, and an apolar cavity providing a hydrophobic matrix, described as a micro heterogeneous environment [33]. Hydrophobic molecules are accommodated within the apolar cavity to form inclusion complexes as it is shown in Figure 1.3. Thus, HOC

solubility is increased according to the complex stability (or equilibrium) constant ( $K_{CD}$ ) [21]. Very large differences are observed in the solubility and/or stability of inclusion complexes formed with different compounds [33].

There are three main native CDs consisting of cyclic oligosaccharides with six ( $\alpha$ -CD), seven ( $\beta$ -CD) or eight ( $\gamma$ -CD) glucopyranose units linked by  $\alpha$ -(1,4) bonds [33,34]. The internal dimension of the apolar cavity varies according to the number of glucopyranose units (Figure 1.3).



**Figure 1.3.** Structure of native cyclodextrins (CDs) and inclusion complex formed with hydrophobic organic compounds (HOCs). Adapted from the reference [34].

There are also many derivative  $\beta$ -CDs such as hydroxypropyl- $\beta$ -CD (HPCD), carboxymethyl- $\beta$ -CD (CMCD), methyl- $\beta$ -CD (MCD) or randomly methylated- $\beta$ -CD (RAMEB). These CDs have higher solubility (in the range 100 to 1000 g L<sup>-1</sup>) compared to the native  $\beta$ -CD (18.5 g L<sup>-1</sup> at 25 °C).

CD-enhanced SW/SF processes have been recently reviewed [21]. CDs enhance water solubilization of many HOCs [35]. The  $\beta$ -CD is considered as the most accessible and less

expensive among the native ones [21]. However, its low solubility increases its soil sorption and limits its application for SW/SF experiments. Consequently, derivative  $\beta$ -CDs have been marketed and proved their high water-solubility and efficiency. Moreover, derivative CDs exhibit better extracting capacity than the native ones [21].

The analysis of the enhancement of HOCs solubility by using different surfactants and CDs revealed that CDs have a lower ability to solubilize HOCs than traditional surfactants [36]. They are usually ten times less efficient, depending on the nature of the CD and surfactant used [21].

#### **2.3.4. Organic cosolvents and vegetable oil**

The use of organic co-solvents (esters, ketones, alcohols, alkylamines and aromatics for example) is no longer considered to be a promising technique. It implies several important drawbacks, such as high costs, risks of handling and storing, toxicity and soil permeability disturbing [29]. Moreover, their effect is usually not significant until the volume-fraction concentration used is above 10% [21].

However, it has been shown that vegetable oil could favorably replace costly, toxic and low-biodegradable organic solvents for HOCs removal from soil [29]. For instance, more than 90% of the total PAHs from a heavily contaminated soil has been removed by using a sunflower oil-soil ratio of 2:1 (v/w) [37]. It is worth to mention that further assessment of costs, ecological risks, and treatment/disposal of contaminated oil is necessary because of huge quantities of vegetable oil needed [38]. Moreover, the production of the vegetable oil also involves large areas of cultivated fields as well as the use of high amounts of pesticides increasing environmental risks.

#### **2.3.5. Other alternative extracting agents**

Some other alternative EAs have also been reported, including salmon deoxyribonucleic acid [16] and humic acids [39] for their amphiphilic properties, soil nano-particles (composed mainly by organic carbon and inorganic clay material) due to their adsorption capacities [40], polymers for their ability to change water viscosity [23],



surfactant foams leading to homogeneous displacement fronts [23] and gemini surfactants for their low CMC [11]. However, further studies are necessary to assess their efficiency in different remediation cases. Moreover, the production at industrial scale of some of them is still the main issue for their extensive application in soil remediation [11].

### 3. Removal of hydrophobic organic compounds from soil washing/flushing solutions by degradation processes

Electrochemical advanced oxidation processes (EAOPs), heterogeneous photocatalysis and technologies based on Fenton reaction chemistry (including homogeneous photocatalysis such as photo-Fenton) have been largely applied to the treatment of SW/SF solutions [41–43]. These AOPs are based on the generation of strong oxidants, in particular, hydroxyl radicals ( $\bullet\text{OH}$ ). The main characteristics of this radical are [44–46]:

- a very strong oxidizing power:  $E^\circ(\bullet\text{OH}/\text{H}_2\text{O}) = 2.8 \text{ V/SHE}$ ;
- a non-selective feature towards organic compounds;
- a very short average lifetime of few nanoseconds in water.

The  $\bullet\text{OH}$  has the ability to degrade most of organic and organo-metallic pollutants [47,48] by dehydrogenation, hydroxylation or redox reactions [49]. The degradation of organic compounds involves the formation of several by-products until total mineralization, i.e., conversion into carbon dioxide ( $\text{CO}_2$ ), water and inorganic ions [50,51]. This is the reason why mineralization rates are much slower than degradation rates [50]. Furthermore, some by-products more toxic than the parent compound can be formed [52]. Therefore, the identification of these by-products, the understanding of degradation pathways [53,54] and the evolution of the treated solution toxicity are also relevant parameters to study [55].

The use of ozone, biological treatments and combined processes is also discussed in this subsection.

The efficiency of each process for SW/SF solutions treatment must be assessed as a function of the following specific objectives [15,16,56]:

- target pollutants removal: influence of operating conditions and specific SW/SF solution characteristics (particularly high EA concentrations) on degradation kinetics;
- operating cost optimization (reagent consumption, treatment time, energy consumption, sludge production etc.);
- recovery of EAs and reuse of SW/SF solutions.

Removal of HOCs from SW/SF is investigated either in synthetic SW/SF solutions [56] or in real SW/SF solutions [17]. With synthetic solutions, chemical substances/pollutants initially present in the solution are totally controlled: concentration of pollutants, surfactants/cosolvents, or other initial parameters such as the presence of dissolved organic matter. The use of simple systems like synthetic solutions makes the control of selected parameters easier and leads to a better understanding of mechanisms involved during the treatment. However, it does not reproduce real parameters affecting the process efficiency. A lot of synergetic, competing or scavenging effects can occur in real SW/SF solutions, depending on the presence of different nature and concentration of pollutants, SOM, or metallic ions, for example. This is the reason why the efficiency of a process for SW/SF solution treatment has to be assessed by using real SW/SF solutions. Therefore, both kinds of studies are complementary.

### 3.1. Heterogeneous photocatalysis

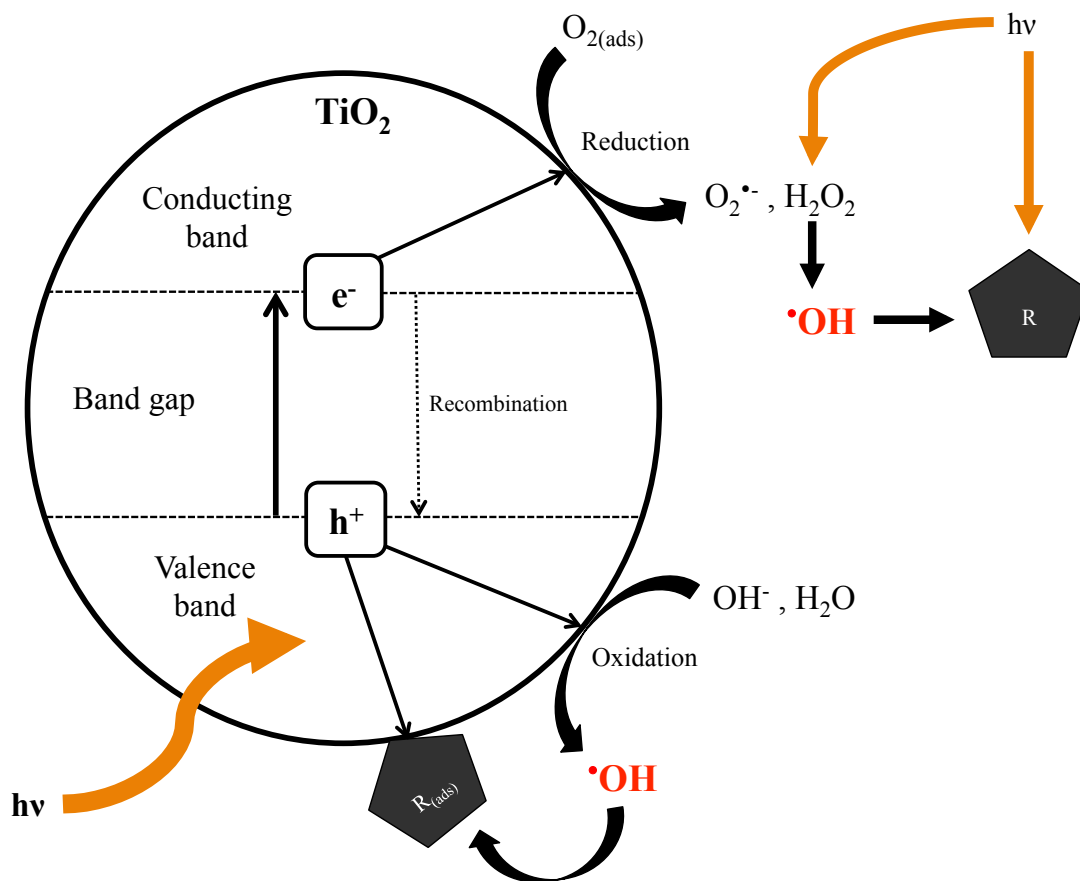
#### 3.1.1. General considerations

Photolysis of organic compounds is an important mechanism in natural environment (solar photolysis) but this process is not effective enough for industrial applications on highly contaminated wastewaters. However, coupling light irradiation with the addition of a photocatalyst increases the efficiency due to the formation of  $\bullet\text{OH}$ . Several authors have reviewed the application of this photocatalytic process for the treatment of hazardous organic compounds in wastewaters [57–62]. The process is based on the use of semiconductors exhibiting a band gap region in which no energy levels are available to promote the recombination of an electron and hole produced by photoactivation in the solid semiconductor (Eq. 2). This band gap ( $E_g$ ) extends from the top of the filled valence band to the bottom of the vacant conduction band.



By far, titanium dioxide ( $\text{TiO}_2$ ) is the most largely used compared to other semiconductor photocatalysts due to its cost-effectiveness, inert nature (i.e. stable under different reaction conditions) and photostability (i.e. able to promote reactions efficiently upon repetitive use). Several authors have reviewed and described the

degradation of organic contaminants by heterogeneous photocatalysis [58,61,63]. This process is schematically described in Figure 1.4.



**Figure 1.4.** Schematic representation of the oxidation mechanism of organic compounds ( $R$ ) by the photocatalytic process. Adapted from the reference [63].

### 3.1.2. Removal efficiency and kinetics

Complete degradation of target pollutants has been achieved with degradation rate constants in the range of  $0.1 - 10 \text{ h}^{-1}$  and by using several kinds of pollutants and EAs (Table 1.1).

A decrease in degradation rates is observed with real SW/SF solutions. Thus, the process needs to last longer in order to reach similar effectiveness than with synthetic SW/SF solutions [64–66]. This is ascribed to adverse effects from the presence of SOM.

Since  $\bullet\text{OH}$  have a non-selective reactivity towards organic compounds, the SOM acts as a strong  $\bullet\text{OH}$  scavenger [67–69].

Most of the studies only investigated the first step of target pollutant degradation. Further studies about total organic carbon (TOC) and chemical oxygen demand (COD) removal as well as toxicity evolution would be necessary since these measurements provide reliable and significant results concerning the efficiency of the treatment and quality of the effluent.

**Table 1.1.** SW/SF solution treatment by photocatalytic processes.

Pollutant (concentration)	Extracting agent (concentration)	Synthetic (S) / Real (R) solution Volume	Operating conditions				Degradation rate constant	Observations	Reference
			Semiconductor (concentration)	Irradiation light	pH	T (°C)			
NAP <sup>1</sup> (0.03 mM)	B35 (1.2 mM)	S 5 mL	TiO <sub>2</sub> (0.4 g L <sup>-1</sup> )	Xe lamp (1500 W) with 340 nm cut-off filter	3	-	2.04 h <sup>-1</sup>	Compared to solutions without B35, degradation rate constant is 4 times lower with B35 and 10 times lower in real SW/SF solution with the same B35 concentration.	[70]
		R 5 mL					0.78 h <sup>-1</sup>		
PCP <sup>2</sup> (0.2 mM)	$\beta$ -CD, MCD, HPCD (0-5 mM)	S 35 mL	TiO <sub>2</sub> (1.7 g L <sup>-1</sup> )	UV lamp (125 W)	7; 11	19	0.3-5.3 h <sup>-1</sup>	The higher CD concentration, the lower PCP degradation rate	[71]
NAP <sup>1</sup> (0.2 mM)	TX100 (0.04-0.13 mM)	S 1 L	TiO <sub>2</sub> (0.1 g L <sup>-1</sup> )	Solar light simulator (50 $\mu$ W cm <sup>-2</sup> )	7	30	1.9-4.2 h <sup>-1</sup>	The higher TX100 concentration, the lower NAP <sup>1</sup> degradation rate and TX100 recovery	[72]
PCB (53 mg L <sup>-1</sup> )	soya lecithin and TX100	R 1 L	TiO <sub>2</sub> (0.5 g L <sup>-1</sup> )	Fluorescent lamp (330-400 nm) (8 W)	-	20	-	Low degradation rate (treatment time = 15 days). Better results for PCB degradation rate with soya lecithin as extracting agent.	[73]
Aromatic compounds	B35 (25 mM)	S 5 mL	TiO <sub>2</sub> (0.5 g L <sup>-1</sup> )	Xe lamp (1500 W) with 340 nm cut-off filter	-	55	0.12-3.48 h <sup>-1</sup> (for individual pollutants)	Addition of peroxydisulfates has improved treatment performances	[66]

SWEP <sup>3</sup> residues (17 mg L <sup>-1</sup> )	C <sub>12</sub> E <sub>8</sub> ; SDS; hexadecyltrimethylammo- nium bromide (8.6 mM)	S; R 500 mL	TiO <sub>2</sub> (0.2-1.0 g L <sup>-1</sup> )	Hg lamp (125 W) with 300 nm cut-off filter	3.0; 5.6; 8.0	25	-	The presence of surfactants largely affects degradation kinetics. Important influence of the nature of the surfactant. Bubbling air improved treatment performances.	[65]
PHE <sup>4</sup> (0.16 mM) and PYR <sup>5</sup> (0.05 mM)	MCD (83 mM)	S -	TiO <sub>2</sub> (1 g L <sup>-1</sup> )	UV (200-280 nm) lamp (150 W)	6	22	-	Very slow degradation rate	[74]
PCP <sup>2</sup> (0.018 mM)	TX100 (0.023-1.01 mM)	S 500 mL	La-B codoped TiO <sub>2</sub> (0.4 g L <sup>-1</sup> )	Visible light (400 W); Xe lamp with 400 nm cut-off filter	5.7	-	0.1-3.3 h <sup>-1</sup>	The higher the TX100 concentration, the lower PCP degradation rate, particularly above the CMC. Photocatalytic degradation kinetics are directly linked to adsorption properties	[75]
				Solar light (39.0-27.5 mW cm <sup>-2</sup> )			1.8-9.3 h <sup>-1</sup>		
alkylphenols	B35 (1 and 10 mM); C <sub>12</sub> E <sub>8</sub> (1 and 10 mM); SDS (15 mM); mixtures	S 5 mL  R 5 mL	TiO <sub>2</sub> (0.1 g L <sup>-1</sup> )  TiO <sub>2</sub> (0.2 and 0.5 g L <sup>-1</sup> )	Xe lamp (1500 W) with 340 nm cut-off filter	-	55	0.1-4.9 h <sup>-1</sup>  0.05-1.86 h <sup>-1</sup>	Important influence of the nature of the surfactant	[76]
PHE <sup>4</sup> (0.006 mM)	TX100 (1.6-4.8 mM)	S -	TiO <sub>2</sub> (0.1-0.5 g L <sup>-1</sup> )	Monochromatic (254 nm) UV lamp (8 W)	3.6; 8.1	25	1.4-3.5 M <sup>-1</sup> min <sup>-1</sup>	Effect of O <sub>2</sub> , H <sub>2</sub> O <sub>2</sub> and radical scavengers has also been studied	[77]

<sup>1</sup> Naphtalene, <sup>2</sup> Pentachlorophenol, <sup>3</sup> Methyl(3,4-dichlorophenyl)carbamate, <sup>4</sup> Phenanthrene, <sup>5</sup> Pyrene

### 3.1.2.1. Influence of extracting agents

The efficiency of the process tightly relies on the adsorption capacity of target pollutants onto the photocatalyst [75] because it promotes the oxidation of organics by highly oxidant species such as  $\bullet\text{OH}$  formed at the surface of the catalyst (Figure 1.4). Adsorption depends on pollutant and surfactant properties and concentration as well as surface characteristics of the photocatalyst.

#### ❖ *Surfactant: influence of nature and dose*

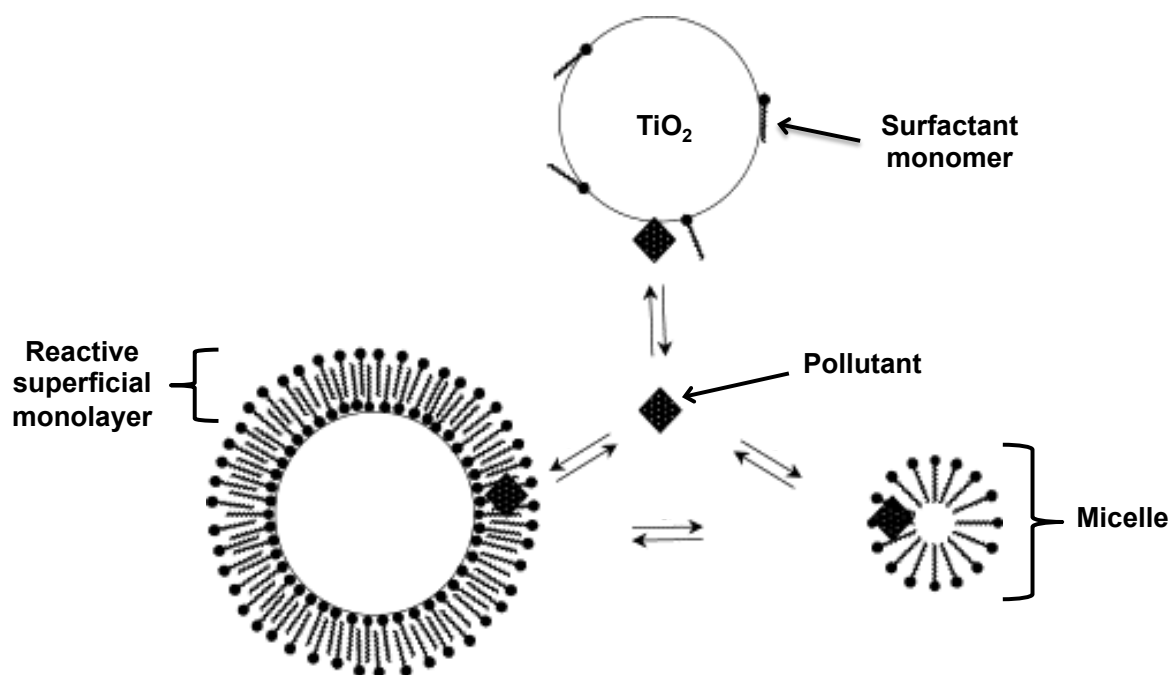
The use of low surfactant concentrations (below or close to the CMC) improves the removal of HOCs. This beneficial effect has been explained by the following mechanism [75]. First, non-ionic surfactant monomers quickly combine with the modified surface of the catalyst. This comes from the interaction with hydrophobic sites on the catalyst surface. Thus, a superficial reactive monolayer is formed on the catalyst surface. Finally, the target pollutant implants into the hydrophobic space among the surfactant head and the catalyst surface system. This promotes its availability to photogenerated oxidant species [75].

Cationic surfactants also greatly enhance the adsorption of target pollutants at low surfactant concentration [78,79]. The superficial reactive monolayer formation at the surface of the catalyst is ascribed to electrostatic interactions. Besides, higher effectiveness for photocatalytic degradation has been obtained in solutions containing mixed cationic–nonionic surfactants compared to solutions with single surfactants, indicating synergistic effects in complex systems [78].

However, it is important to mention that the effect of surfactants on more hydrophilic compounds (such as oxidation by-products) is less favorable, even at low concentration [79]. This may be attributed to the lower fraction of organic compounds implanted in the superficial hydrophobic reactive monolayer (lower  $K_m$ ) and/or to a different locus of implementation of these organic compounds inside this monolayer (closer to the hydrophilic heads of surfactants), which decrease their availability for oxidant species.



Lower effectiveness for degradation of HOCs by photocatalysis has been obtained by increasing surfactant concentration higher than the CMC (such as in SW/SF solutions) [75]. This is due to the competitive partition of target pollutants in the micelle that cannot adhere or react at the surface of catalysts [75,79,80]. A scheme of this mechanism is proposed in Figure 1.5. It is also ascribed to surfactant degradation, which competes with target HOCs for oxidation by  $\cdot\text{OH}$  at the catalyst/solution interface.



**Figure 1.5.** Partition equilibria of target pollutant during the heterogeneous photocatalytic treatment of a SW/SF solution. Adapted from the reference [79].

The nature of the surfactant for concentrations much higher than the CMC has an important influence [65]. In real SW/SF solutions containing methyl(3,4-dichlorophenyl)carbamate (SWEP) residues, the process was more efficient by using SDS compared to hexadecyltrimethylammonium bromide (cationic surfactant) and poly(oxyethylene) dodecyl ether ( $\text{C}_{12}\text{E}_8$ , non-ionic surfactant) [65]. Alkylphenol degradation was also less inhibited with SDS than with non-ionic surfactants for high surfactant concentrations [76]. In a similar study from the same research group, three non-ionic surfactants (at 10 mM, much higher than the CMC) have been tested and the

following order of effectiveness for bentazone degradation was obtained [64]: B35 ( $C_{12}E_{23}$ ) > poly(oxyethylene) dodecyl ether ( $C_{12}E_8$ ) >  $C_{12}E_5$ . The lower inhibitory effect of B35 has been explained by the bigger dimension of its hydrated polar head. It reduces the surfactant adsorption on  $TiO_2$  surface and, therefore, the competition between bentazone and B35 for occupation of active sites on the catalyst surface.

❖ *CDs: influence of nature and dose*

At low concentrations (<0.5 mM), CDs enhance the photocatalytic degradation of target pollutants. This has been shown with a dye [81], bisphenol A [82], bisphenol E [83], 4,4'-biphenol [84]. Using low concentration, the enhancement of target pollutant degradation is explained by the adsorption of the complex CD-pollutant onto the surface of the photocatalyst [84]. This promotes interactions between oxidant species and target pollutants [81]. Therefore, a high inclusion constant between CDs and HOCs promotes the photocatalytic degradation of HOCs. Without formation of this complex, a delay in the degradation of target pollutants can occur [84]. This is ascribed to the higher affinity of CDs onto the  $TiO_2$  surface compared to organic pollutants and competition reactions with  $\bullet OH$ .

Studies using high CD concentrations reported strong inhibitory effects. Using 83 mM MCD, very low efficiency for the photocatalytic degradation of pyrene (PYR) and phenanthrene (PHE) has been reported [74]. It has also been shown that the higher the CD concentration (in the range 1 - 5 mM), the lower the degradation rate of pentachlorophenol (PCP) [71]. Similarly to solutions containing high concentrations of surfactants, high CD concentrations inhibit the photocatalytic degradation of target pollutants by occupying all active sites on the surface of the photocatalyst and by providing a protective environment in the bulk [74].

### 3.1.2.2. Influence of operating conditions

#### ❖ *Nature and dose of the photocatalyst*

The nature of the photocatalyst has a great influence on the efficiency of the process [61]. For example, Liu et al. [75] showed that La-B co-doped TiO<sub>2</sub> has better performances than the commercial P25 TiO<sub>2</sub> for the treatment of SW/SF solutions, due to higher adsorption of pollutants on the catalyst surface and stronger absorption in the visible light.

Regarding the amount of photocatalyst used, an optimal dose has to be determined according to specific characteristics of the SW/SF solution and nature of the photocatalyst used. For example, it has been observed that the higher the dose (in the range 0.1 - 0.5 g L<sup>-1</sup>), the higher the photocatalytic degradation rate of PHE [77]. However, further addition of TiO<sub>2</sub> caused the light obstruction and increased filtration costs [77], decreasing thus the cost-efficiency of the process.

#### ❖ *Irradiation light*

The nature of the irradiation light (intensity and wavelength) strongly influences the efficiency of the process. In a comparative study, Liu et al. [75] showed that solar light leads to faster PCP degradation rate compared to visible light (Table 1.1). This could be explained by:

- the larger amount of electron-hole pairs resulting from a higher light strength [75];
- the larger amount of photons with wavelengths shorter than the absorption edge of TiO<sub>2</sub>, which are the only ones to result in reaction [61];
- PCP photolysis caused by the UV portion of solar light [75].

### ❖ *pH*

The pH can also influence oxidation mechanisms and surface properties of photocatalysts, leading to adverse effects such as aggregation of semiconductor particles, repulsion force between organic compounds and the photocatalyst surface or lower production of  $\cdot\text{OH}$  from hydroxide ions reaction with holes [61,77]. Therefore, the pKa of target pollutants and the isoelectric point of photocatalysts have to be taken into consideration for optimal pH adjustment [64].

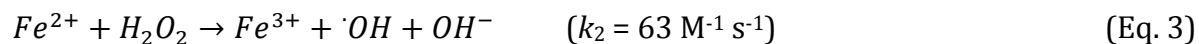
### ❖ *Oxygen supply*

Molecular oxygen plays an important role on the photocatalytic process: its main role is to act as an electron sink for photogenerated electrons (Figure 1.4) in order to avoid their recombination with holes [63]. Moreover, UV photolysis of  $\text{H}_2\text{O}_2$  formed from oxygen reduction can generate additional free  $\cdot\text{OH}$  in the bulk (Figure 1.4). Oxygen can also either hinder or support the reaction according to degradation mechanisms of pollutants [61]. As regards to SW/SF solutions, it has been observed a significant increase of SWEP residues degradation by saturating the irradiated suspension with air bubbling [65].

## **3.2. Technologies based on Fenton reaction chemistry**

### **3.2.1. General considerations**

Technologies using Fenton reaction chemistry have been widely studied due to the production of large amounts of  $\cdot\text{OH}$  for the oxidation of organic pollutants [89]. The effectiveness of these AOPs has been recently reviewed [44,90]. They are based mainly on the use of the Fenton's reagent, which is a mixture of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ferrous iron ( $\text{Fe}^{2+}$ ). Fenton reaction is the catalytic decomposition of  $\text{H}_2\text{O}_2$  by iron salts. It is initiated by the formation of  $\cdot\text{OH}$  in accordance with the classical Fenton reaction (Eq. 3) at acidic pH ( $\text{pH} \approx 3$ ) [47,91]:



Then, the process is propagated by the catalytic behavior of the Fe(III)/Fe(II) couple. It can also be coupled to catalytic processes leading to further ferrous ions production. This process presents some drawbacks such as the use of high reagent concentration, occurrence of parasitic reactions consuming  $\cdot OH$  and formation of process sludge under the form of  $Fe(OH)_3$  [90]. One of the well-known way for improving the efficiency of Fenton's chemistry is to combine the classical Fenton process with UV-A [92–96] or solar light [97] irradiation (photo-Fenton process). The action of photons is complex but mainly described by the following reaction (Eq. 4) [98].



$Fe(OH)^{2+}$  is the pre-eminent form of Fe(III) in the pH range 2.8 - 3.5 and UV light has the ability to perform the reductive photolysis of  $Fe(OH)^{2+}$ . The benefits are twice: *in situ* generation of  $Fe^{2+}$  that catalyzes the Fenton reaction (Eq. 3) and formation of further  $\cdot OH$ .

A major drawback of the Fenton process is the production of sludge from iron (III) hydroxides precipitation. This has been partly solved by the development of Fenton-like processes (*i.e.* the use of solid iron-containing catalysts such as zeolites, alumina, pyrite or other iron oxides) [99–102].

The use of other metallic ions as catalyst has also been studied. For example, Co, Cu and Mn could be used to act as catalysts of the Fenton reaction [103].

Some authors have also reported promising results by coupling sonochemistry and Fenton's chemistry for organoxenobiotic degradation [104,105]. Further combination of processes have also been investigated such as sono-photo-Fenton [106] or photo-Fenton-like [107].

### 3.2.2. Removal efficiency and kinetics

Results obtained by different research groups are summarized in Table 1.2. Fenton process has been applied to different kinds of SW/SF solutions with low efficiency. For

example, it has been reported 46% removal of 365 mg  $\Sigma$ PAHs L<sup>-1</sup> in a solution containing 0.1 g L<sup>-1</sup> of CAS (amphoteric surfactant) by using 1.7 mM of Fe<sup>2+</sup> and 17.6 mM H<sub>2</sub>O<sub>2</sub> at pH 4 for the Fenton process [108].

Bandala et al. [109] reported the higher efficiency of the photo-Fenton process by using SDS as EA: the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) after 50 min of treatment was < 5%, 50% and > 99% for UV irradiation, Fenton and photo-Fenton processes, respectively.

**Table 1.2.** SW/SF solution treatment by technologies based on Fenton reaction chemistry.

Process	Pollutant (concentration)	Extracting agent (concentration)	Synthetic (S) / Real (R) solution - Volume	Operating conditions				Degradation rate constant (h <sup>-1</sup> )	Remarks	Reference
				[H <sub>2</sub> O <sub>2</sub> ] (mM)	[H <sub>2</sub> O <sub>2</sub> ]/[Fe <sup>2+</sup> ]	pH	Irradiation light			
Fenton	Anthracene (0.28 mM), BaP <sup>1</sup> (0.20 mM)	Biosoft, Sorbax, Igepal, Witcomul, Marlipal (1 g L <sup>-1</sup> )	S 50 mL	150 mM	15	-	-	-	Between 24 and 88% degradation after 48 h. Coupling with biodegradation has also been studied	[110]
Fenton	PAH	CMCD (0.05-1 mM)	S 10 mL	Continuous addition	-	2.5	-	-	Several assessments about the influence of scavengers and the formation of a ternary complex	[111]
Fenton	PCB	CMCD (1 - 10 mM)	S 2 mL	86 mM	4.3	-	-	-		
Fenton	BAP <sup>1</sup> (0.02 mM and 10 <sup>-5</sup> mM)	β-CD, HPCD, RAMEB (5 mM)	S 5 mL	1 and 10	5	5.5	-	-	Influence of organic scavenger and formation of inclusion complex have been studied	[112]
Fenton	Creosote oil (1.9 mM for Σ PAH)	CAS (0.2 mM)	S 250 mL	1.1-12.1	1.1-11	2-9	-	-	Maximum of 46% PAHs degradation. Higher efficiency obtained with electro-oxidation	[108]
Fenton	p-Cresol (0.19 mM)	TW80 (0.66 mM)	R 500 mL	3 mM	16	-	-	-	Rapid total conversion of p- Cresol (<10 min). TOC and toxicity evolution have also been studied	[15]
Photo- Fenton	TNT <sup>2</sup> (0.5 mM)	None (water)	R -	30 mM (continuous addition)	-	3	UV lamp (150 W)	4.86	Addition of MCD reduced the inhibitory effect of hydroxyl radical scavengers present in the	[113]

		MCD (5 mM)						10.5	SW solution	
Photo-Fenton	PCB (6.4 mg L <sup>-1</sup> )	LAS (0.86 mM)	R 1.1 L	8.6-860	-	2.8	UV lamp (254 nm, 36 W)	-	Degradation of different homologous groups, influence of illumination source and Fenton's reagent dose have been studied	[114]
Photo-Fenton	PCB (6.4 mg L <sup>-1</sup> )	LAS (0.86 mM)	R -	8.6-860	-	2.8	UV lamp (254 nm, 36 W)	-	The use of a perfluorinated surfactant has also been studied	[115]
Solar photo-Fenton	DDT <sup>3</sup> (0.05-0.11 mM), DDE <sup>4</sup> (0.03-0.05 mM), diesel (230-350 mg L <sup>-1</sup> )	TX100 (2.2-8.9 mM)	R 250 mL	18 injection of 80 mM every 20 min	6.6	2.8	sunlight	-	High degradation efficiency (>98%). Dissolved organic carbon evolution has also been studied	[17]
Fenton and photo-Fenton	2,4-D (0.02 mM)	SDS (17 mM)	R -	0-6	10-60	-	- UV lamp (365 nm, 150 W m <sup>-3</sup> )	-	Much higher efficiency of the photo-Fenton process	[109]

<sup>1</sup> Benzo[a]pyrene, <sup>2</sup> Trinitrotoluene, <sup>3</sup> Dichlorodiphenyltrichloroethane, <sup>4</sup> Dichlorodiphenyldichloroethylene



### 3.2.2.1. Influence of extracting agents

#### ❖ *Surfactants: influence of nature and dose*

Similarly to adverse effects from SOM, the presence of high surfactant concentration has strong adverse effects on the efficiency of the Fenton process [116]. For example, Yang and Wang (2009) [117] reported a decrease in methyl orange degradation rate with surfactant concentration increasing. Much higher reagent doses are necessary to reach degradation of target pollutants in SW/SF solutions containing surfactants and SOM [115]. As  $\bullet\text{OH}$  act in a non-selective way, a significant amount is wasted in the reactions with the SOM and surfactants. This is one of the main limiting factor in determining the economic feasibility of the process [116]. Therefore, it could be concluded that the classical Fenton process is not enough efficient for the treatment of SW/SF solutions containing high surfactant concentrations. Besides, the use of the photo-Fenton improves performances but also increases process cost.

#### ❖ *CDs: influence of nature and dose*

A study has compared the treatment of a SW solution containing trinitrotoluene (TNT) as target pollutant by the photo-Fenton process, with and without the use of CDs as EA [113]. It has been shown that the process efficiency is improved by using MCD. The use of 5 mM MCD increased the concentration of TNT in the SW solution by a factor of 2.1; it also improved the photo-Fenton oxidation efficiency. The TNT degradation rate was 1.3 times higher compared to the degradation in distilled water, despite the presence of SOM in the real SF solution. In fact, MCD reduced the  $\bullet\text{OH}$  scavenging effect from non-target organic compounds. This has been ascribed to the formation of a ternary complex (TNT-CD-Fe(II)) [113]. The enhanced Fenton degradation of PCBs and PAHs by simultaneous iron and pollutant complexation with CDs has also been emphasized by another study [111]. CMCD is able to remove HOCs from SOM binding sites while complexing  $\text{Fe}^{2+}$  at the same time [111]. The formation of the ternary complex allows the formation of radical species close to the included target molecule [56]. Interestingly, it has also been shown that too low concentrations of iron could decrease the pollutant degradation rate. This is ascribed to an isolation of pollutants away from  $\bullet\text{OH}$ , because a

too small fraction of CMCD is bounded to iron [111]. The formation of the ternary complex depends on the functional group present on the external shape. Iron is coordinated in different functional groups with each CD [111]. For example, metal binding is stronger with the oxygen in the carboxyl group of CMCD compared to the alcohol groups of native  $\beta$ -CD. This is the reason why  $\beta$ -CD and  $\alpha$ -CD have lower ability to form this ternary complex compared to CMCD [111]. Moreover, Fenton degradation of benzo[a]pyrene (BAP) in the presence of a radical scavenger was improved with HPCD but not in the presence of RAMEB [112]. This confirms the importance of CD nature. Analysis bringing evidence of the ternary complex formation include spectrophotometry [56], fluorescence and nuclear magnetic resonance spectroscopy [118,119].

### 3.2.2.2. Influence of operating conditions

#### ❖ *Fenton's reagent dose*

As the oxidizable organic matter in the reaction medium is comprised of target pollutants as well as EAs and SOM, the Fenton's reagent dose has to be greatly increased. By using PCB as target pollutant ( $6.4 \text{ mg L}^{-1}$ ) and LAS as surfactant ( $300 \text{ mg L}^{-1}$ ),  $3 \text{ g L}^{-1}$  of  $\text{H}_2\text{O}_2$  has been used to reach more than 99% of PCB degradation at the end of 2 h of treatment by the photo-Fenton process [115]. However, this high  $\text{H}_2\text{O}_2$  concentration was not sufficient to reach a sufficient mineralization rate, which stopped around 19%.  $30 \text{ g L}^{-1}$  of  $\text{H}_2\text{O}_2$  has been necessary to reach a mineralization rate of 96%. Therefore, similarly to the classical Fenton process, the photo-Fenton process also requires the use of large amounts of Fenton's reagent during the treatment of SW/SF solution [109]. Another example, more than 95% degradation of dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE), diesel and at least 95% COD removal has been reported after 6 h of treatment by the photo-Fenton process [17]. However, operating conditions included high Fenton's reagent dose:  $\text{FeSO}_4$  at 12 mM and a sequential addition of 80 mM of  $\text{H}_2\text{O}_2$  every 20 min (i.e. 1440 mM of  $\text{H}_2\text{O}_2$  addition during the whole treatment).

The use of CDs as EA favors the removal of HOCs by Fenton's reaction based processes [111], however, further comparative studies would be necessary in order to determine

how much Fenton's reagent is saved with the use of CDs, compared to the use of synthetic surfactants.

It is also well known that the efficiency of the Fenton process depends on the ratio  $R = [\text{H}_2\text{O}_2]/[\text{Fe}]$  [94,120]. In most of cases, the ratio  $R$  used for SW/SF solutions treatment is chosen according to previous studies. For example, Tang and Huang [120] determined the optimal  $R$  as 11 for the degradation of 2,4-dichlorophenol in pure aqueous solution.

Interestingly, it has been noticed that the Fenton process could be performed without external iron addition, due to the extraction of iron and other transition metals from the soil during the SW/SF process [15]. The use of EAs with high chelating ability could also be investigated in order to improve this phenomenon. However, it would involve the investigation of other issues such as cost and toxicity of the chelating agent, extraction of toxic metals, etc. [15].

#### ❖ *pH*

It has been reported that the best pH to perform the Fenton process is 2.8 [98]. However Fenton oxidation of real SW/SF solutions could be successfully performed without pH adjustment. This is ascribed to the presence of substances able to keep  $\text{Fe}^{3+}$  in the solution at near neutral pH (SOM or CDs when it is used as EA) and/or to the formation of acidic degradation by-products (particularly carboxylic acids) allowing the decrease of the pH around 3 during the treatment [15].

#### ❖ *Irradiation light (for the photo-Fenton process)*

In regards to the photo-Fenton process, the choice of the irradiation light is an important parameter. Both UV lamp [115] and sunlight [43] have been used as irradiation light for the treatment of SW/SF solutions. However, it is not possible to clearly determine the influence of the irradiation light since other operating conditions ( $[\text{H}_2\text{O}_2]$ ,  $[\text{Fe}]$ ,  $R$ , pH) must be taken into account for the comparison. A study has investigated the effect of illumination source wavelength on the degradation of PCBs in

SW/SF solutions [114]. Iron (III) complexes absorb more the radiation at 254 nm than at 366 and 440 nm. This allows a higher photoreduction rate of iron (III) to iron (II) (Eq. 4) at 254 nm. Therefore, higher effectiveness was obtained by using an illumination source centered at 254.

### 3.3. Ozone processes

#### 3.3.1. General considerations

Ozone ( $O_3$ ) is a strong oxidant with the fifth highest standard redox potential ( $E^\circ = 2.07$  V/SHE, at 25 °C) [45]. Thus, ozone processes have the ability to oxidize many organic compounds [123–126]. Ozone is produced by electrical discharge over site where it will be used, because of its unstable nature. Then, it is bubbled inside the effluent and transferred from the gas phase to the liquid phase. Ozonation can be limited by the difficulty to reach high ozone concentrations in water.

The degradation of organic pollutants in water by ozone processes depends strongly on the pH of the solution [126]. If the ozonation is developed under acidic conditions, the main pathway for degradation of organics is the direct oxidation. Ozone acts in a selective way with lower kinetic rate constants (for example, in the range  $1 - 10^3$   $M^{-1} s^{-1}$  with chlorophenols) than  $\cdot OH$  [57,127]. It reacts with functional groups of organic pollutants through electrophilic, nucleophilic, and dipolar addition reactions [128]. At higher pH, the decomposition of ozone by hydroxyl ions is faster and the indirect process occurs following a complex pathway described by Pera-Titus et al. [57]. The indirect oxidation occurs through  $\cdot OH$  generation, which react immediately and non-selectively with the organic matter. Overall, at  $pH < 4$  the direct oxidation dominates; at  $4 < pH < 9$  both mechanisms are present; at  $pH > 9$  the indirect pathway is the main reaction [57].

Ozonation can also be combined with homogeneous promoters in presence or absence of UV light ( $O_3/H_2O_2$ ,  $O_3/H_2O_2/UV$ ,  $O_3/Fe^{2+}$ ,  $O_3/Fe^{2+}/UV$ ) in order to increase the production of  $\cdot OH$  [123,124,129]. Moreover, the photolysis of ozone leads to the formation of  $H_2O_2$  which is further degraded into two  $\cdot OH$  under UV-C irradiation [125].

### 3.3.2. Removal efficiency

Ozone is often used for *in situ* chemical oxidation, particularly by combining ozone oxidation with a post-biological treatment of the soil [13]. Some data have also been obtained for the treatment of SW/SF solutions by ozone processes. First, the influence of pH and ozone dose on the efficiency of the treatment of a SW solution containing 200 mg L<sup>-1</sup> of PAHs has been studied [130]. It has not been observed any significant effect from the pH in the range 3 - 10. Only the higher doses (more than 500 mg O<sub>3</sub> L<sup>-1</sup>) decreased the amount of PAHs (45-65% removal) in the solution. Similar efficiency has been obtained for the treatment of SW/SF solutions containing 340 - 600 mg L<sup>-1</sup> of chlorophenols [131]. Interestingly, for lower doses (less than 50 mg L<sup>-1</sup> of O<sub>3</sub> consumed), an increase in total PAH concentration has been observed. This has been attributed to the better extraction efficiency of PAHs for analysis, due to the release of PAHs entrapped in humic substances after a mild ozonation [130].

The NAP removal in Brij 30 (B30) containing solutions by an ozone process has also been investigated [132]. It has been observed that an increase in B30 concentration (in the range 100 - 1000 mg L<sup>-1</sup>) strongly decreases NAP removal efficiency. The presence of the surfactant decreased gas-liquid mass transfer for both NAP and ozone. This directly affects NAP removal mechanisms *i.e.* volatilization and ozonolysis (lower ozone transfer from the gas to the liquid phase). Therefore, the use of a rotating packed bed as ozone contactor would be more suitable. It allows increasing gas-liquid mass transfer coefficients compared to conventional contactors [132].

As only few authors have studied the use of ozone processes for the treatment of SW/SF solutions, there is a lack of data on the influence of operating conditions and nature of SW/SF solutions.

### 3.4. Electrochemical processes

#### 3.4.1. General considerations

In electrochemical processes, the application of an electric current or potential between two electrodes in an electrochemical reactor induces electron transfer (redox) reactions resulting in direct or indirect destruction of organic compounds [133–136]. Different mechanisms are involved according to operating conditions [5,46,137–139].

Direct electrolysis results from electron exchange between organic pollutants and the electrode surface without involvement of other substances. This is theoretically possible in the potential region of water stability (low potential). However, adsorption of organic compounds onto the anode material and formation of a polymer layer on the anode surface can lead to the deactivation of the anode (poisoning effect) [5]. The anode fouling effect is avoided by performing oxidation in the potential region of water discharge *i.e.* high anodic potentials. In this case, formation of heterogeneous  $\cdot\text{OH}$  ( $\text{M}(\cdot\text{OH})$ , M being the anode material) from oxidation of water can occur at the surface of the anode material. This is an EAOP named as anodic oxidation (AO) process [5]. Two classes of anodes are distinguished in AO: “active” and “non-active” electrodes [137]. Particularly, anodes with high oxygen evolution overpotential (called non-active electrodes) allow the accumulation of large amounts of physisorbed  $\text{M}(\cdot\text{OH})$  at the anode surface, leading to the complete mineralization of organics to  $\text{CO}_2$  [5] (Eq. 5).



The production of some other electrochemically generated redox reagents can simultaneously occur with the generation of  $\text{M}(\cdot\text{OH})$ . This can come from the oxidation of compounds used as electrolyte. For example, active chlorine species ( $\text{Cl}_2$ ,  $\text{HOCl}$ ,  $\text{ClO}^-$  and oxychloro species formed by oxidation of  $\text{Cl}^-$  on the anode surface) are the most traditional ones used [140,141]. It is named mediated oxidation. However, chlorinated organic compounds can also be produced, leading to the increase of wastewater toxicity [142]. Indirect electrolysis can also occur through production of ozone, persulfate, percarbonate, perphosphate [143–145].

Electrochemistry can be combined with Fenton’s chemistry; this has been extensively studied during the last decades [44,46]. The very popular EAOP called electro-Fenton

(EF) allows avoiding the main drawbacks of the classical Fenton process, i.e. reagent's cost, waste reactions and sludge formation [138]. It is based on the *in situ* electrocatalytic generation of the Fenton's reagent (the mixture of H<sub>2</sub>O<sub>2</sub> and iron (II)) in the homogeneous medium [136]. H<sub>2</sub>O<sub>2</sub> is continuously supplied to the solution from the two-electron reduction of dissolved O<sub>2</sub> on the cathode, as follows (Eq. 6):



Oxygen required for H<sub>2</sub>O<sub>2</sub> production can be partially formed at the anode by oxidation of water (particularly with Pt anode) and/or directly injected as compressed air [136]. The oxidation power of H<sub>2</sub>O<sub>2</sub> is strongly enhanced in acidic medium in the presence of a catalytic amount of Fe<sup>2+</sup> ions [136]. This comes from the production of •OH via the Fenton reaction (Eq. 3). Ferric iron formed by this reaction is then reduced at the cathode [146] (Eq. 7).

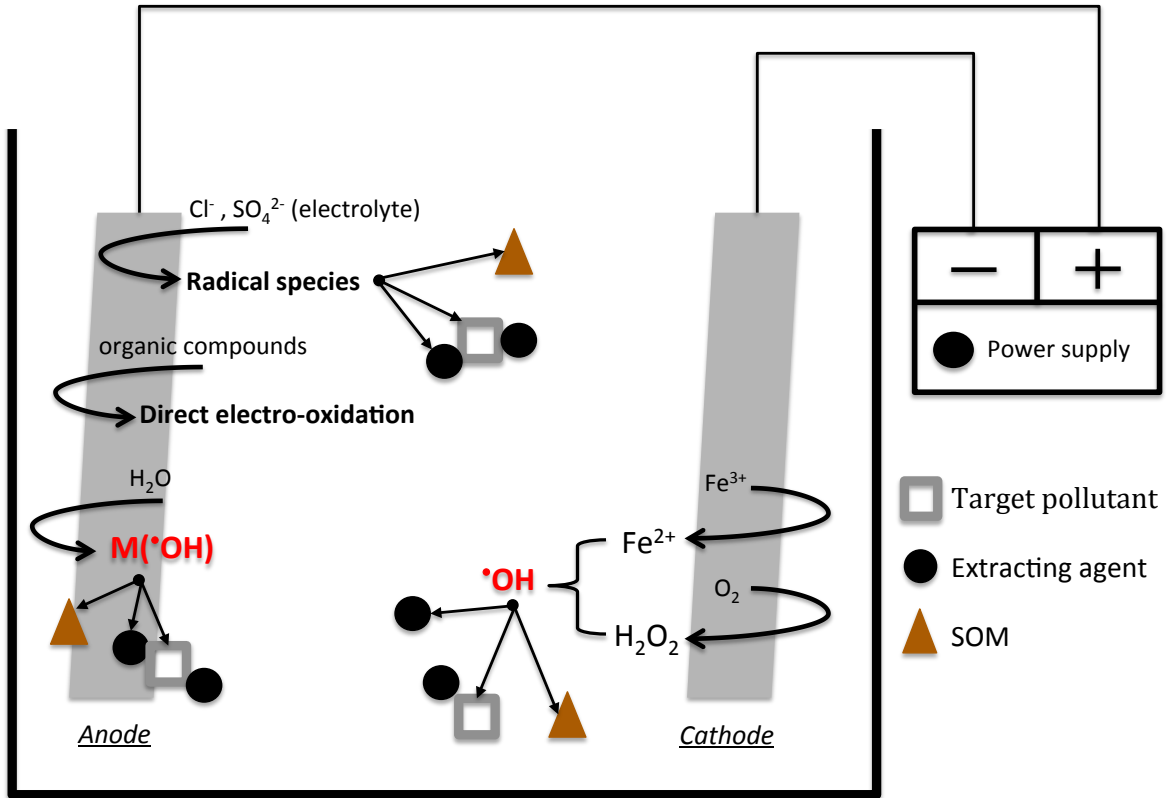


This allows catalyzing efficiently the Fenton reaction, through continuous regeneration of ferrous iron. Thus, •OH are continuously produced in the solution to be treated via the electrochemically assisted Fenton reaction. Several studies reported the degradation of a large range of persistent organic pollutants by the EF process [46,147–150]. This process can also lead to high TOC and COD removal from wastewaters, indicating total mineralization of organics to CO<sub>2</sub> [151].

The efficiency of the EF process can be enhanced by irradiating the EF reactor with an UV lamp (photo-EF process) or solar light (solar photo-EF process) [152,153]. As explained above (see technologies based on Fenton reaction chemistry), the interest is double: additional production of •OH and ferrous iron regeneration enhancement.

### 3.4.2. Removal efficiency and kinetics

Electrochemical processes have been successfully applied for the treatment of SW/SF solutions by using different operating conditions involving different mechanisms (Figure 1.6). This is why a large range of kinetics has been obtained (0.01 - 2 h<sup>-1</sup>) (Table 1.3).



**Figure 1.6.** Schematized view of mechanisms and competition effects, which can occur during the treatment of SW/SF solutions by EAOPs.



**Table 1.3.** SW/SF solution treatment by electrochemical processes.

Process	Pollutant (concentration)	Extracting agent (concentration)	Synthetic (S) / Real (R) solution - Volume	Operating conditions			Degradation rate constant (h <sup>-1</sup> )	Remarks	Reference
				Anode- Cathode material	Electrolyte (concentration)	Power supply			
EF	PCP (0.1 mM)	HPCD (5 mM)	S -	Pt-Carbon felt	-	10 mA cm <sup>-2</sup>	0.546	A 5 fold increase in apparent rate constant of PCP degradation was observed with HPCD	[154]
EF	PHE (0.1 mM)	HPCD (8.8 mM)	S 400 mL	Pt-Carbon felt	Na <sub>2</sub> SO <sub>4</sub> (0.15 M)	13.3 mA cm <sup>-2</sup>	1.56	Toxicity and biodegradability evolution and extracting agent recycling have also been studied.	[56]
		TW80 (0.6 mM)					0.78		
AO	Creosote oil (1.3 mM for Σ PAH)	CAS (2.2 mM)	S 1 L	Ti/IrO <sub>2</sub> -SS <sup>1</sup> ; Ti/SnO <sub>2</sub> -SS <sup>4</sup>	Na <sub>2</sub> SO <sub>4</sub> (0.0035 M)	4.0-23 mA cm <sup>-2</sup>	0.90	Recirculation flow rate, retention time and continuous electro-oxidation have been studied	[155]
AO	Creosote oil (1.5-3.0 mM for Σ PAH)	CAS (0.22-1.1 mM)	S 1.5 L	Ti/RuO <sub>2</sub> -SS <sup>1</sup>	Na <sub>2</sub> SO <sub>4</sub> (0.0035-0.028 M)	3.08-12.3 mA cm <sup>-2</sup>	-	Toxicity evolution and COD removal have also been studied	[156]
AO	NAP (0.83 mM)	CAS (9.1 mM)	S 1.5 L	Ti/RuO <sub>2</sub> -SS <sup>1</sup>	Na <sub>2</sub> SO <sub>4</sub> (0.0035 M)	9.23 mA cm <sup>-2</sup>	0.90	Oxidation by-products have been analyzed and degradation mechanisms have been proposed	[108]
	PYR (0.27 mM)	CAS (9.1 mM)	S 1.5 L	Ti/RuO <sub>2</sub> -SS <sup>1</sup>	Na <sub>2</sub> SO <sub>4</sub> (0.0035 M)	9.23 mA cm <sup>-2</sup>	0.66		
AO	PHE	SDS, TW80, alkylbenzyl-dimethylammonium chloride	R 600 mL	BDD <sup>2</sup> -SS <sup>1</sup> ; DSA <sup>3</sup> -SS <sup>1</sup>	Na <sub>2</sub> SO <sub>4</sub> (0.021 M)	30 mA cm <sup>-2</sup>	-	Much higher efficiency with BDD <sup>2</sup> as anode	[157]

AO	PHE (0.1 mM)	TW80 (7.6 mM)	S 1.5 L	Graphite- Graphite	Na <sub>2</sub> SO <sub>4</sub> (0.035 M); NaCl (0.035 M)	5 V	-	The use of two different electrochemical cell configuration has been compared	[158]
	PHE, Anthracene, BaP	TW80, B35, Tyloxapol	R 1.5 L	Graphite- Graphite; Ti/Pt-Ti	Na <sub>2</sub> SO <sub>4</sub> (0.1 M)				
	Fluoranthene (0.1 mM)	TW80 (7.6 mM)	S 400 mL	Graphite- Graphite	Na <sub>2</sub> SO <sub>4</sub> (0.1 M)	5 V	0.050		
AO	Benanthracene (0.1 mM)	TW80 (7.6)	S 400 mL	Graphite- Graphite	Na <sub>2</sub> SO <sub>4</sub> (0.1 M)	5 V	0.020	PAH mixture degradation rate has also been studied	[159]
	PYR (0.1 mM)	TW80 (7.6 mM)	S 400 mL	Graphite- Graphite	Na <sub>2</sub> SO <sub>4</sub> (0.1 M)	5 V	0.012		
AO	PHE (0.21 mM)	TW80	R 400 mL	Graphite- Graphite	-	5 V	-	Extracting agent recycling has also been studied	[160]
AO	PHE	HPCD	R 400 mL	Graphite- Graphite	-	5 V	0.19	Extracting agent recycling has also been studied	[161]
AO	PYR, Anthracene, Fluoranthene	TW80 and TX100	S and R 400 mL	Graphite- Graphite	Na <sub>2</sub> SO <sub>4</sub> (0.1 M)	5 V	-	PAH mixture degradation rate and extracting agent recycling have also been studied	[162]
AO	Atrazine	SDS	R 1 L	BDD <sup>2</sup> -Steel	-	30 mA cm <sup>-2</sup>	-	PAH mixture degradation rate and extracting agent recycling have also been studied	[163]

<sup>1</sup> Stainless steel, <sup>2</sup> Boron doped diamond, <sup>3</sup> Dimensionally stable anode

### 3.4.2.1. Influence of extracting agents

Concentration and nature of the EA greatly influence the efficiency of the process. Particularly, the high carbon content (EAs, target HOCs and SOM) leads to high competition effects for oxidation with  $\bullet\text{OH}$  (Figure 1.6). However, similarly to Fenton and photo-Fenton processes, higher efficiency is usually obtained with the EF process by using CDs as EA due to the formation of the ternary complex HOC-CD-Fe(II) [56].

A variety of behaviors and efficiencies have also been observed according to the nature of the surfactant used, due to different degradation pathways [157]. For example, the COD removal of model solutions containing alkylbenzyltrimethylammonium chloride (a cationic surfactant) was higher compared to the use of SDS. The aromatic structure of the cationic surfactant enhanced the organic load removal through the formation of insoluble species, while the generation of oxidation-refractory compounds took place with SDS (aliphatic structure) [157].

Besides, using continuous treatment, it has been reported more than 80% of PAH degradation during the first 18 h of treatment by electro-oxidation with DSA anode [155]. Thereafter, removal efficiency decreased owing to the formation of a polymeric film on the anode surface leading to its. This fouling phenomenon has been studied by investigating the influence of surfactants and anode materials during electro-oxidation of phenols [164]. By using graphite as anode, Sripriya et al [164] observed that both cationic (cetyltrimethylammonium bromide) and anionic (SDS) surfactants had an adverse effect on phenol removal. These surfactants adsorbed onto the anode surface, leading to a blocking effect. Using oxide coated titanium anode, negative effects have been observed with SDS and TW80, while positive effects have been obtained with cetyltrimethylammonium bromide. In fact, this surfactant may have blocked the adsorption onto the electrode surface of cation radicals generated from phenol oxidation and facilitated the chlorine evolution reaction by increasing the surface concentration of chloride ions through formation of a complex with chloride ions [164].

Recently, it has been studied the influence of particle size of micelles (organic compound micro-drop covered by a layer of surfactant) during the treatment of real SW solutions containing atrazine and SDS (anionic surfactant) by AO using boron doped diamond (BDD) anode [163]. Particularly, it has been reported that the higher the amount of SDS

used during the washing process, the lower the particle size and the more negative the superficial charge of particles [163]. This is an important parameter to take into consideration since steric hindrance of the large micelles could prevent their oxidation on the anode surface [165]. This is why homogeneous production of oxidant species in the bulk by mediated oxidation has to be considered for the understanding of surfactant degradation during electro-oxidation of SW solutions [163]. Therefore, despite the steric hindrance phenomenon, it has been observed a continuous decrease of the size of particles during electrolysis and a complete mineralization of organic compounds [165].

#### 3.4.2.2. Influence of operating conditions

##### ❖ *Electrode material*

The use of active anode materials with low oxygen overpotential such as platinum or graphite led to kinetic degradation rates in the range  $0.01 - 0.2 \text{ h}^{-1}$  (Table 1.3). Better results have been obtained for EF and AO processes using anodes with higher oxygen overpotential (rate constants in the range  $0.5 - 2 \text{ h}^{-1}$ ). These latter EAOPs have the ability to produce significantly larger amounts of  $M(\cdot\text{OH})$ , leading to higher degradation/mineralization kinetics [147].

In a comparative study, better results have been obtained by using  $\text{Ti}/\text{SnO}_2$  compared to  $\text{Ti}/\text{IrO}_2$  as anode material [155]. This is explained by the fact that  $\text{Ti}/\text{SnO}_2$  has a higher  $\text{O}_2$  overpotential (1.9 V vs SHE in 0.05 M of  $\text{H}_2\text{SO}_4$  for  $\text{Ti}/\text{SnO}_2$  versus 1.52 V vs SHE in 0.5 M of  $\text{H}_2\text{SO}_4$  for  $\text{Ti}/\text{IrO}_2$  [5]), leading to higher  $M(\cdot\text{OH})$  accumulation on the anode surface [5,155]. The same trend has been reported with SDS, which has been more efficiently degraded and mineralized on BDD anode than on  $\text{PbO}_2$  anode [166]. For similar reasons, it has also been reported that a dimensionally stable anode (DSA) was inefficient for the treatment of SW solutions containing PHE,  $10 \text{ g L}^{-1}$  surfactant and COD of  $20,000 \text{ mg O}_2 \text{ L}^{-1}$  [157]. In contrast, a BDD anode exhibited much higher efficiency [157]. Recently, BDD anodes have shown very promising results, due to their corrosion stability, inert surface and high oxygen overpotential (2.3 V vs SHE in 0.5 M of  $\text{H}_2\text{SO}_4$ ) [5,167]. However, their main drawback is currently their high investment cost.

Regarding the EF process, the choice of the cathode has a significant influence on the efficiency of the process, particularly for  $\text{H}_2\text{O}_2$  accumulation and  $\text{Fe}^{2+}$  regeneration. Best results for practical applications are usually obtained with gas diffusion electrodes (GDEs) and three-dimensional electrodes using carbon-based porous materials, in particular carbon felt cathodes [168].

Other mechanisms than the production of  $\cdot\text{OH}$  on the anode surface or in the bulk from the Fenton reaction can also occur during electrochemical processes, depending on the choice of operating conditions. Particularly, oxidation mechanisms involved in the electrochemical treatment applied by the Sanromán's group also include direct electro-oxidation and oxidation mediated by oxidants generated from during the treatment from salts contained in the wastewater [159]. However, lower degradation kinetics have been obtained by comparison with the EF process and the AO process using anode with higher oxygen overpotential (due to the production of larger amounts of  $\cdot\text{OH}$ ) (Table 1.3).

Finally, the efficiency of electrochemical processes depends on the experimental design of the electrolytic cell. This parameter is difficult to compare between the different research groups.

#### ❖ *Nature and dose of the electrolyte*

Nature and concentration of electrolyte is of great importance. It has been shown that the addition of  $\text{Na}_2\text{SO}_4$  is required to reduce energy consumption and treatment costs [156]. Moreover, the increase  $\text{Na}_2\text{SO}_4$  concentration up to 0.1 M improved PAH degradation rates [158]. The effectiveness of electrochemical oxidation is often influenced by the choice of the supporting electrolyte ( $\text{K}_3\text{PO}_4$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ ), due to the formation of oxidant species from the electrolyte (mediated oxidation) [169]. Furthermore, it can also affect the degradation pathway of organic compounds: a mechanistic study on NAP and PYR electro-oxidation showed that the oxidation pathway included both oxidation by  $\cdot\text{OH}$  produced on the anode surface and chlorine mediated electrolysis [108].

### ❖ *Current*

The increase of the current density can improve degradation rates of organics but also increases the energy consumption of electrochemical processes. The high COD content of SW/SF solutions usually allows reaching high current efficiency [5]. However, a too high current density can increase the portion of current wasted due to the increase of secondary reactions (such as oxygen evolution at the anode and H<sub>2</sub> evolution at the cathode) [5]. Besides, degradation efficiency of organic compounds can also decrease when too high potentials are applied. For example, Tran et al. defined an optimal current density of 9.2 mA cm<sup>-2</sup> for the treatment of a mixture creosote oil / synthetic surfactant with a Ti/RuO<sub>2</sub> anode[156]. The optimization of the current density applied to the electrochemical cell is also particularly important during the EF process. A too high potential favors waste reactions and can decrease H<sub>2</sub>O<sub>2</sub> accumulation in the solution [46]. Finally, the balance between the effectiveness of electrochemical processes and the energy consumption has to be further investigated.

### ❖ *pH*

A pH between 2 and 4 is usually required for the EF process, while the optimal pH has been defined as 3.0 [46]. However, in the area of SW/SF solutions, the presence of compounds such as SOM or CDs can allow keeping Fe<sup>3+</sup> in the solution at near neutral pH, thus allowing starting the process at pH >4 [56]. Moreover, the accumulation of carboxylic acids during the electrochemical treatment of SW/SF solutions also lead to decrease the pH around 3 during the treatment [154,157]. Besides, by using a Ti/RuO<sub>2</sub> anode for the electro-oxidation of creosote oil in the presence of CAS, the initial pH did not have any significant influence in the range 2 – 9 [156]. However, contradictory results have also been reported on the influence of the pH during AO [164].

## 3.5. Biological treatments

### 3.5.1. General considerations

Biological treatment is nowadays one of the most popular and cost-effective process in water treatment for removal of organic compounds [165]. It is based on the metabolism of organics by a large range of microorganisms. Physical, chemical, and microbiological aspects of a particular environment have to be taken into consideration for understanding biological degradation mechanisms of a given compound. Different microorganisms and degradation pathways are involved depending on operating conditions in reactors, including composition of the effluent to be treated, oxygen concentration, pH, temperature, etc. [166,167]. Particularly, biological processes are divided into three main categories depending on the final electron acceptor: aerobic, anaerobic and anoxic. Mainly aerobic biodegradation processes have been applied to SW solutions due to higher microbial growth rates leading to faster removal kinetics [18].

Microorganisms have evolved an extensive range of enzymes, pathways, and control mechanisms that are responsible for catabolism of a large range of organic compounds [168]. Thus, biological degradation is a powerful treatment used to alleviate a lot of environmental pollution issues. For example, several studies reported that biological processes are able to treat a variety of organic compounds such as halogenated organics [168], nitroaromatic compounds [169], petroleum hydrocarbons [170], polychlorinated dibenzodioxins [171] or PCBs [172].

However, some organic compounds can be recalcitrant to biodegradation for different reasons such as the absence of microorganism able to use them as substrate, the presence of toxic concentrations of a specific organic compound or the decrease of bioavailability of organic compounds due to the physicochemical parameters of the environment [173].

### 3.5.2. Removal efficiency

Only few authors have reported kinetic studies, data at pilot or real scale and used real SW/SF solutions [174,175]. In the area of biological processes, these kinds of studies are particularly important to raise understanding of biodegradation mechanisms and efficiency. However, some authors have investigated biodegradation effectiveness by using batch reactors (Table 1.4). With different solution characteristics and microorganism cultures, they obtained a large range of effectiveness. Treatment times necessary to achieve sufficient removal effectiveness can reach several weeks (Table 1.4). Biodegradation effectiveness strongly depends on SW/SF characteristics such as nature of the target pollutant as well as nature and dose of the EA (Table 1.4). Different surfactants may have different influence for a same bacterial culture. Likewise, biodegradation effectiveness can differ for a same surfactant when different microorganisms are used [173]. Therefore, the adaptation and acclimatization of microorganisms to the mixture surfactant-target pollutant is an important parameter [173]. Besides, the removal of (semi-) volatile HOCs can also occur through volatilization during aerobic treatment.



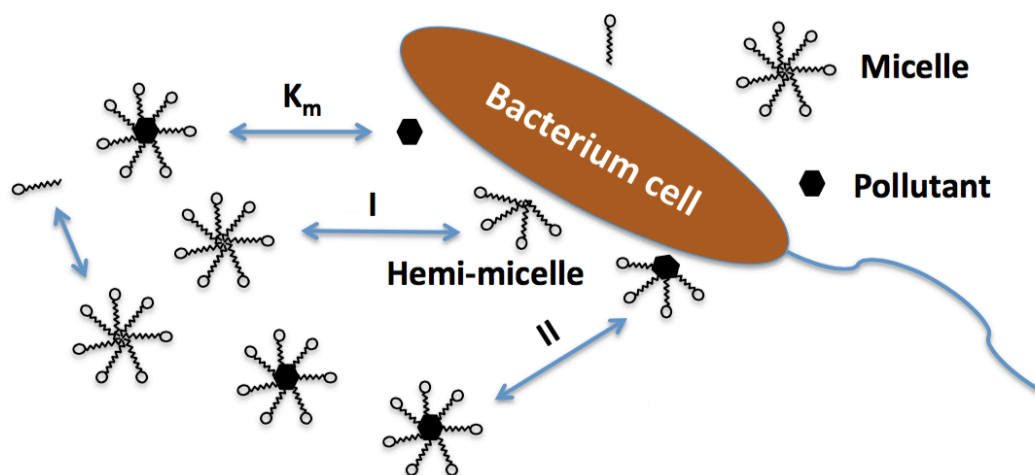
**Table 1.4.** Removal effectiveness for biological treatment in batch reactors of solutions containing HOCs and extracting agents.

Biodegradation experiment	Target HOC (mg L <sup>-1</sup> )	Extracting agent (g L <sup>-1</sup> )	Treatment time	% Removal	Reference
Aerobic treatment. Microorganisms obtained from the contaminated soil during the SW step	anilines, benzenes, thiophenes and PAHs (pollutant concentration: 85 - 167 mg L <sup>-1</sup> )	TX100 (10)		2	[176]
		β-CD (10)		23	
		HPCD (10)	63 d	19	
		RHA (10)		28	
		humic substances (10)		40	
Aerobic treatment. Pure culture of PAH-degrading bacteria, <i>Sphingomonas</i> sp. AJ1 (10 <sup>8</sup> CFU mL <sup>-1</sup> )	ANT (0.6) PHE (12.7) PYR (14.4) BAP (4.1) Benzo[ghi]perylene (0.7)		1 h	100	[16]
		Deoxyribonucleic acid (10)	1 h	100	
			1 d	87	
			5 d	82	
Aerobic treatment. Pure culture of PHE-degrading bacteria, <i>Burkholderia CRE 7</i> (10 <sup>7</sup> CFU mL <sup>-1</sup> )	PYR (50)	None	24 w	< 5	[177]
		HPCD (10)	24 w	14	
Aerobic treatment. Pure culture of marine bacteria, <i>N. naphthovorans</i>	PHE (1.64)	Tergitol 15-S-12 (0.2)	4.5 d	80	[178]
		Tergitol 15-S-12 (0.4)	4.5 d	67	
		Tergitol 15-S-12 (0.6)	4.5 d	42	
		Tergitol 15-S-12 (1.0)	4.5 d	27	

### 3.5.3. Influence of extracting agents

Uptake of organic compounds by microorganisms is assumed to occur mainly via the aqueous phase. Therefore, the influence of EAs on biodegradation of HOCs is related to solubility enhancement of HOCs by EAs and to partition of HOCs in the CD inclusion complex or in the surfactant micellar pseudo-phase [174,175,179].

Different mechanisms are involved for biodegradation of target pollutants in surfactant-containing solutions [173]. First, aqueous extra-micellar pollutants can be directly utilized by bacteria (Figure 1.7). Thus, pollutants diffusing from the micellar (or inclusion complex) to the aqueous phase (kinetics in the range of milliseconds to few seconds) according to the micellar phase / aqueous phase partition coefficient ( $K_m$ ) (or  $K_{CD}$ ) can be degraded. Biodegradation of pollutants solubilized in micelles can also occur due to the formation of a hemi-micellar layer around the bacteria cells (step I, Figure 1.7) and transfer of pollutants from the micellar phase to this hemi-micellar layer (step II, Figure 1.7) [173]. However, these two steps might be kinetic limiting steps for biodegradation [173].



**Figure 1.7.** Organic pollutant uptake by bacteria in soil washing solutions.  $K_m$  is the micellar phase / aqueous phase partition coefficient of the target pollutant. I is the equilibrium between the hemi-micellar layer around the bacteria cells and micelles in the aqueous phase. II is the equilibrium between pollutants solubilized in hemi-micelles around the bacteria cells and micelles in the aqueous phase.

Only few authors have investigated the influence of EAs on biodegradation mechanisms and kinetics. Therefore, it is difficult to discuss results obtained and to highlight clear trends. Certain authors [174,175] have assumed that some EAs (non-ionic surfactants, biosurfactants) do not alter HOC degradation kinetics in the aqueous phase. Therefore, based on Monod equation, the following model has been proposed (Eq. 8 and 9) in order to describe substrate and biomass evolution during the biological treatment of HOCs in the presence of EAs [174,175]. Kinetic parameters obtained are reviewed in Table 1.5. Large differences have been obtained for maximum specific growth rates. This is ascribed to the use of different nature of microorganisms (pure culture, mixed culture) and substrate (including target HOCs and EAs).

$$\eta \frac{dS}{dt} = -\frac{1}{Y} \frac{\mu_{max} \cdot S(1 + \gamma)}{K_S + S(1 + \gamma)} X - \nu \quad (\text{Eq. 8})$$

$$\frac{dX}{dt} = \frac{\mu_{max} \cdot S(1 + \gamma)}{K_S + S(1 + \gamma)} X - bX \quad (\text{Eq. 9})$$

where  $\mu_{max}$  is the maximum substrate utilization rate;  $S$  is the concentration of target substrate (HOC);  $K_S$  is the half-saturation constant;  $X$  is the biomass concentration;  $Y$  is the yield coefficient (mass of bacteria per mass of substrate consumed);  $b$  is the first-order endogenous respiration coefficient;  $\eta$  is a term linked to HOC solubility enhancement by surfactant;  $\gamma$  is a term linked to the bioavailable fraction of micelle bound contaminants;  $\nu$  is a term linked to the mass transfer between air and gas phase.

The model considers that the enhanced biodegradation in solutions containing EAs is mainly attributed to an increased aqueous solubility of HOCs (parameter  $\eta$  in Eq. 8) [177,178,180,181]. In contrast, high EA concentrations exhibit adverse effects due to the inhibition of the direct contact between microbial cells and target pollutants by partition into CD inclusion complex or micelles (parameter  $\gamma$  in Eq. 8; parameters  $\alpha$  in Table 1.5) [174,175]. Particularly, this approach introduced a bioavailability parameter ( $\gamma$  in Eq. 8,  $\alpha$  in Table 1.5) assessing the bioavailability of a pollutant in the micellar pseudo-phase. The value 1 means a total bioavailability of the target pollutant while the value 0 means a total non-bioavailability. This parameter is strongly dependant on the nature and concentration of the EA, as reported in Table 1.5. This is ascribed to various micelle characteristics and HOC partitioning, leading to a different level of inhibition of the

contact between microbial cells and target pollutants. For example, the low bioavailability of pollutants in solutions containing Brij® 35 was attributed to its very long hydrophilic chain, which may reduce the interaction and the transfer of PHE from the micelle to the microbial cell [174].

Overall, the following trend is usually observed for both surfactants and CDs: the presence of low concentration of EAs (below or close to the CMC for surfactants) enhances biodegradation of HOCs, but the bioavailability and biodegradability is reduced with increasing the EA concentration [173] (Table 1.5). Other potential mechanisms of biodegradation inhibition include toxicity of EAs to microorganism [182,183] and preferential microbial uptake of EAs as substrate [183–185].

Finally, surfactants can also affect the oxygen transfer coefficient from the gas to the liquid phase, which is an important parameter in aerobic biological degradation [186,187]. It has been observed that surfactants influence the process of bubble generation. Particularly, specific interfacial area, bubble diameters, volumetric mass transfer coefficient and liquid-side mass transfer coefficient can be modified [187].

**Table 1.5.** *Biological kinetic parameters obtained for the treatment of solutions containing HOC and extracting agent.*

Biodegradation experiment	Target HOC (mg L <sup>-1</sup> )	Extracting agent	$\mu_{\max}$ (h <sup>-1</sup> )	$K_s$ (mg L <sup>-1</sup> )	Y	Bioavailability ( $\alpha$ <sup>1</sup> )	Reference
Aerobic treatment. Samples inoculated with <i>Pseudomonas putida</i> CRE 7 culture pregrown on minimum salts medium containing PHE as sole carbon and energy source at 23 °C for 3 days	PHE (130)	None	0.4	1.95	1	-	[175]
		Mono-RHA (0.35 mM)				0.1	
		Mono-RHA (3.5 mM)				0.01	
		Di-RHA (0.35 mM)				0.3	
		Di-RHA (3.5 mM)				0.03	
Aerobic treatment. A mixed enrichment culture was used, which has been isolated from a petroleum-contaminated soil sample	PHE (1)	B30 (150 mg L <sup>-1</sup> )	0.0011	0.09	0.39	0.86	[174]
		B30 (300 mg L <sup>-1</sup> )				0.32	
		B30 (1300 mg L <sup>-1</sup> )				0.08	
		B35 (300 mg L <sup>-1</sup> )				< 0.02	
		TX100 (300 mg L <sup>-1</sup> )				0.32	
Triton N 101 (300 mg L <sup>-1</sup> )	0.34						

<sup>1</sup>  $\alpha$  comes from the expression of  $\gamma = \alpha \cdot K_p$  with  $K_p = C/C_m$  (C: aqueous phase solute concentration;  $C_m$ : micelle phase solute concentration).  $\alpha$  is a fitted parameter that characterizes availability of micellar phenanthrene for transport into actively growing cells.

### **3.6. Combination of advanced oxidation processes and biological processes**

SW/SF solutions have high content of toxic organic compounds and can exhibit low biodegradability [42,56]. Besides, a complete mineralization of target pollutants is often expected since some degradation by-products are highly toxic [55]. AOPs have the ability to degrade compounds with low biodegradability properties. However, the total mineralization of organics by AOPs requires longer treatment times and high energy consumption. Recently, the treatment of toxic effluents by the combination of an AOP with a post-biological treatment has been proposed [188]. Indeed, AOPs allow the formation of more biodegradable by-products, which are then completely mineralized by the post-biological treatment in a more cost-effective way compared to the only use of AOPs. Some studies reported the application of this combined process to several kinds of effluent such as industrial wastewaters [189] or landfill leachates [189] by using ozone, Fenton or electrochemical processes [190] as oxidation step. Furthermore, successful treatment of SW/SF solutions has also been observed by using the Fenton process [106,191] or ozonation [130] as oxidation stage and an aerobic treatment as post-biological treatment. Regarding EAOPs, the use of high-O<sub>2</sub> overvoltage electrodes like BDD showed the best results for biodegradability enhancement of SW/SF solutions [42]. This is ascribed to the lower production of toxic oxidation by-products. However, further investigations are necessary in order to improve the use of this kind of combined process for the treatment of SW/SF solutions.

The combination of a biological treatment as a prior step followed by an AOP could also be investigated [192]. This approach could be suitable for SW/SF solutions containing biodegradable EAs. First, it could lead to the removal of the effluent biodegradable fraction in a cost-effective way by the biological treatment. Then, a faster removal of low-biodegradable compounds could be observed during the AOP since biodegradable compounds removed in the first step, would not act anymore as strong inhibitor.

### 3.7. Selective degradation of target pollutants

The best way to save EAs is to implement a process allowing a selective removal of target pollutants. It aims at reaching both maximum removal of target pollutants and minimum degradation of EAs [18]. Thus, the treated SW/SF solution could be used for additional SW/SF steps without addition of further EAs and with similar effectiveness than a fresh SW/SF solution. However, there are two main issues hindering the achievement of this objective during degradation processes: (i) the protective environment for target pollutants formed by surfactant micelles and CDs, which usually decrease the availability of target pollutants ( $K_m$  and  $K_{CD}$  are crucial parameters), (ii) the degradation of organic compounds in a non-selective way [18] by oxidant species such as  $\bullet\text{OH}$ .

Few authors have investigated SW solution recycling for further SW steps after biological treatment. Navarro et al. [16] observed a selective biodegradation of PYR from a SW solution containing deoxyribonucleic acid (DNA) as EA. PYR removal reached 99% after 1 day of treatment, while more than 98% of deoxyribonucleic acid was recovered. This has been explained by the stability of the polymer against the PAH-degrader used in this study (*Sphingomonas* sp.). Thus, the treated solution was re-used for 4 SW cycles (synthetic contaminated soil) with high extraction capacity. Recently, it has also been reported that the use of a bacterial consortium (isolated from a contaminated soil) could allow effective reuse of a biologically-treated SW solution containing PHE and TW80 as EA (synthetic contaminated soil) [193]. However, dilution of the SW solutions was required in order to avoid toxic effects of TW80 on the bacterial consortium and fresh TW80 was always added before SW solution reuse in order to compensate the dilution effect. Moreover, none study has achieved selective biodegradation of target pollutants by using an inoculum from a conventional wastewater treatment plant.

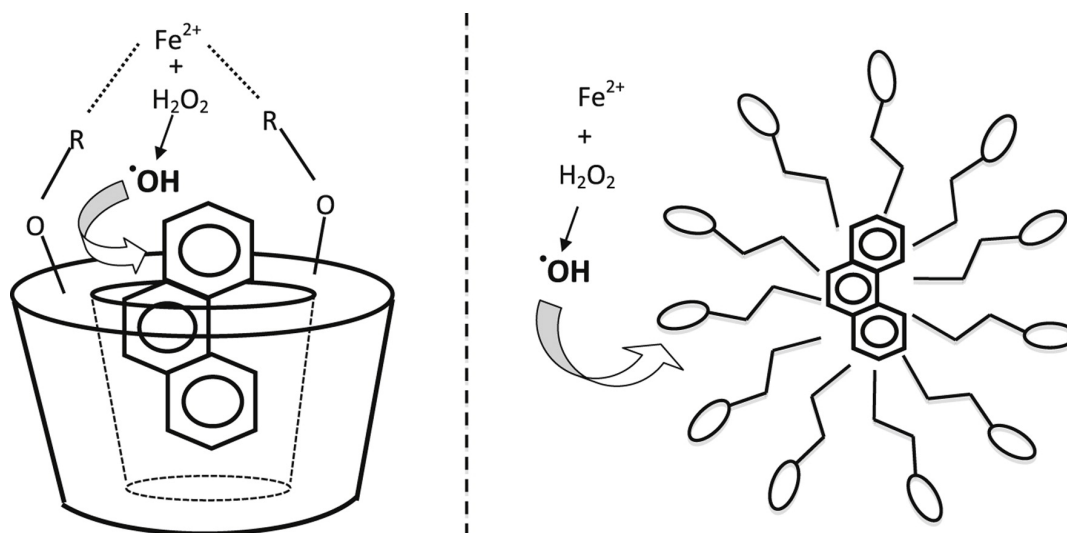
Several authors have investigated EA recycling by optimizing operating conditions of AOPs in order to promote the degradation of target pollutants and avoid the degradation of EAs. First, perfluorinated surfactants have the important characteristic to be highly refractory to oxidation by  $\bullet\text{OH}$ , however, they are considered as toxic persistent organic pollutant and they cannot be used for soil remediation by SW/SF processes [115]. Besides,  $\bullet\text{OH}$  have also different reaction kinetics with target pollutants and other EAs,

according to their chemical structure. Particularly, aromatic compounds are the most reactive species [46]. A slower degradation rate of EAs compared to target pollutants can be used for partial recovery of EAs. Some studies reported the following absolute rate constants for degradation of TX100, HPCD and TW80 by  $\bullet\text{OH}$ :  $3.5 \times 10^9$ ,  $2.6 \times 10^9$ ,  $1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , respectively [56,194]. It could be interesting to select EAs with low reactivity with  $\bullet\text{OH}$  in order to improve their recovery from SW/SF solutions.

It is worth to mention that only degradation of pollutants can be achieved. Complete mineralization of target pollutants requires higher treatment times and lead to high degradation rates of EAs [18]. Therefore, the toxicity of target pollutant degradation by-products should also be assessed [52,55]. This has been investigated by Mousset et al. [195], who observed that a second SW step with a SW solution (containing PAHs and TW80 as EA) partially oxidized by the EF process did not affect negatively the soil microbial activity, compared to the use of a fresh SW solution. This has been attributed to the production of hydroxylated by-products with higher biodegradability and solubility than initial compounds [195,196].

As regards to Fenton-based processes, the best results for EA recovery have been observed by using CDs as EA. This has been emphasized during the EF process by a comparative study using either TW80 or HPCD as EA and PHE as target pollutant [56]. This behavior has been explained by two different ways of forming complexes between TW80-PHE and CD-PHE. In the latter case, PHE is entrapped inside the CD cavity and the formation of the ternary complex (PHE-HPCD-Fe(II)) allows the production of  $\bullet\text{OH}$  close to the contaminant (PHE) and its direct oxidation. In contrast, in the case of TW80, PHE is entrapped inside the micelle core; this strongly reduces its availability towards oxidant species.  $\bullet\text{OH}$  have to degrade the micelle before degrading the contaminant [56]. Figure 1.8 depicts an explicative scheme of this mechanism.





**Figure 1.8.** Two different mechanisms for PHE degradation according to two different ways to form complexes between CD-PHE and surfactant-PHE. Reprinted from the reference [56].

During photocatalytic processes, the formation of micelles in the bulk reduces the availability of surfactants towards oxidant species [75,79,80]. This is an interesting behavior for reducing degradation rates of EAs but it has been reported higher recovery of TX100 after full removal of pentachlorophenol when low concentration of TX100 is used [75]. This has been ascribed to the much faster degradation kinetic of pentachlorophenol at low TX100 concentration.

Besides, the phenomenon of steric hindrance reducing the availability of micelles during AO process [165] could be further investigated as regards to the objective of selective degradation of target pollutants.

Here are some interesting results reported in the literature:

- Photocatalytic treatment during 2 h of a solution containing dibenzothiophene and 250 mg L<sup>-1</sup> of TX100 led to full degradation of the pollutant, while none degradation of TX100 (140 – 250 mg L<sup>-1</sup>) was observed [197].

- EF treatment of a synthetic SW solution containing PHE (17.8 mg L<sup>-1</sup>) and either HPCD (10 g L<sup>-1</sup>) or TW80 (0.75 g L<sup>-1</sup>) as EA led to full degradation of PHE, while 10% and 50% of EA was removed, respectively [56].
- Electro-oxidation of a SW solution containing PHE (35 mg L<sup>-1</sup>) and TW80 (10 g L<sup>-1</sup>) as EA led to 95% removal of PHE, while the reuse of the treated SW solution allowed the removal of 82.4% of PHE from a spiked contaminated soil, similarly to the extraction capacity obtained with the fresh TW80 solution (87%) [160].
- Electro-oxidation of a SW solution containing PHE and HPCD as EA led to full removal of PHE, while the extraction capacity of the treated solution was only 3% lesser than the value obtained with a fresh solution [161].
- Fenton treatment of a SW solution containing p-Cresol (20 mg L<sup>-1</sup>) and TW80 (0.86 g L<sup>-1</sup> TW80) as EA led to complete degradation of p-cresol, while 90% of TW80 was recovered [15].
- Higher selective removal of the target pollutant (nitrobenzene and sodium dodecylbenzenesulfonate as EA) was observed by using a Fe<sup>2+</sup>/persulfate system compared to the Fenton process, due to a preferential oxidation of nitrobenzene by persulfates [198].

However, a lot of contradictory results are observed and the details of mechanisms leading to selective removal of pollutants entrapped inside micelles have never been sufficiently investigated and fully understood.

It is also worth to mention that the crucial parameter is not the amount of EA recovered but the extraction power of the treated solution, which can differ because of EA analysis artefacts, generation of degradation by-products still solubilized in micelles and production of EA degradation by-products with extracting properties [18].

For example, it has been observed that a partially oxidized solution (by using the EF process) containing 11% less of HPCD than the initial solution allowed reaching slightly higher PAH removal from soil than a fresh HPCD solution [195]. This has been attributed to the extraction capacity of hydroxylated HPCD (degradation by-products), since the

internal hydrophobic space may have remained intact. By comparison, the reduction of 21% of the TW80 concentration by the EF process strongly decreased the extraction capacity of the partially oxidized solution compared to a fresh TW80 solution [195].

Finally, the extraction capacity of fresh and recovered SW solutions should be always assessed with real contaminated soils. The use of artificial and spiked soils usually leads to a strong overestimation of the efficiency of SW and SW solution treatment due to the lower sequestration of pollutants, lower surfactant sorption onto soil and lower mobilization of natural SOM.

## 4. Selective separation of target pollutants from soil washing/flushing solutions

### 4.1. Gas-liquid extraction

VOCs readily partition into the gas phase in contrast to non-volatile EAs. This is why air stripping and related technologies based on gas-liquid extraction are relevant processes for the removal of VOCs from SW solutions [199–202]. This method is usually applied for organic compounds with Henry's constant below  $0.01 \text{ mol m}^{-3} \text{ Pa}^{-1}$ . VOCs can be also defined as compounds with saturated vapour pressure above 10 Pa (0.075 mmHg) at 20°C and atmospheric pressure. Air stripping systems are based on the formation of a large air-water interfacial area in order to improve the mass transfer of VOCs from the aqueous phase to the gas phase. However, gas injection in the presence of EAs can lead to significant foam formation [203]. This is considered as one of the main drawback of this process [204]. The use of hollow fiber membranes instead of the usual packed towers and tray air strippers can reduce these foaming issues [205,206]. Lower foaming formation is also observed with CD, compared to synthetic surfactants. For example, air stripping was successfully performed at field-scale [207,208] for recycling HPCDs for several successive SF steps. Then, contaminated air was treated using granular activated carbon reactors.

Solubilization of target pollutants inside surfactant micelles or inclusion complex with CDs has an important impact on the efficiency of the process. The creation of an extra interfacial resistance is often considered to have a low impact on the global mass transfer [186,203]. However, EAs reduce the mole fraction of free organic compounds in the aqueous phase and act as a competing pseudo-phase with the gas phase for partitioning of the organic contaminant [209,210]. This adverse effect increases for more hydrophobic target pollutants and EAs with higher solubilization capacity (high  $K_m/K_{CD}$ ) [203]. This is also why lower efficiency are usually observed at high EA concentration [202]. For example, tetrachlorethylene removal efficiency was 83, 61 and 37% when performing air stripping with hexadecyl disulfonate as EA at 0, 10 and 55 mM, respectively [203]. Thus, Lipe et al. [203] developed a surfactant air stripping model (SASM) for assessing the efficiency of air stripping systems by taking into account

the effect of surfactants. It is based on the conventional non-equilibrium mass transfer model and was successfully validated by experiments at both bench and field scales [203,206].

Vacuum processes have been investigated in order to improve air stripping processes [211]. Vacuum is used as driving force for the transfer of VOCs from the liquid to the gas phase. SW/SF solutions can also be heated in order to increase the vapor pressure of target pollutants. This process allows the improvement of the separation effectiveness for contaminants with a lower volatility and the reduction of foaming problems [203].

Pervaporation has also been successfully applied to SW solutions [212] containing VOCs such as tetrachlorethylene [213], trichloroethylene [214], 1,1,1-trichloroethane [212,215] and toluene [215]. It is based on the vaporization of the SW solution through a VOC selective non-porous polymeric membrane. Field demonstration and pilot-scale experiments showed the high efficiency of the process for VOC removal without affecting the performance of the recovered solution [213,215]. Different configurations can be used such as spiral wound modules [215] or hollow fiber membranes [214]. Similarly to previous processes, the use of high surfactant concentrations can decrease the performances of the process in terms of selectivity and flux [212,213].

## **4.2. Liquid-liquid extraction**

An organic liquid can be used as the partitioning phase for the extraction of target HOCs from SW solutions [202]. Liquid-liquid extraction is based on the mass transfer of target pollutants from the wastewater to the solvent. Several studies successfully applied this process at both laboratory and field scales for the removal of semi- and non-volatile organics with high Henry's constants making them unsuitable for air stripping processes [216,217]. Using surfactants as EA, it has been reported a similar extraction capacity for the treated SW solutions and the fresh solutions [216,217]. However, the process is sometimes complicated by emulsification of the extracting solvent by the surfactant solution, leading to solubilization of solvent molecules into the micellar pseudo-phase. The selection of a proper solvent can reduce this phenomenon, particularly by using highly hydrophobic solvents [216–218]. Hollow fiber membranes filled by the extracting

solvent have also been used in order to eliminate emulsification and reduce the amount of solvent used [219]. As another example, Petitgirard et al. [74] used either micro-emulsion or impregnation of an organic membrane with the oil in order to reduce the amount of solvent used. Lower amount of solvent allows decreasing the loss of surfactant and facilitating the disposal of the contaminated solvent [202]. Distillation systems can also be used for solvent/contaminant separation in order to reuse the solvent for further contaminant/EA separation steps [201].

Hasegawa et al. [216] developed a model for surfactant liquid-liquid extraction in order to predict the efficiency of this process, which depends on the solvent-water partition coefficient ( $K_d$ ),  $K_m$ , solvent-water ratio and solvent-water contact conditions (column height, retention time, water velocity). Particularly, the partition of target pollutants in micelles ( $K_m$ ) is a crucial parameter. The increase of surfactant concentration significantly decreases the efficiency of the process due to micellar-reduced contaminant activities (the micellar pseudo-phase acts as a competing partitioning phase) [216]. Moreover, it is usually observed that the higher the hydrophobicity of target pollutants (high  $K_m/K_{CD}$ ), the higher the adverse effects of EAs on removal efficiency [216].

This process has also been applied to solutions containing CDs as EA. For example, it has been observed that liquid-liquid extraction with rapeseed oil could be efficiently used to regenerate a SW solution containing MCD [74]. This lab-scale experiment included a step of contact between the rapeseed oil and the contaminated SF solution, which allowed the regeneration of the MCD solution for continuous SF. After two days of SF, almost complete decontamination of the spiked sandy soil was achieved (96-98% of PAH removal), pollutants were concentrated in the organic phase and the loss of MCD was negligible.

It is worth to mention that such liquid-liquid extraction process lead to the production of highly contaminated solvent, for which disposal is very challenging. Moreover, it also involves high risks of handling (leaking storage tanks, exposure of workers via skin contact or inhalation).

### 4.3. Membrane processes

The use of membrane technologies has also been investigated for the treatment of SW solutions. Most of studies did not report selective surfactant-contaminant separation. However, in SF processes, EAs are often diluted in recovery wells by groundwater. Thus, membrane processes are often used for re-concentration of the SW solution (for example, after air stripping treatment) before reinjection in the contaminated zone [206].

By using ultrafiltration membranes, it has been observed 93-99% of surfactant-contaminant retention from a SW solution containing NAP and trichloroethylene as contaminant and linear alkyl diphenyloxide disulfonate as surfactant [203]. In fact, the formation of micelles improves the effectiveness of the process [220]. This micellar-enhanced ultrafiltration process (MEUF) is based on the formation of colloid-sized surfactant micelles retained by the ultrafiltration membrane, while surfactant monomers and aqueous extra-micellar pollutants pass through the membrane [203]. Thus,  $K_m$  is a crucial parameter for the effectiveness of this process [203] and high concentration of surfactant increases the separation efficiency (SE) due to the lower ratio of surfactant monomers and extra-micellar pollutants. A model has been developed by Lipe et al. [203] for the assessment of the separation efficiency by the MEUF process (Eq. 10 and 11).

$$SE = \left(1 - \frac{C_0}{S_m \times K_s}\right) \times 100 \quad (\text{Eq. 10})$$

with,

$$K_s = \frac{C_m}{C_{aq}} \times \frac{C_o}{S_m} \quad (\text{Eq. 11})$$

whereby,  $C_o$ ,  $C_m$ ,  $C_{aq}$  are the molar pollutant concentration in the total solution, in the micellar phase and in the aqueous phase, respectively,  $S_m$  is the molar surfactant concentration in micelles and  $K_s$  is a simplified micellar partition coefficient.

In this simple approach, it is assumed that  $C_m \ll S_m$  and concentration polarization is not taken into consideration, while it has been reported that this can significantly improve separation efficiency [203]. It is also worth to note that the CMC of the surfactant is an

important parameter to consider, since it influences the amount of surfactant monomers passing through the membrane.

Besides, the main drawback of membrane technologies is related to fouling issues, which lead to a dramatic increase of operating costs. Particularly, natural organic matter is widely recognised to be involved in the fouling of low-pressure membranes [221,222]. Thus, SW solutions containing high load of fouling materials and the increase of the surfactant concentration at the membrane surface can lead to the formation of a stable viscous phase resistant to the permeate flow [223]. This effect of concentration polarization depends on nature and concentration of the surfactant [203] and can strongly increase operating costs of the process. However, a field demonstration showed that the operation of MEUF for surfactant re-concentration after an air-stripping unit was simple and trouble free [206].

In contrast to most studies, Ang et al. [224] reported a selective removal of target pollutants by using an ultrafiltration system: 67% of the surfactant was recovered in the permeate, while more than 90% of polychlorobiphenyls and 83% of oils were retained, due to the formation of oil droplets readily rejected by the membrane.

#### **4.4. Adsorption processes**

Adsorption processes recently received great attention, due to promising results obtained for EA recovery [18]. Activated carbon is the most widespread sorbent material used (Table 1.6). Several studies observed much higher removal rates of target pollutants than EAs because of the higher partition coefficient for adsorption, higher hydrophobicity and lower concentration of target pollutants, compared to EAs [225,226].

The effectiveness of this process for EA recovery can be assessed in batch experiments by using the selectivity ratio ( $S$ ) (Eq. 12) [226]. Values reported in the literature usually range between 5 and 100, according to operating conditions (concentration/nature of EA, target pollutant, sorbent material, dose etc.). For example, a higher selectivity ratio for PHE removal (with Triton X-100 (TX100) as EA) was observed by using activated carbons with the higher sorption capacities [226]. Regarding the activated carbon dose,



a moderate amount (around 2 g L<sup>-1</sup>) was reported to be sufficient to reach 60% removal of 100 mg L<sup>-1</sup> of PHE with a selectivity ratio of 10 (initial concentration of TX100 was 5 g L<sup>-1</sup>) [226]. Much higher effectiveness was also achieved with a lower PHE concentration [226].

$$S = \frac{C_{SM,j}}{C_{l,j}} \times \frac{C_{l,SA}}{C_{SM,SA}} \quad (\text{Eq. 12})$$

whereby  $C_{SM,j}$  is the concentration of the target pollutant sorbed onto the sorbent material (mg g<sup>-1</sup>),  $C_{l,j}$  is the concentration of the target pollutant in the liquid phase (mg L<sup>-1</sup>),  $C_{l,SA}$  is the concentration of EA in the liquid phase (g L<sup>-1</sup>) and  $C_{SM,SA}$  is the concentration of EA onto the sorbent material (g g<sup>-1</sup>).

By using a configuration with a continuous flow through column, this process lead to much shorter exhausting times of EAs compared to breakthrough times of target pollutants [227]. Sorbent materials and mixtures pollutant-EA already studied are reported in Table 1.6.

**Table 1.6.** *Extracting agent recovery by using adsorption processes – an overview of the existing studies.*

Sorbent	Pollutant	Extracting agent	Configuration	Reference
Activated carbon	PHE <sup>1</sup>	TX100 <sup>2</sup>	Batch	[225,226]
Activated carbon	PHE <sup>1</sup> , FLUO <sup>3</sup> , BaA <sup>4</sup>	TX100 <sup>2</sup>	Column	[227]
Activated carbon	Trichloroethylene	HPCD <sup>5</sup>	Batch	[228]
Activated carbon	Mineral oil	RAMEB <sup>6</sup>	Column	[229]
Activated carbon	PHE <sup>1</sup>	Mixture SDS <sup>7</sup> -TX100 <sup>2</sup>	Batch	[230]
Activated carbon	PHE <sup>1</sup>	SDS <sup>7</sup>	Batch	[225,226]
Activated carbon	PHE <sup>1</sup>	TX100 <sup>2</sup>	Column	[231]
Activated carbon	FLUO <sup>2</sup>	TX100 <sup>2</sup>	Batch	[232]
Activated carbon	Chlorinated solvents	TX100 <sup>2</sup> , TX165 <sup>8</sup>	Column	[233]
Activated carbon	PHE <sup>1</sup>	TW40 <sup>9</sup> , TW80 <sup>10</sup> , B30 <sup>11</sup> , B35 <sup>12</sup>	Batch	[234]
Organo-bentonite	Various PAH <sup>13</sup>	TX114 <sup>14</sup> , TX100 <sup>2</sup> , TX305 <sup>15</sup>	Batch	[235]
Activated carbon	Hexachlorobenzene	Rhamnolipid	Column	[236]
Activated carbon	p-Cresol	TW80 <sup>10</sup>	Batch	[237]
Biochar	PHE <sup>1</sup> , FLUO <sup>3</sup> , PYR <sup>16</sup>	TX100 <sup>2</sup>	Batch	[238]

<sup>1</sup> Phenanthrene; <sup>2,8,14,15</sup> Triton X 100, 165, 114, 305; <sup>3</sup> Fluoranthene; <sup>4</sup> Benzo(a)anthracene; <sup>5</sup> HPCD <sup>6</sup> Randomly methylated  $\beta$ -cyclodextrin; <sup>7</sup> Sodium dodecyl sulfate; <sup>9,10</sup> Tween<sup>®</sup> 40, 80; <sup>11,12</sup> Brij<sup>®</sup> 30, 35; <sup>13</sup> Polycyclic aromatic hydrocarbon <sup>16</sup> Pyrene

Even if promising results have been obtained, further investigations are necessary. A better understanding of competition mechanisms between solubilization of target pollutants inside micelles or inclusion complex and their adsorption onto the sorbent material is required since it has been observed that a high HPCD concentration lowers the efficiency of the process [228].  $K_m$  and  $K_{CD}$  should be important parameters [239] to take into consideration for assessing the availability of pollutants for the adsorption. Compounds such as native natural organic matter could also have strong adverse effects on the selectivity ratio, therefore, the efficiency of the process should also be assessed by using real SW solutions. For example, two times lower selectivity ratio has been observed in a fluoranthene/TX100 mixture by adding  $0.10 \text{ g L}^{-1}$  of fulvic acid [232]. Finally, the efficiency of this process should be investigated for additional EAs, target pollutants and sorbent materials. Particularly, the EA and the sorbent material have to be carefully chosen in order to limit the phenomenon of pore blocking, which can lead to a reduction of active sites available for adsorption of target pollutants. For example, it has been observed that the reduction of the activated carbon surface area after TX100 adsorption is mainly ascribed to the blocking of micropores [226].

The regeneration of sorbent materials is also a critical issue because of their high cost. Thermal processes are currently the most conventional processes for activated carbon regeneration. However, it requires a huge energy consumption, post-treatment of the contaminated gas stream is required and it can reduce the specific surface area and adsorption capacity of the activated carbon [240]. Therefore, alternative regeneration processes are currently investigated, such as biological treatments [241,242], microwave irradiation [227,243], ozone [244] or EF processes [240,245]. The latter is a promising technique since activated carbon can be used as cathode for hydrogen peroxide production [246], leading to the production of  $\cdot\text{OH}$  close to target pollutants. Moreover, EF may have low adverse effects on the evolution of the adsorption capacity of the activated carbon, due to cathode polarization [240].

## 5. Conclusions and recommendations

Treatment of SW/SF solutions must face two main challenges:

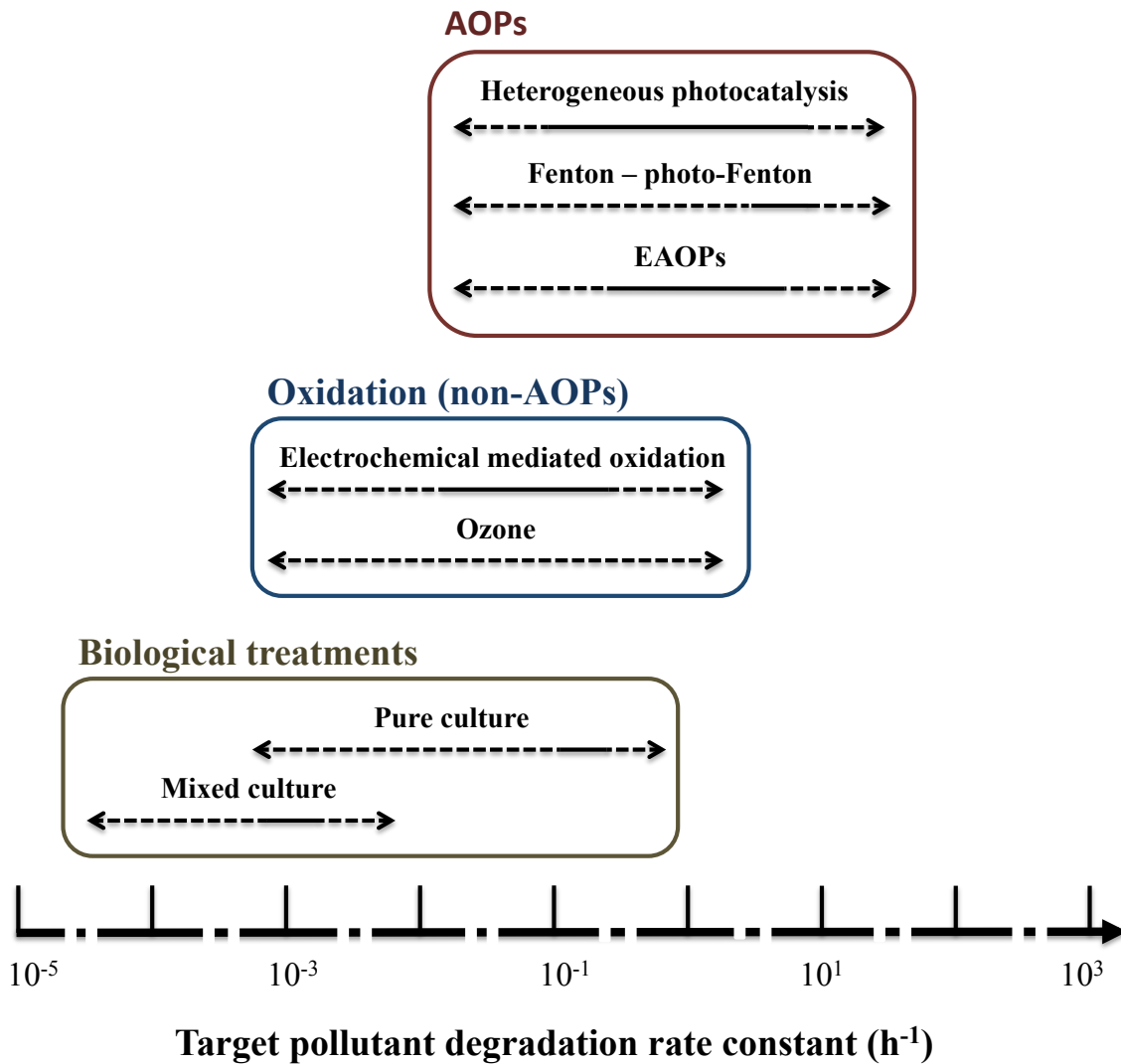
- the removal of pollutants in a cost-effective way in order to avoid contamination of the environment by SW/SF solution discharge,
- the recovery of EAs for SW/SF solution reuse in order to ensure the cost-effectiveness, sustainability and low ecological footprint of the process.

This requires the implementation of different treatment strategies. Main conclusions and recommendations for future studies are emphasized in this sub-section.

### 5.1. Decontamination of SW/SF solutions by degradation processes

There are technological solutions for the removal of organic compounds from SW solutions. However, the main issue is to perform the process in a cost-effective way because SW/SF solution characteristics (high SOM and EA concentration) have usually great adverse effects on the removal efficiency of the organic load and target pollutants.

Figure 1.9 shows target pollutant degradation kinetics that could be achieved as regards to the degradation process used. Table 1.7 shows an overview of main advantages and drawbacks of each process previously described. However, further studies about global treatment costs would be necessary, including energy consumption, reagent consumption, transport of soil and/or effluent, implementation and maintenance costs of the treatment plant.



**Figure 1.9.** Target pollutant degradation kinetic ( $\text{h}^{-1}$ ) in SW/SF solutions as regards to the degradation process (built from Table 1.1, 2.2, 2.3 and 2.5). Solid lines correspond to kinetics reported in literature, while dotted lines correspond to the variability of results which could be obtained depending on the nature of target pollutants, extracting agents, operating conditions, etc.

**Table 1.7.** Overview of main advantages and drawbacks of degradation processes for the treatment of SW/SF solutions (built from references of part II) “+” corresponds to a positive side for the use of the process considered, while “-” corresponds to a negative side.

Process	Influence of SW/SF solution characteristics	Operating costs		
		Reagent consumption	Energy consumption	Sludge production
Heterogeneous photocatalysis	--	+	-	+
Fenton	--	--	+	-
Photo-Fenton	--	-	-	-
Ozone	--	+	--	++
Electrochemical processes	--	++	--	++
Biological treatments	-	++	+	--

Among oxidation processes, heterogeneous photocatalysis, photo-Fenton and EAOPs are the most effective processes for the degradation of HOCs in SW/SF solutions with kinetic degradation rates in the range 1 – 10 h<sup>-1</sup>. This is attributed to the production of a sufficient amount of •OH for the treatment of these high-strength effluents. However, these AOPs lead to the consumption of a large amount of energy and/or reagents because EAs and natural SOM act as strong •OH scavengers. Moreover, micelles/CDs can act as a protective environment for target pollutants and prior degradation of micelles is often required for improving the availability of target pollutants towards •OH [56,163]. Besides, further studies are required on:

- the influence of the nature and concentration of target pollutants and EAs on degradation kinetics, by doing comparative studies;
- the availability of target pollutants towards oxidant species when they are entrapped inside micelles formed by surfactant molecules or inclusion complex formed with CDs;

- the amount and the influence of non-target compounds mobilized during the SW/SF process (particularly SOM and metallic ions) on the efficiency of degradation processes;
- the assessment of parameters such as COD, TOC, toxicity and biodegradability evolution of the solution during the treatment. Prior to the discharge of SW/SF solutions in the environment, an effective treatment should include the removal of the organic load.

Contrary to AOPs, biological treatment is a more cost-effective process, but its efficiency is limited by the presence of low biodegradable compounds and adverse effects arising from the presence of high concentrations of EAs. Moreover, it would be necessary to carry out further investigations about the influence on biodegradation kinetics of operating conditions and SW/SF solution characteristics. Particularly, biodegradability of EAs and interactions of EAs with microbial cell surface are crucial parameters. There is also a lack of studies performed in continuous reactors and/or at a pilot scale.

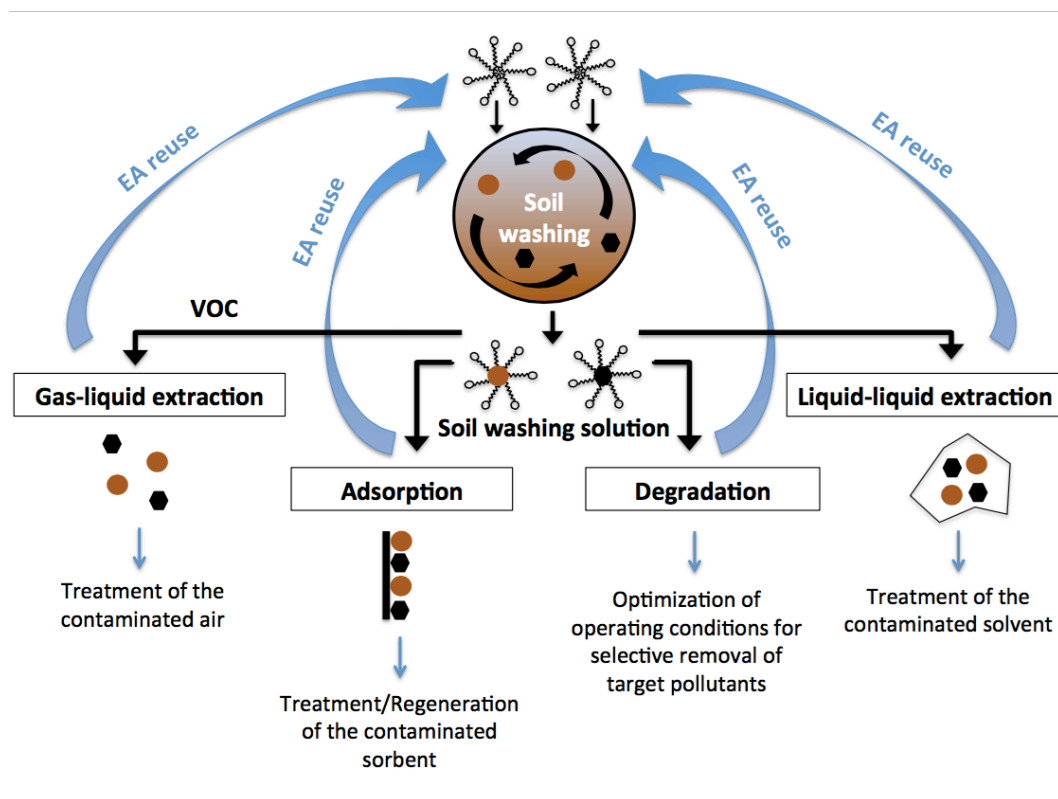
Finally, further studies should be carried out on the combination of AOPs with a pre- or post-biological treatment. This treatment strategy allows reaching high mineralization rates of organic compounds with optimized operating costs.

## **5.2. Recovery of extracting agents and SW/SF solution reuse**

The optimization of operating parameters (nature of the EA and other operating conditions) is the most direct approach to save EAs and improve the cost-efficiency of the process. However, an adapted management of SW/SF solutions allowing the recovery of EAs and reuse of SW/SF solutions is a crucial step in order to save large amounts of EAs.

Several technologies have been critically reviewed in this chapter (Figure 1.10). The choice of the most suitable technique depends strongly on characteristics of the SW/SF solution (Table 1.8). Gas-liquid extraction (air stripping and related technologies such as vacuum extraction or pervaporation) allows the selective removal of VOCs from SW/SF solutions. However, foaming issues have to be managed. As regards to HOCs, the choice

of an adapted organic solvent for a liquid-liquid extraction can lead to the concentration of HOCs in the organic phase while large amounts of EAs are recovered. Adsorption processes are also very promising for the separation of target pollutants from SW/SF solutions. However, high EA concentrations usually reduce the effectiveness of these separation processes due to the partition of target pollutants in the micellar pseudo-phase or inclusion complex with CDs ( $K_m/K_{CD}$  are crucial parameters). Thus, the optimal conditions for SW/SF processes (high EA concentration and high  $K_m/K_{CD}$ ) have adverse effects on the efficiency of selective separation processes. Furthermore, it is worth to mention that a post-treatment of the contaminated air/solvent/sorbent is required, thus increasing the global cost of the whole treatment strategy.



**Figure 1.10.** Treatment strategies for the recovery of extracting agents (EA) from contaminated soil washing solutions.

Optimization of operating parameters of degradation processes can also lead to higher degradation rates of target pollutants compared to EAs. This is mainly ascribed to



different reactivity of target pollutants and EAs towards oxidant species. However, further studies should be carried out on mechanisms of selective degradation of pollutants entrapped inside micelles or inclusion complex. In contrast to separation processes, these processes allow the degradation of target pollutants but a lower amount of EA is usually recovered.

**Table 1.8.** *Important operating conditions, target pollutant and extracting agent characteristics to consider according to the choice of the process used for extracting recovery from SW/SF solutions. CMC: critical micellar concentration;  $K_m$ : micellar phase / aqueous phase partition coefficient;  $K_{CD}$ : complex stability (or equilibrium) constant between organic compounds and cyclodextrins.*

Process	Important target pollutant characteristics (optimal*)	Important EA characteristics (optimal*)	Important operating conditions
Gas-liquid extraction	Henry constant (low), saturated vapor pressure (high), $K_m/K_{CD}$ (low)	Henry constant (high), concentration (low), $K_m/K_{CD}$ (low)	Limitation of foaming (hollow fiber membranes, vacuum processes)
Liquid-liquid extraction	Solvent-water partition coefficient (high), $K_m/K_{CD}$ (low)	Solvent-water partition coefficient (low), concentration (low), $K_m/K_{CD}$ (low)	Limitation of emulsification and amount of solvent used (hollow fiber membranes), highly hydrophobic solvent
Membrane processes	Oil-containing mixture (for selective removal), $K_m$	Concentration, $K_m$ , micelle size, CMC, effect on concentration polarization	Ultrafiltration (for micellar-enhanced ultrafiltration), fouling control
Adsorption processes	Partition coefficient on the sorbent material (high), $K_m/K_{CD}$ (low)	Partition coefficient on the sorbent material (low), concentration, $K_m/K_{CD}$ (low)	Sorbent material and dose
Degradation processes	Degradation kinetic (fast), $K_m/K_{CD}$	Degradation kinetic (slow), concentration, nature, $K_m/K_{CD}$	Optimized for selective degradation of target pollutants

\* This refers to optimal conditions for EA recovery from SW/SF solutions (different from the optimal conditions for the SW/SF process)

Besides, further studies on real contaminated soils are required in order to assess the efficiency of these processes at real field scale. Particularly, the characteristics of the contaminated soil may have a strong influence on the extraction capacity of recovered SW/SF solutions according to the amount of natural SOM still present in the treated solution, sequestration level of target pollutants in soils and soil sorption of EAs.

Nature and concentration of the EA used during SW/SF processes are crucial parameters for the treatment of SW/SF solutions (Table 1.7). Thus, the implementation of optimal operating conditions for SW/SF processes should also consider the impact of the EA chosen on the efficiency of SW/SF solution treatment. Particularly, its capacity to be recovered and reused for several SW/SF steps should be assessed in order to improve the sustainability of the whole process. An ideal EA would have the following properties:

- high extraction capacity of target pollutants by using low concentration;
- low soil sorption and low influence on soil structure and microbial activity;
- low mobilization of SOM, low inhibitory effect on the efficiency of degradation processes and suitable for a treatment allowing its recovery.

Finally, the choice of the most suitable process for the treatment of a SW/SF solution should be based on a cost-benefit analysis. Selective separation/degradation of target pollutants involve the implementation of costly processes (in terms of reagents and/or energy consumption). Therefore, it would be interesting to compare these additional costs to savings made by EA recovery and SW solution reuse. The development of effective processes for EA recovery could encourage industrials to use more expensive EAs with higher eco-friendliness and effectiveness. Moreover, EA recovery from SW/SF solutions could improve the suitability of SW/SF processes for the treatment of historically contaminated soils, for which several successive SW/SF steps are often required for reaching sufficient removal rates due to the higher sequestration of pollutants in aged soil.

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## **CHAPTER 2**

### **CHARACTERISTICS OF PAH TAR OIL-CONTAMINATED SOILS – BLACK PARTICLES, RESINS AND IMPLICATIONS FOR TREATMENT STRATEGIES**

This chapter has been submitted for publication in Journal of Hazardous Materials as:

Trellu C., Miltner A., Gallo R., Huguenot D., van Hullebusch E.D., Esposito G., Oturan M.A., Kästner M., Characteristics of PAH-tar oil contaminated soils - Visualization of black particles and new treatment strategies.



## Abstract

Tar oil contaminations are a major environmental concern due to health impacts of polycyclic aromatic hydrocarbons (PAHs) and the difficulty of reaching acceptable remediation end-points. Six tar oil-contaminated soils with different industrial histories were compared to investigate contamination characteristics by black particles (BPs). Here we provide a simple method tested on 6 soils to visualize and identify large amounts of BPs as either solid aggregates of resinified and weathered tar oil or various wood/coke/coal-like materials derived from the contamination history that contain 2 to 10 times higher PAH concentration than the average soil and lead to the accumulation of 42 to 86% of PAHs in the sand fraction. The PAH contamination in the different granulometric fractions was directly proportional to the respective total organic carbon content, due to the association of PAHs to various carbonaceous particulate materials. Significantly lower (bio)availability of PAHs associated to these carbonaceous phases is widely recognized, thus limiting the efficiency of remediation techniques. In addition, we provide a conceptual model of the limited mass transfer of PAHs from resinated tar oil phases to the water phase. Finally, we emphasize the options to physically separate BPs, based on their lower bulk density and slower settling velocity.

**Keywords:** Polycyclic aromatic hydrocarbons (PAHs), tar oil, resin, black carbon, remediation

### Highlights:

- The characteristic particles of aged tar oil-contaminated soils are visualized
- Resins of tar oil and wood/coal/coke particles are identified in 6 soils
- A large amount of PAHs is sequestered inside these materials in the sand fraction
- The low mass transfer of PAHs from resinated particles is described by a model
- Selective separation of these materials is a promising treatment strategy



## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals of environmental concern, consisting of two or more condensed aromatic rings. They are generated by pyrolysis or incomplete combustion of biomaterials and other organic compounds above 800°C [1,2], and are also common constituents of coals, and thus, also of coal tars and mineral oils. PAHs mainly enter the environment from wildfires, soot emissions of combustion processes, and spills of mineral and tar oils [3]. Due to the development of industrial activities during the 19<sup>th</sup> and 20<sup>th</sup> century (especially manufactured gas plants and rising tar oil use), the anthropogenic emissions and contaminations increased. PAHs do not enter the environment as pure compounds: they are mostly components of soot particles or tar oils. Their hydrophobicity leads to strong interactions with solid surfaces, non-aqueous liquid phases (NAPL) and soil organic matter, leading to low or non-biodegradability in the environment [4]. Many compounds of this group have severe toxic, cancerogenic and mutagenic potentials to higher organisms and humans [5,6]. Therefore, they represent an important long-term contamination of the environment and the US Environmental Protection Agency (USEPA) considers them as priority pollutants. Sixteen model PAHs have been selected by the USEPA for a relevant and easy monitoring of contaminated sites [7].

There is a need for industry, authorities, and environmental engineering companies to find sustainable remediation techniques for decontamination of PAH-polluted soil. Soil washing and biodegradation are currently the most widespread treatment techniques [8]. Soil washing is based on the transfer of PAHs from the sorbed fraction to the washing solution [9]. Sufficient removal effectiveness usually requires the use of large amounts of extracting agents (cyclodextrins, surfactants, solvents) [10,11]. The main drawbacks of this process are the high cost of the extracting agents, their potential toxicity, and the management of the resulting concentrated soil washing solution [12–14]. Much knowledge has been accumulated on PAH removal and biodegradation pathways [15], including mineralization by specific bacteria or fungi and cometabolic degradation by specific enzymes up to the process of ‘enzymatic combustion’ [16,17]. However, biodegradation approaches in real-world contaminated sites often led to unexpected low effectiveness [8], whereby the reasons were not analyzed with respect

to the detailed contamination characteristics determining the unexpected very poor PAH bioavailability. Relevant parameters for extraction effectiveness, bioavailability and microbial biodegradation are the PAH solubilization properties and partitioning in multi-phase systems [18]. The octanol-water ( $K_{ow}$ ) and organic carbon-water ( $K_{oc}$ ) partitioning coefficients are usually used to express the behavior of organic compounds in different environments. However, tar oils are a liquid to highly viscous mixture of various organic compounds, forming NAPL [19,20]. Therefore, Raoult's law determines the mass transfer into the aqueous phase, because it takes into account the chemical activity of each compound in the oil matrix [18,21–23]. Sequestration and ageing also result in increasing soil sorption and decreasing (bio)availability of PAHs over time [24,25]. Various general phenomena have been observed such as tar oil weathering [20,22] or association of tar oils to black carbon (BC) materials [26,27] but have not been considered for specific sites. Contamination history is thus a crucial issue for better understanding the behavior of PAHs in contaminated soils. Ignoring the different pollution characteristics at each site, caused by the contamination history, is one important reason for the failures of remediation measures, contradictory results about PAH (bio)availability and partitioning behavior reported in the literature [28–33].

Tar oil contaminations are complex because PAH contamination is frequently accompanied by the presence of solid carbonaceous particles [32]. Moreover, tar oil ageing can modify the physical and chemical characteristics of the initial NAPL [19,27,34,35]. Therefore, we analyzed 6 different polluted soils in order to provide a better understanding of the dominating characteristics of soils contaminated by tar oils, thus providing a basis for recommendations for remediation approaches. Specific objectives were: (i) to visualize, characterize, and understand the impact of solid carbonaceous particles on PAH-tar oil contamination of various soils, with a particular focus on the resinification process of the tar oil phase, (ii) to evaluate and discuss the effect of the contamination history on PAH distribution and treatability of PAH tar oil-contaminated soils, including testing of new treatment strategies.

## 2. Material and methods

### 2.1. Soil sites

Soil samples were collected at 6 different contaminated sites with a current need for decontamination. They have all been impacted by historic dumping and spillage of tar oil, and provide various levels of PAH contaminations. 'Michle' soil came from a former municipal gas works (coal carbonization until 1965 and hydrocarbon cracking until 1975) in Prague (Czech Republic). 'Sobeslav' soil was sampled at a production site for pressure-treated wooden poles and railway sleepers (based on impregnation by creosote and distillation products of gas-tar) in the south of Czech Republic. Ile de France (IdF) and North of France (NoF) were two sites located in France producing bituminous mixtures and coating materials, respectively. 'Rositz' soil came from a carbo-chemical plant situated near Altenburg (Germany) which produced coke and coal tar from lignite over a period of 75 years, until 1990; contamination came from leakage of storage tanks, waste and by-products stored in unstable ponds, and war damage. The contamination of the Veringstrasse (VS) soil in Hamburg (Germany) was related to a site of general gas manufacturing and tar oil storage, and historically a trading site of carbonized conifer oils for caulking wooden ship planks.

### 2.2. Acetone and full oxidation procedure

Two rapid, simple methods were developed in order to identify qualitatively the nature of solid particles in the sand fraction. First, the acetone treatment for assessment of tar oil products only required the addition of some drops of acetone at the surface of a soil sample. Turning black of the soils indicates tar oil presence.

In order to assess the BC particles and the mineral matrix, a method for full oxidation of the brown humic matter was developed [36]. Briefly, 0.5 g of the soil to be analyzed was added to 5 mL concentrated  $\text{H}_2\text{SO}_4$  and was carefully heated to 80 °C. This solution was supplemented with 100 mg  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ;  $\text{H}_2\text{O}_2$  solution (30%, w/w) was added drop-wise until the brown color vanished. Finally, the solution was neutralized with NaOH, the liquid phase discarded and the residual particulate material dried at 40 °C.

### 2.3. Particle size separation

Wet sieving was performed for particle size separation [31]. Three fractions were analyzed: (i) <63  $\mu\text{m}$  (fine fraction, silt and clay), (ii) 63-200  $\mu\text{m}$  (fine sand) and (iii) 200-2000  $\mu\text{m}$  (medium to coarse sand). The duration of wet sieving and volume of water used were minimized (ratio soil:water <1:3) in order to limit the loss of low molecular weight PAHs. Particle size separation on the soil VS was not performed due to limited amount of sample available.

### 2.4. Optical evaluation

Soil particles of various samples (initial soil, fully oxidized soil, acetone-treated soil and the different granulometric fractions) were optically inspected using a stereomicroscope (Carl Zeiss, Stemi DRC, Germany) with digital camera (Carl Zeiss, AxioCam ERc 5s, Germany) (total magnification of 10-20 fold). The nature of the particles was assessed according to their respective size, color and shape. Black particles (BPs) (*i.e.* particles identified as either solid aggregates of resinified and weathered tar oil (RWTO) or wood, coke and coal-like materials) were then manually separated with tweezers from the sand fraction.

### 2.5. Total organic carbon (TOC) and black carbon analysis

Analyses were performed using a combustion furnace (Ströhlein Instruments, Germany) coupled with an infrared detector (Seifert Laborgeräte, C/S max, Germany). TOC was obtained from the analysis of initial soil samples, whereas BC was analyzed after oxidation at 375 °C of the non-BC materials [32]. TOC and BC content in Rositz and VS soils were not analyzed due to limited amount of sample available.

### 2.6. PAH extraction and analysis.

PAH extraction from soil was performed following the method of Eschenbach et al. [37] based on two successive steps, including an organic solvent extraction and a methanolic

hydrolysis (saponification). Briefly, organic solvent extraction was performed using 0.5 - 3 g of soil mixed with 3 mL ethylacetate (HPLC grade) into 10 mL glass Hughte tube sealed with screw caps (Schott Duran, US) and ultrasonicated the mixture for 30 min (Bandelin, Sonrex Super, Germany). After centrifugation of the slurry (3500 rpm, 15 min), the extract was sampled for analysis of its PAH content. Then, methanolic hydrolysis was performed using saponification leach (2.8 mL methanol (HPLC grade), 0.2 mL 2 N KOH) and incubating the samples at 95 °C for 1 h. Samples were centrifuged, an aliquot of the supernatant was pipetted and PAHs were extracted by means of three successive extractions with 1 mL hexane. PAHs were quantified using a gas chromatograph (7890A, Agilent Technologies) equipped with a BPX5 column (30 m × 0.25 mm id, 0.25 µm film, SGE Analytical Science, Melbourne, Australia) coupled to a quadrupole mass spectrometer (5975C, Agilent Technologies). The GC oven temperature was programmed as follows: initial 40 °C, hold for 2 min, then heat to 180 °C at 40 °C min<sup>-1</sup>, 2-min hold, heat to 240 °C at 5 °C min<sup>-1</sup>, 2-min hold and heat to a final temperature of 300 °C at 15 °C min<sup>-1</sup>, 5-min hold, with a helium flow of 1.5 mL min<sup>-1</sup>. The injector was set to 280 °C. The mass spectrometer was operated in the electron impact ionization mode at 70 eV. Concentration of the 16 USEPA PAH was obtained by means of the internal standard method, using deuterated phenanthrene and chrysene from Sigma Aldrich as internal standard. Total PAH concentration in soil samples was calculated from the analysis of both organic solvent extraction and methanolic hydrolysis. All soil samples were analyzed in triplicate, allowing the calculation of standard deviations for the PAH concentration of each soil sample.

## 2.7. Enrichment factors

Enrichment factor ( $EF_{S,f;i}$ ) of the compound S (*i.e.* PAH, TOC or BC) in the fraction  $f$  (BPs or the different granulometric fractions) of the soil  $i$  was calculated as follows:

$$EF_{S,f;i} = \frac{[S]_{f;i}}{[S]_i} \quad (\text{Eq. 1})$$

whereby  $[S]_{f,i}$  is the concentration of the compound S in the fraction  $f$  of the soil  $i$  and  $[S]_i$  is the concentration of the compound S in the total soil  $i$ .

## 2.8. Selective separation procedure

A simple procedure was proposed in order to test the possibility of developing a selective separation process for the most contaminated fraction. All particles were suspended in water (ratio soil:water of 1:2) by agitation on a rotary flatbed shaker. The agitation was then stopped and particles settled according to their respective settling velocity. The procedure was applied to the total soil as well as to different granulometric fractions. Low-density BPs in the sand fraction allowed the formation of an upper black layer. The supernatant was discarded; the upper layer was carefully removed manually, weighted and analyzed for its PAH content. Resuspension and sedimentation were repeated with the remaining lower layer. Once again, the two different layers were manually separated, weighted and analyzed for their respective PAH contents.



## 3. Results

### 3.1. Identification of black particles

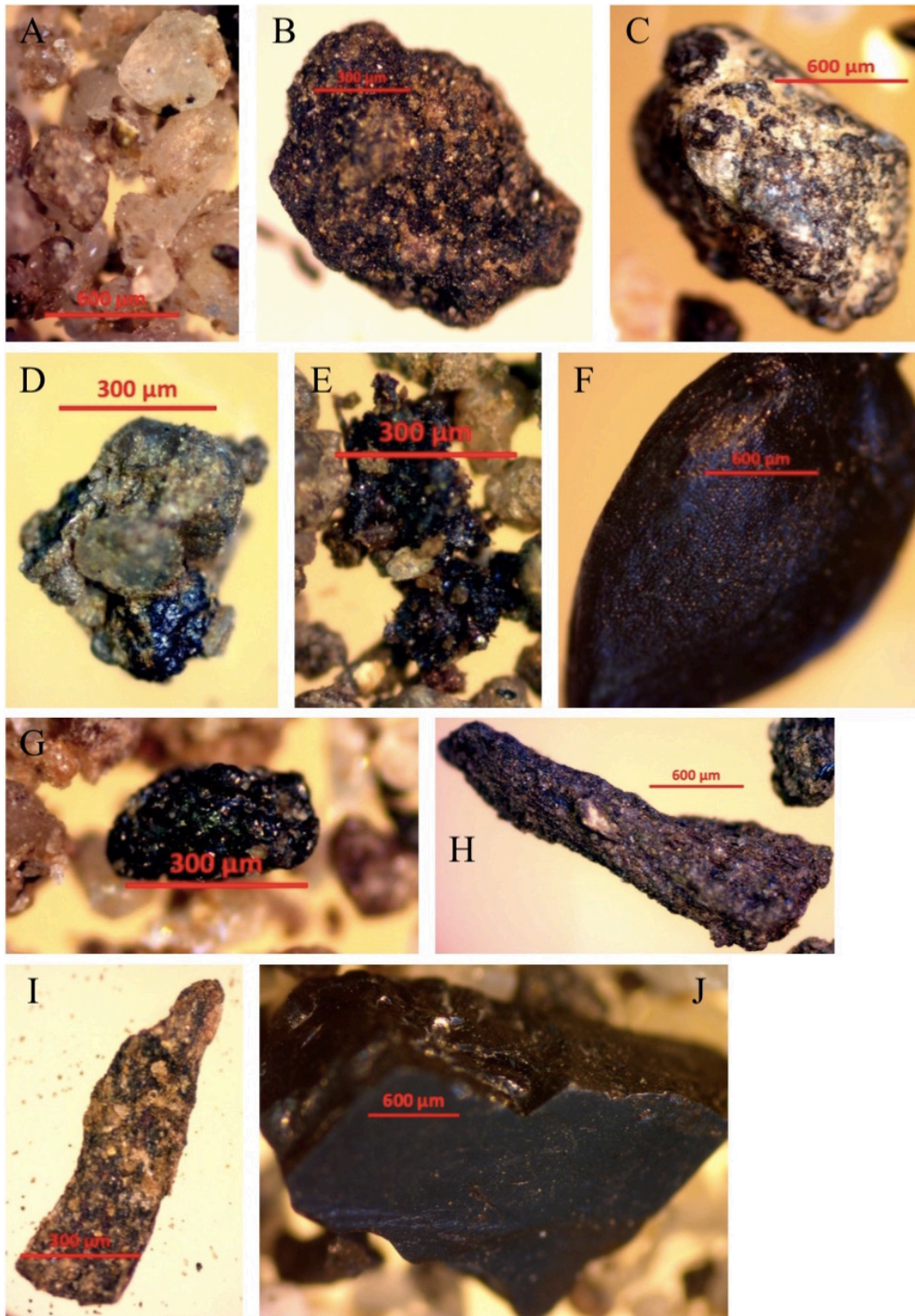
At first sight, a historically tar oil polluted soil often does not show visual evidence of its contamination, e.g. the untreated brown soil VS shown in Figure 2.1 A1. However, adding several drops of acetone to the parent soil material causes a black color to appear on some particles from solubilization of residual resinified and weathered tar oil (RWTO; Figure 2.1 A2). The full oxidation method for brown humic matter qualitatively indicates the presence of solid-state BC materials in the white or glassy solid mineral phase (Figure 2.1 A3). Similarly, wet sieving of the soil IdF allowed many distinct BPs to appear, mainly in sand fractions (63-200 and 200-2000  $\mu\text{m}$ ) (Figure 2.1 B), due to the removal of fine materials adhering on the surface of sand particles.

Particular consideration was given to the identification of BPs by stereomicroscopic analysis, resulting in Figure 2.1 C-F: (i) coal-like particles, (ii) porous materials such as coke particles, (iii) glassy slag particles, (iv) solid aggregates of RWTO, often mixed with sand, silt, clay or natural soil organic matter. Various other types of BPs observed, such as wood-like particles, are given in Figure 2.2. Based upon these analyses, BPs were divided into two main classes: RWTO particles and wood/coke/coal-like particles. BPs were observed in all 6 soils analyzed, as shown for the 63-200  $\mu\text{m}$  fractions in Figure 2.3; however, differences were observed in terms of amount and nature. A lower amount of BPs was observed in the Sobeslav and NoF soils. Many wood-like materials were identified in the Sobeslav soil, while mainly RWTO particles were identified in NoF. A large variety of coal- and coke-like materials as well as RWTO aggregates were observed in the Michle, VS, Rositz and IdF soils.

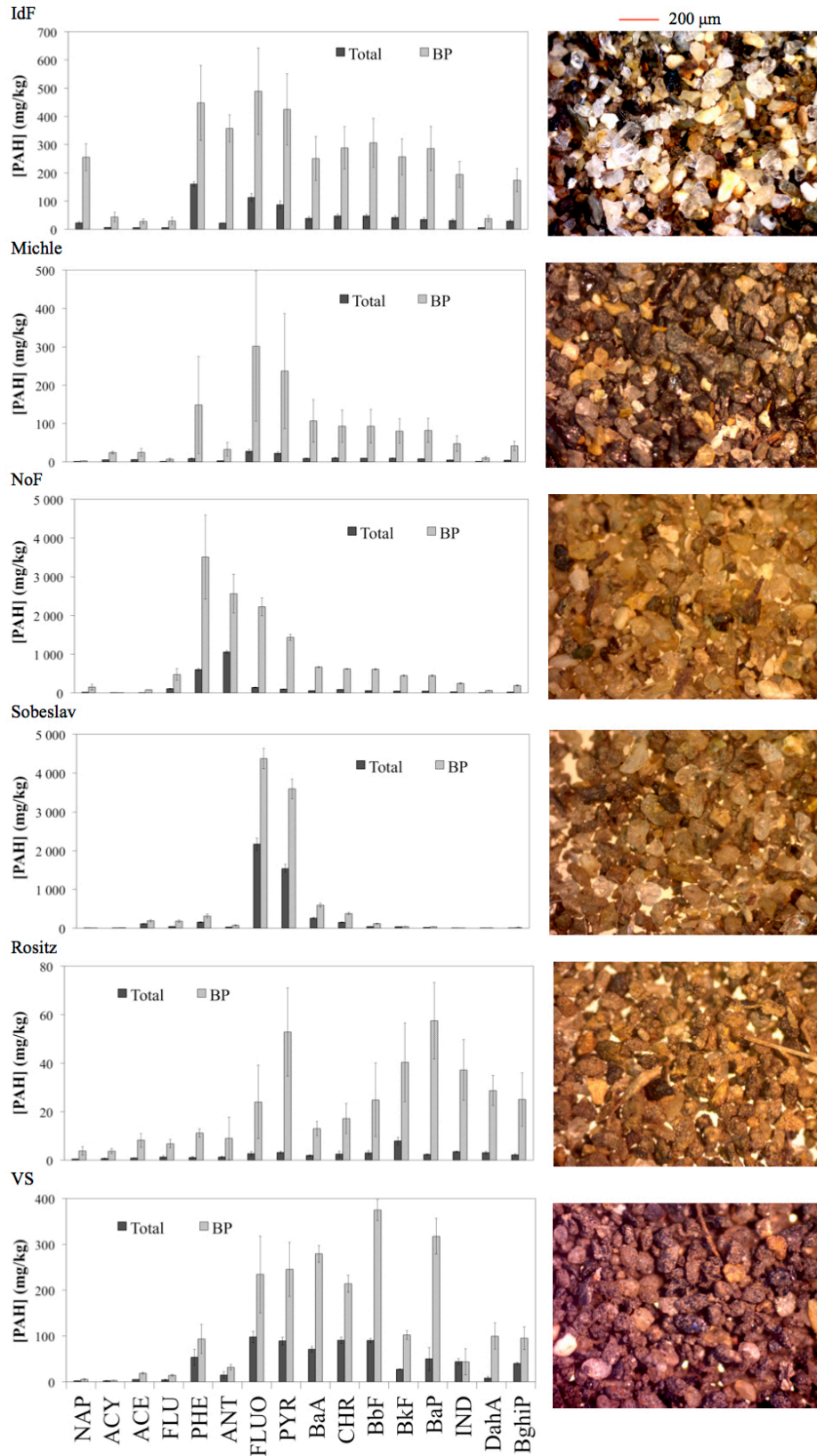


**Figure 2.1.** Stereomicroscopic pictures. A1: VS soil untreated; A2: VS soil acetone-treated; A3: VS soil fully oxidized; B1: IdF soil untreated; B2: 200-2000  $\mu\text{m}$  fraction of IdF soil; B3: 63-200  $\mu\text{m}$  fraction of IdF soil; B4: <63  $\mu\text{m}$  of IdF soil; C: coal particle (from IdF); D: coke particle (from VS); E: glassy slag particle (from NoF); F: solid aggregates of resinified/weathered tar oil and embedded soil particles (F1: from VS, F2: from IdF, F3: from Michle).





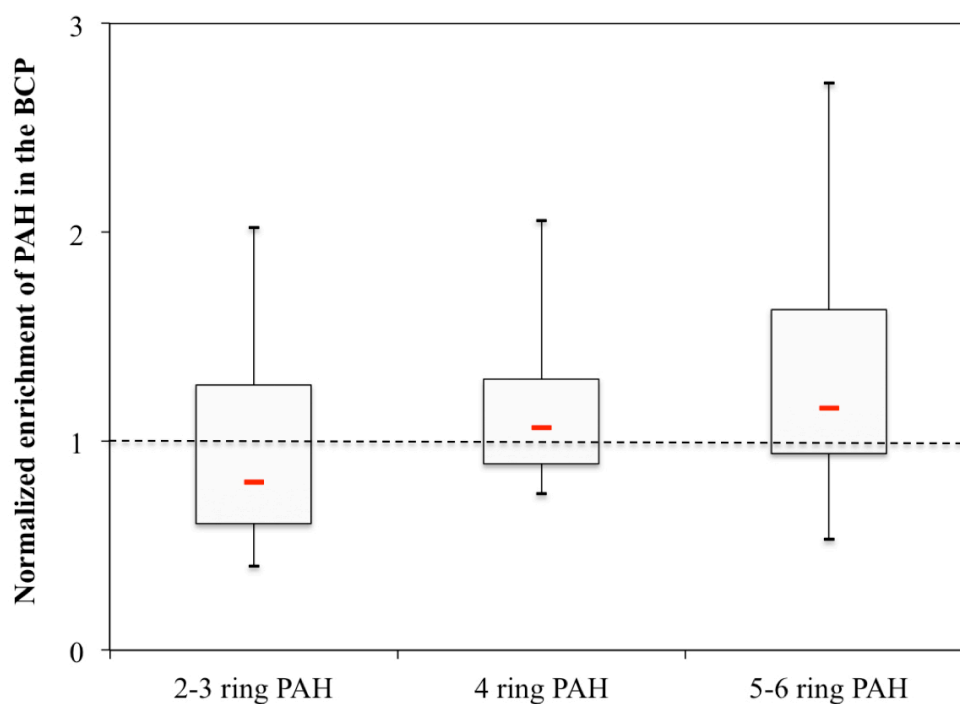
**Figure 2.2.** Stereomicroscopic pictures of different kinds of particles observed in the sand fraction of contaminated soils. A: mineral particles (NoF); B-G: solid aggregates of weathered tar oil from Rositz (B), IdF (C), Michle (D), Rositz (E), IdF (F), VS (G); H, I: wood-like particles (Sobeslav); J: coal-like particle (IdF).



**Figure 2.3.** Concentration of the 16 USEPA PAHs in total soil and in manually separated black particles from IdF, Michle, NoF, Sobeslav, Rositz and VS soils. Stereomicroscopic pictures of the respective 63-200  $\mu\text{m}$  fraction of each soil.

### 3.2. Role of black particles in PAH distribution for aged tar oil-contaminated soils

BPs were manually separated from the sand fraction of each soil and analyzed for their PAH content (Figure 2.3). The enrichment factor for the sum of the 16 USEPA PAHs in BPs was 10, 10, 6, 6, 3 and 2 for the Michle, Rositz, IdF, NoF, VS and Sobeslav soils, respectively. A slight but significant higher enrichment of the heaviest PAHs was observed in BPs, as shown by the statistical analysis in Supporting Information (Figure 2.4). The patterns of 16 USEPA PAHs distributions were also different between the sites. While the full PAH spectrum was observed in the IdF, Rositz and VS soils, the other soils contained a lower amount of heavy PAHs.

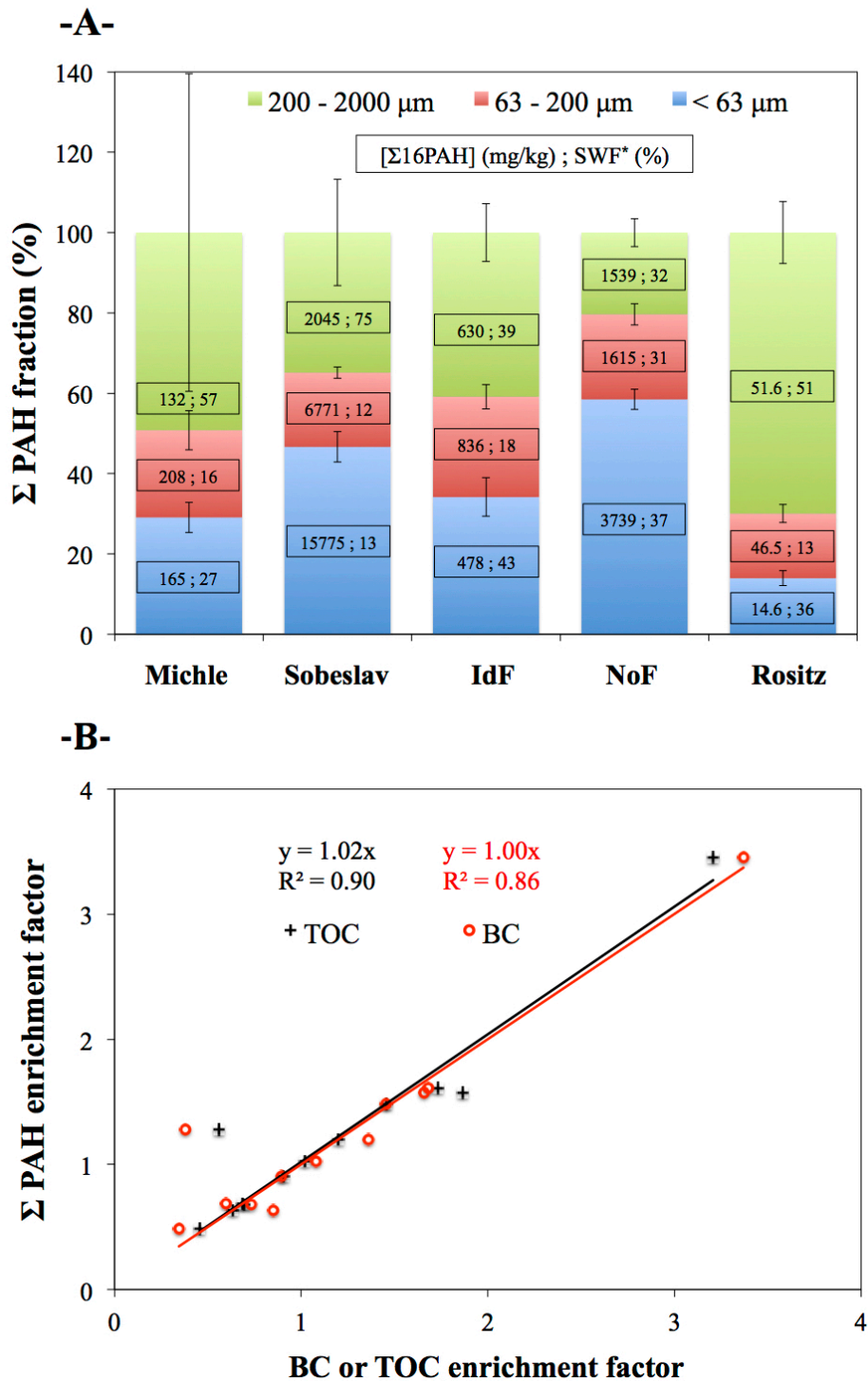


**Figure 2.4.** Box plot of the evolution towards heavier PAHs of the distribution of the 16 USEPA PAHs in BPs of the 6 soils analyzed, compared to the respective PAH distribution in the bulk soils. Normalized enrichment factor of PAHs in BPs refers to the ratio between the enrichment factor of the PAH  $j$  in the BPs of the soil  $i$  and the enrichment factor of the average of the 16 PAHs in the BPs of the soil  $i$  ( $EF_{PAH_j;BP;i} / PAH_{16PAH;BP;i}$ ). Boxes indicate first and third quartile values; red lines indicate median values; the extremity of lines indicates maximum and minimum values. The two higher and lower values of each data set were not considered.

PAH distribution within the granulometric fractions <63, 63-200 and 200-2000  $\mu\text{m}$  was then investigated (Figure 2.5 A). The fraction of PAH in the sand fraction (>63  $\mu\text{m}$ ) amounted to 86, 71, 66, 53 and 42% of the total PAH content for the Rositz, Michle, IdF, Sobeslav and NoF soils, respectively.

TOC and BC contents of bulk soils and of the various granulometric fractions were determined (see Table 2.1). Good linear correlation (factor 1.02;  $R^2 = 0.90$ ) was observed between PAH and TOC enrichment factors within the various granulometric fractions. Similar correlation was observed between PAH and BC enrichment factor (factor 1.00;  $R^2 = 0.86$ ) (Figure 2.5 B).





**Figure 2.5.** Impact of the presence of black particles on PAH partitioning behavior in aged tar-oil-contaminated soils. A - PAH fraction according to granulometric fraction in Michle, Sobeslav, IdF, NoF and Rositz soils. PAH recovery after wet sieving was always above 90% compared to the bulk soil. \*Soil weight fraction. B - Correlation between the enrichment factor of the sum of the 16 USEPA PAHs and the enrichment factor of BC and TOC content in the granulometric fractions.

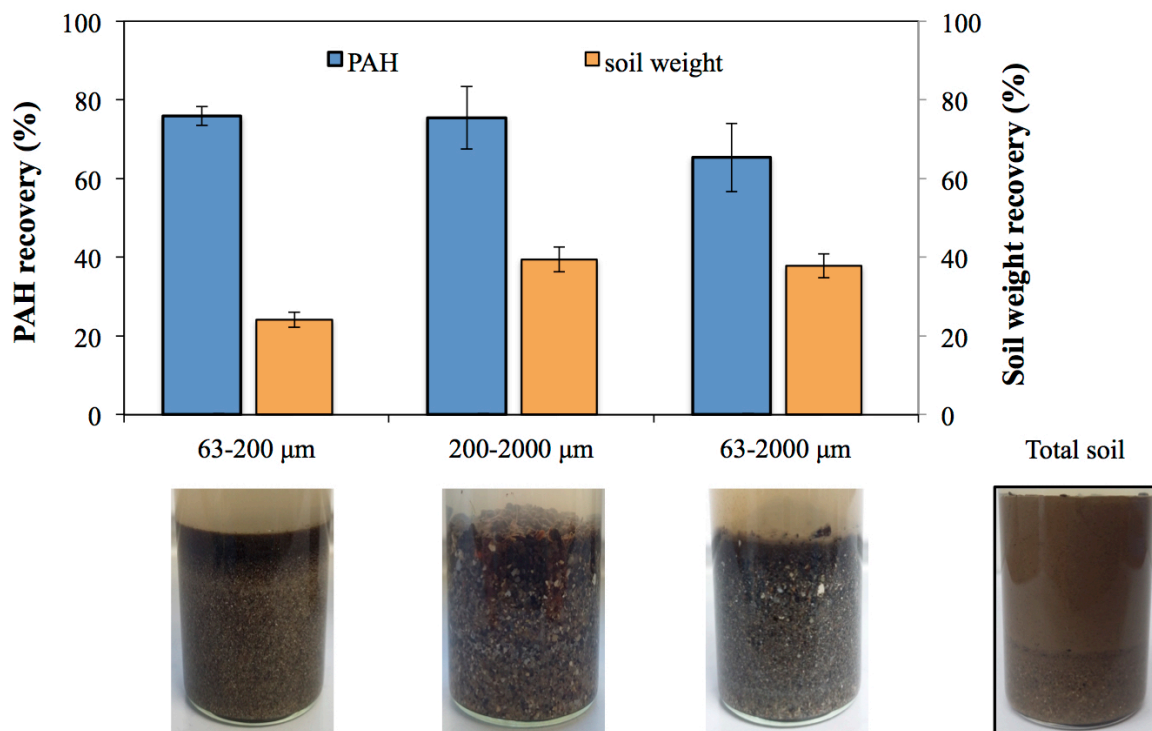
**Table 2.1.** Total organic carbon (TOC) and black carbon (BC) of soils Michle, Sobeslav, IdF and NoF, according to granulometric fractions. VS and Rositz were not analyzed. Tot: total soil; 2000: 200-2000  $\mu\text{m}$ ; 200: 63-200  $\mu\text{m}$ ; <63: <63  $\mu\text{m}$ .

Fraction	Michle				Sobeslav				IdF				NoF			
	Tot	2000	200	<63	Tot	2000	200	<63	Tot	2000	200	<63	Tot	2000	200	<63
BC (%)	8.1	8.8	13.7	3.1	0.7	0.3	1.1	2.5	1.1	1.0	1.5	0.7	0.6	0.5	0.5	1.1
TOC (%)	10.7	10.9	18.5	6.0	2.3	1.1	3.4	7.4	2.5	1.8	3.2	2.1	2.1	1.2	1.4	3.8

### 3.3. Implication for remediation actions – New treatment strategy

For assessing potential treatment options, a simple BP-separation technique was tested based upon the differences of bulk density and settling velocity. IdF was selected as the model soil due to the high amount of PAHs in its sand fraction and the observation of nearly all BP types. Unfortunately, no selective separation was achieved for the total soil and the fine fraction, but the application of the procedure to various sand fractions allowed the formation of a visible black upper layer representing 10 to 25% of the total height and containing a greater amount of BPs and PAHs (Figure 2.6). Manual separation of the upper layer resulted in the following order of separation effectiveness (*i.e.* ratio between the percentage of PAHs removed and the percentage of soil removed) for the most contaminated fraction: 63-200  $\mu\text{m}$  > 200-2000  $\mu\text{m}$  > 63-2000  $\mu\text{m}$ . For example, the PAH concentration in the upper layer of the 63-200  $\mu\text{m}$  fraction was 9.9 times higher than in the residual fraction. Thus, 76% of PAHs contained in this fraction was recovered, while only 24% of the weight of this soil fraction was removed (separation effectiveness = 3.2).





**Figure 2.6.** PAH recovery and soil weight recovery after the two-step separation procedure, according to granulometric fraction of IdF soil. The PAH concentration in the upper black layer is much higher than in the lower layer.

## 4. Discussion

### 4.1. Characteristics of aged tar oil-contaminated soils and role of black particles in PAH distribution

Various tar-oil-contaminated soils with a wide range of properties were analyzed, including contaminations by raw tar oils (full PAH spectrum) and specific tar oil products or distillates such as creosote, wood impregnation products or middle-distillates. However, these soils are obviously characterized by the absence of free tar oil phases. Only RWTO and wood/coke/coal-like particles were identified, resulting in the accumulation of PAHs in the sand fraction and mostly exclusive association of BPs and PAHs in these aged tar oil-contaminated soils. The nature and amount of BPs in a soil thus strongly depend on the contamination history at the site, leading to impacts on the characteristics of the contamination that are different from what was previously considered. The following discussion aims at explaining these results and emphasizing their implications for remediation actions. Based upon the present results, a new treatment approach for such contaminated soils was proposed and tested.

Tar-oil contaminations are complex because the industrial history of each site is unique. For example, tar oil residues were often dumped in open pits and later solidified with other waste materials present at these sites, e.g. coal powders, coke particles, and ashes [38]. These particles were observed in sand fractions of all contaminated soils studied (Figures 3.1, 3.2 and 3.3). Moreover, the BC/TOC ratios for the Michle (0.76), Sobeslav (0.32), IdF (0.44) and NoF (0.30) soils were high, *i.e.* similar or greater than values observed for fire-impacted soils (0.30 – 0.45) [26]. This is related to the nature of these carbonaceous materials being dumped and spilled.

Tar oil weathering and resinification, leading to solid aggregate formation, is a major phenomenon which must be considered when describing real historically contaminated sites and assessing bioavailable fractions [39]. Pure RWTO particles and various mixed aggregates with native soil organic matter or mineral particles were visualized (Figure 2.1 F and Figure 2.2 B-G). Weathering of tar oil from a NAPL to a solid phase can be attributed to various mechanisms. Luthy et al. [20] were the first to report that short-term experiments with fresh coal tar may not accurately reflect field conditions due to

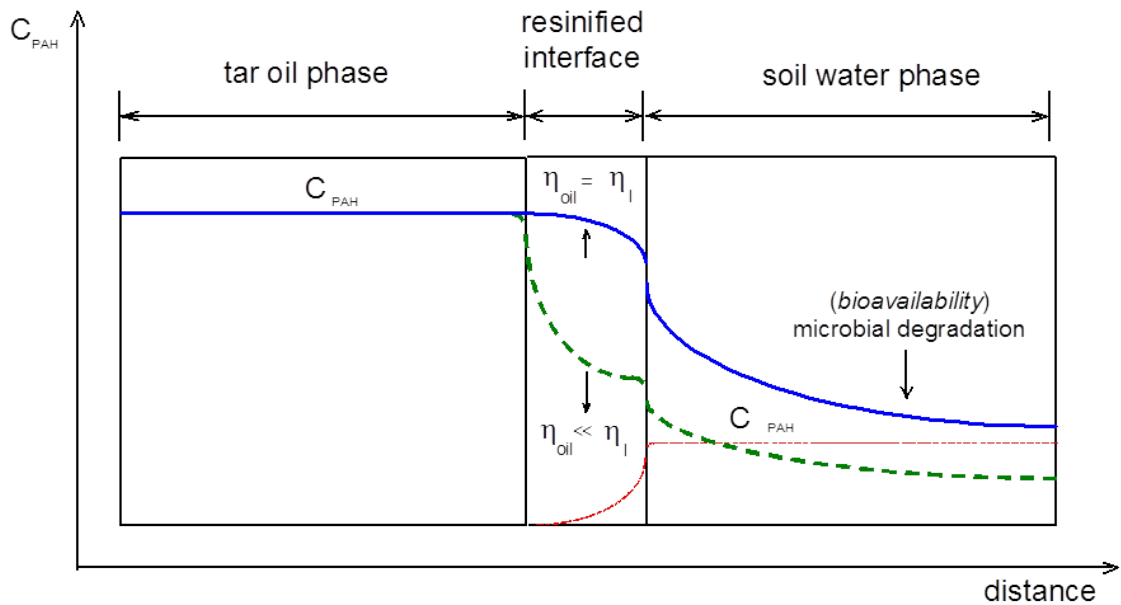
the formation of a viscous film at an undisturbed coal tar oil-water interface after only 3 days. This was identified as an interaction phase, embedding water into amphiphilic molecules of the interface. Interaction between water and tar oil compounds was reported to lead to the formation of highly viscous phase [40]. This formation of solidified films could also result from the adsorption of high molecular weight compounds at the interface, as reported for crude-oil / water systems [20]. However, this process may also be accelerated by enrichment of amphiphilic molecules from soil organic matter (e.g. from microbial lipids) at the oil phase / water interface and polymerization of organic compounds by oxidative coupling [41], finally resulting in resinification of the interface. According to Fick's 1<sup>st</sup> law [40], the diffusion over this rigid interface (Eq. 2 and 3) mostly depends on the viscosity  $h$  of the interface layer, since all the other parameters including the gradient are more-or-less similar.

$$J_{PAH} = \frac{\delta n}{\delta t} = -D \cdot A \cdot \frac{\delta c}{\delta x} \quad (\text{Eq. 2})$$

$$D = \frac{k \cdot T}{6 \cdot \pi \cdot \eta \cdot r_{RWTO}} \quad (\text{Eq. 3})$$

where  $J_{PAH}$  = flux of PAH,  $n$  = amount of PAH;  $t$  = time,  $D$  = diffusion constant,  $A$  = interface area,  $c$  = concentration,  $x$  = thickness of the interface,  $k$  = Boltzmann constant,  $T$  = temperature,  $h$  = viscosity,  $r_{RWTO}$  = radius of RWTO particle.

The following model can describe the mass transfer processes. Interfaces of increasing viscosity result in two mass-transfer-limiting interface layers: one towards the water phase and one towards the oil phase of lower (original) viscosity (Figure 2.7). This leads to PAH concentration shifts at each interface, finally resulting in much lower mass transfer in comparison to an interface of a tar oil drop with homogeneous viscosity. Furthermore, this also results in behavioral differences between externally added PAHs and the aged PAH matrix in experiments with real contaminated sites, e.g. when spiked with radiolabeled PAHs.



**Figure 2.7.** Scheme of the course of PAH concentrations ( $C$ ) from a tar oil phase over the oil-water interface into the surrounding water phase. Upper curve: concentration profile of a tar oil phase with homogeneous viscosity; lower dashed curve: concentration profile from the tar oil over the resinified (solidified) interphase with two mass-transfer interfaces ( $\eta_{oil}$  of the tar oil phase is much lower than  $\eta_I$  of the interfacial layer); dotted line: external mass transfer from the water phase into the tar oil phase with solidified interface.

Increasing extension of the resinified interface towards the center of the oil drop finally results in the formation of (semi-)solid particles with very low mass transfer; this effect was technically applied for caulking wooden ship planks with pine tar oil. At later stages, the depletion in the NAPL of the most soluble and biodegradable compounds may lead to the precipitation of a portion of the coal tar, due to the increase of the mole fraction of barely soluble compounds above their solubility limit [42,43]. This could explain the higher enrichment of heavy PAHs in BPs (Figure 2.4), compared to respective bulk soils, due to their lower solubility limit, in particular in WRT0 [44]. Higher shifts towards heavy PAHs in the PAH pattern distribution would be observed compared to the initial tar oil, since light PAHs are more easily biodegraded [45]. Overall, these processes lead to coal tar ageing and formation of organic particles with a grain size similar to that of sand materials [22]. These particles contain large amounts of PAHs, which are integral to the material and present throughout the interior [32]. This may explain the high PAH

concentrations and behavior observed in BPs and in the sand fraction of tar oil-contaminated soils, where this kind of particles was widely observed. This is also consistent with the analysis of sediments from manufactured gas plant sites, where coal tar pitch appeared to be the dominant partitioning matrix [32].

This study provided evidence that the dominant amount of PAHs in the sand fraction is contained in various BPs. However, it was reported in the literature that mechanisms other than sorption to BPs can also occur, particularly in the fine fraction, in which PAH behavior may also depend on sorption to native soil organic matter [31,46]. For example, Ghosh et al. [31] observed a high fraction of PAHs associated to materials other than BPs only in the fine fraction of several sediments; Talley et al. [45] observed that PAHs in the fine fraction were more (bio)available than PAHs associated to BPs in the sand fraction [45,47], which is consistent with the behavior observed for industrially contaminated sites. The higher surface area of fine particles may also participate in enhancing the (bio)availability of PAHs in the fine fraction.

Different industrial histories of each site studied (wood impregnation, tar oil handling, manufactured gas production) lead to specific trends in contamination characteristics. For example, high PAH concentration was observed in the  $<0.63 \mu\text{m}$  fraction of the Sobeslav soil (Figure 2.5 A). BPs in this soil were mainly identified as wood fragments and wood-like particles (presumably sawdust) with adsorbed tar oils. This results in higher PAH concentrations in the small particle size fraction, due to higher specific surface area. This is also consistent with the lower enrichment factor (2) of the PAH content in BPs manually separated from the sand fraction, compared to the other soils (Figure 2.3). Furthermore, 58% of PAHs of the NoF soil was found in its fine fraction (Figure 2.5 A). In this case, some RWTO particles were observed but only a very low amount of wood/coke/coal-like particles was present. Therefore, these particles were not the only material acting as a sink for PAHs transferred from the tar oil phase; PAHs may have accumulated in the fine fraction due to sorption to native soil organic matter.

The present study highlighted a linear correlation (factor 1) between PAH enrichment factor in the different granulometric fractions of various sites and the respective TOC and BC enrichment factors (Figure 3). The intimate correlation between PAHs, TOC and BC content appears logical: the high BC and TOC values reported for these soils

(Table 2.1) are attributed to the contamination by PAH-containing carbonaceous phases, e.g. tar oil or wood/coke/coal-like particles. By comparison, Li et al. [48] observed better correlation between PAH and BC than between PAH and TOC content within the different granulometric fraction of a soil from a coke oven plant, which may be attributed to specific BC-based partitioning behavior of PAHs arising from soot emissions from combustion processes. The observed outlier point is for the <63  $\mu\text{m}$  fraction of the Michle soil (Figure 2.5 B); the PAH concentration was higher than would be expected from the TOC and BC distribution. Presumably the presence of higher amount of fine coal/coke particles with high specific surface area increased the PAH sorption capacity of this fine fraction much more than in the other soils.

#### 4.2. Implications for remediation actions

$K_{oc}$  values observed in the literature for RWTO particles are usually several orders of magnitude higher than values predicted by the fresh tar-oil / water partitioning model. These observed effects could be explained by the theoretical considerations shown in Figure 2.7. Differences in  $K_{oc}$ , desorption and biodegradation rates of PAHs associated to RWTO particles [31,49] may be attributed to different levels of weathering and resinification. It has also been observed that a high organic compounds / BC ratio could lead to the saturation of BC sorption sites and the formation of a tar-oil layer at the surface of BC materials [50]. Thus, similar resinification processes may also occur at the surface of some coal/coke particles. Furthermore,  $K_{oc}$  values of organic compounds associated to BC particles such as coke or coal particles are also higher than values predicted by the equilibrium between amorphous organic matter and water [26,31,51].

Tar oil ageing thus has critical implications for PAH sequestration and biodegradation effectiveness. Since uptake of organic compounds by microorganisms is assumed to occur mainly via the aqueous phase, the low flux of PAHs from the aged tar oil phase to the aqueous phase becomes the limiting kinetic step for dissolution and biodegradation. Thus, after decades of being dumped in the subsurface, a fraction of the tar oils is biodegraded and non-biodegraded tar oil residues remain associated to RWTO, wood/coke/coal-like materials. These BPs limiting the flux of PAHs into the water phase lead to highly limited biodegradation rates [18], unsatisfactory bioremediation end-

points in terms of target pollutant concentrations, and thus, to the often observed failure of bioremediation attempts. A promising technique is to increase the (bio)availability of sequestered target pollutants by adding solvents or (bio)surfactants. The concentration in the aqueous phase then depends on the relative rates of biodegradation and desorption. However, bioavailability should only be increased with caution: it may increase the potential for exposure to toxic concentrations of PAHs.

Washing processes are reported to lead to the exhaustion of extractable organic compounds from aged coal tar [42]. This could be considered as acceptable remediation end-points since PAH sequestration in BPs also limits their bioaccumulation and uptake in higher organisms [26]. However, the presence of PAHs in an integral way inside resinated particles strongly reduces the efficiency of washing processes since extracting agents mainly act at the particle-water interface [10]. Moreover, Benhabib et al. [35] observed the transfer of highly toxic organic compounds from aged coal tar to water, particularly high molecular weight PAHs and so-called N-S-O compounds such as relatively polar aza-aromatic compounds, thus leading to potential long-term toxicity of these solid coal tar materials.

According to results and discussion provided in the present paper, it is necessary to find improved and new treatment strategies in order to meet requirement objectives based on total PAH concentration. Several studies [31,49,51] showed that flotation in a CsCl solution having a specific gravity of  $1.8 \text{ g cm}^{-3}$  allows the separation of coal tar pitch, coal-like and wood-like particles from sediments. Therefore, we made a first attempt at developing a cost-effective method for the separation of the most contaminated fractions based on density differences of BPs. Using water as the separation medium adds to cost-effectiveness and sustainability. The different settling velocities of sand particles in the IdF soil allowed the formation of a clearly visible black upper layer containing a large amount of BPs (Figure 2.6). The separation effectiveness was improved by reducing the range of particle sizes of the fraction treated (Figure 2.6), mainly because the influence of particle size on the differences of settling velocity was reduced. Thus, low-density particles (*i.e.* BPs) are more easily recovered in the upper fraction. The technique used did not allow selective separation in the  $<63 \text{ }\mu\text{m}$  fraction. This may be due to the greater influence of particle size on settling velocity. Firstly, the fine fraction contained a relatively large range of particle sizes. Secondly, much longer

times were required after stopping the agitation for total sedimentation of the fine fraction (>1 h) compared to the sand fractions (<5 s). Therefore, particle settling occurred under laminar or turbulent conditions for the fine fraction or sand fractions, respectively. In both cases, the settling velocity changes linearly with the difference of the densities, but it changes linearly or with the square of the particle diameter for turbulent or laminar conditions, respectively [52]. The development of such a method would lead to the recovery of three different fractions: (i) sandy non-polluted fraction, (ii) sandy BP-associated contaminated fraction, and (iii) residual contamination in the fine fraction with an expected higher (bio)availability than in the sandy BP-associated fraction [45].

### **4.3. Conclusion**

We provided evidence in the present paper that ageing of the tar oil and the history of contaminations in soils lead to the presence of a highly PAH-contaminated fraction associated to BPs in the sand fraction, which explains the widely recognized low to non-(bio)availability and severe implications for the potential success of remediation attempts. The separation of the sandy-BP associated fraction may be a feasible and suitable step for remediation of aged PAH-tar oil contaminated soils. Specific and adapted disposal of each fraction could then be managed in a more cost-effective way. Presented experiments indicated that an upflow-fluidized-bed reactor might be a promising process for the separation of particles with different physical properties; this is currently under investigation.



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## **CHAPTER 3**

### **COMPARATIVE STUDY ON THE REMOVAL OF HUMIC ACIDS FROM WATER BY ANODIC OXIDATION AND ELECTRO- FENTON PROCESSES: MINERALIZATION EFFICIENCY AND MODELING**

This chapter has been published as:

Trellu C., Pechaud Y., Oturan N., Mousset E., Huguenot D., van Hullebusch E.D., Esposito G., Oturan M.A., 2016. Comparative study on the removal of humic acids from drinking water by anodic oxidation and electro-Fenton processes: mineralization efficiency and modeling. *Applied Catalysis B: Environmental*, 94, 32-41. doi:10.1016/j.apcatb.2016.04.039.

## Abstract

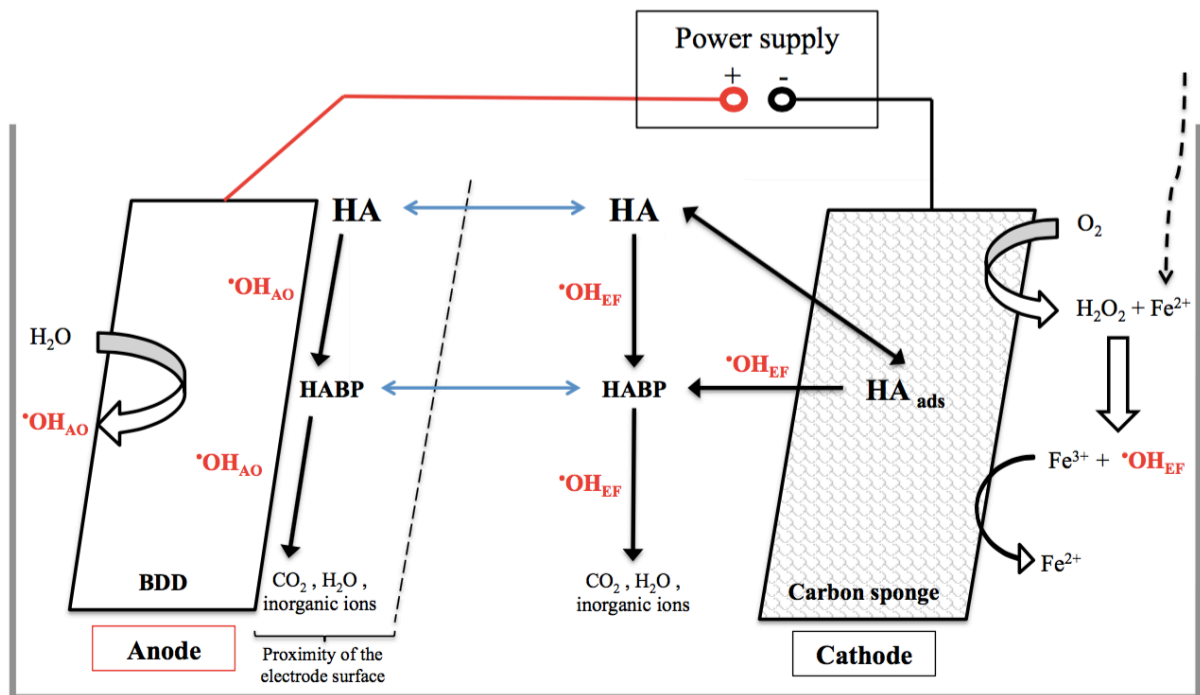
The management of natural organic matter in drinking water treatment plants is an important matter of concern. It can generate toxic disinfection by-products as well as decrease the efficiency of membrane filtration and oxidation processes. This is the first study that investigates the use of anodic oxidation (AO) and electro-Fenton (EF) for the removal of humic acids (HAs) from aqueous solutions. Both sorption and catalytic oxidation of HAs are assessed and discussed. These electrochemical advanced oxidation processes are based on the *in situ* production of hydroxyl radicals, a highly oxidant agent. The EF process involves the use of carbon-based porous materials (carbon sponge) as cathode, leading to the fast adsorption of hydrophobic HAs. It was observed that adsorbed HAs can react with hydroxyl radical produced in the bulk from Fenton's reaction. Then, the release in the solution of more hydrophilic by-products from the oxidation of HAs leads to a rebound effect of the organic matter concentration. Therefore, the AO process using non-carbonaceous cathode materials appears to be more suitable for removal of HAs. Using boron-doped diamond anode and stainless steel cathode, the mineralization efficiency of a HA solution ( $\text{TOC}_0 = 16.2 \text{ mg L}^{-1}$ ) reached more than 99% after 7 h of AO treatment with a current intensity of 1000 mA. By considering both sorption and oxidation processes, this study proposed a new modeling approach to monitor TOC evolution during AO and EF processes.

**Keywords:** Humic acid, Anodic oxidation, Electro-Fenton, BDD anode; Carbon sponge; Adsorption, Modeling.

### Highlights:

- First study on the removal of humic acids from water by electrochemical AOPs
- The main advantage of BDD anode is the complete mineralization of humic acids
- CS cathode is a less suitable cathode material due to adsorption of humic acids
- Adsorbed humic acids are subject to removal by  $\cdot\text{OH}$  produced in electro-Fenton
- Modeling of TOC removal by taking into account sorption and oxidation processes

## Graphical abstract



HA: Humic acid  
HABP: Humic acid by-product

## Electrochemical cell

•OH<sub>EF</sub>: Hydroxyl radical from Fenton's reaction  
•OH<sub>AO</sub>: Hydroxyl radical from anodic oxidation



## 1. Introduction

Humic substances (HSs) are major components of the natural organic matter (NOM) in soil and water. They are complex and heterogeneous mixtures of polydispersed materials formed by biochemical and chemical reactions during humification of plant and microbial remains [1]. The major extractable component of HSs in peat and grassland soils is humic acids (HAs) (70–80%) [2]. They are complex aromatic macromolecules containing phenolic groups, quinone structures, aliphatic compounds, nitrogen and oxygen as bridge units and carboxylic groups variously placed on aromatic rings [1,2].

HSs are non-toxic compounds, but they have a significant influence on selection, design and operation of water treatment processes. The greatest concern is their precursor role in the formation of highly toxic disinfection by-products such as trihalomethanes [3–5]. NOM can be removed from drinking water by several treatment options. The most common and economically feasible process is considered to be coagulation and flocculation followed by decantation and sand filtration [6]. Concentrations of dissolved organic carbon can range from 0.1 mg L<sup>-1</sup> in groundwater to 50 mg L<sup>-1</sup> in bogs [7]. These concentrations depend on the nature of the watershed, but are also strongly influenced by seasonal variations and particulate organic carbon inputs such as runoff or algae bloom [7]. Therefore, the increased requirements in drinking water quality lead to invest additional methods for NOM removal. The following methods can constitute alternative processes: advanced oxidation processes (AOPs) [8,9], ozonation [10], sonolysis [11] or UV-based processes [12]. However, the preferential degradation of hydrophobic organic compounds was observed in many studies. Moreover, incomplete oxidation can lead to increase the potential of formation of disinfection by-products [8].

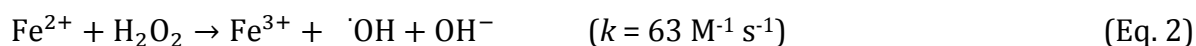
Electrochemical advanced oxidation processes (EAOPs) are new attractive techniques for water treatment [13–20]. They are based on the *in situ* generation of hydroxyl radicals ( $\bullet\text{OH}$ ), the second strongest oxidizing agent known [21]. Their high efficiency for the removal of a large range of persistent organic pollutants (POPs) with complete mineralization to CO<sub>2</sub> has already been shown [22–29]. However, NOM can reduce removal efficiency, due to complexation with POPs as well as  $\bullet\text{OH}$  scavenging [30]. The

management of the NOM is also crucial for the treatment strategy combining EAOPs and membrane processes because it is the main responsible of membrane fouling [31,32].

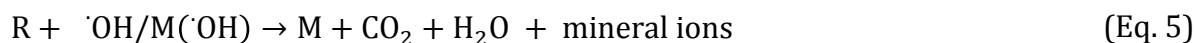
Hydroxyl radicals react with a wide spectrum of NOM of both hydrophobic and hydrophilic character. Rate constants for reactions with NOM have been measured at  $1-5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  [33]. One of the most popular EAOPs is the anodic oxidation (AO) process, where organic compounds directly react with heterogeneous hydroxyl radicals  $\text{M}(\cdot\text{OH})$  [34] formed by oxidation of water at the surface of anodes (M) with high oxygen overpotential [35,36] (Eq. 1). Particularly, boron doped diamond (BDD) anode have very high catalytic activity and allows producing large amount of  $\cdot\text{OH}$ .



The other popular EAOP is the electro-Fenton (EF) process, in which  $\cdot\text{OH}$  are produced homogeneously in the bulk of treated solution from the electrochemically generated Fenton's reagent (mixture of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ ) [37–40] (Eq. 2).  $\text{H}_2\text{O}_2$  is *in situ* electrogenerated at the cathode from the two-electrons reduction of dissolved  $\text{O}_2$  (Eq. 3) [17,40]. A catalytic amount of ferrous iron salt is sufficient to turn up the process, due to the catalytic electro-regeneration of ferrous iron at the cathode (Eq. 4) [41–43].



These homogeneous and heterogeneous  $\cdot\text{OH}$  can then react with the organic matter (R) and oxidize it until ultimate oxidation state is reached, i.e., mineralization (Eq. 5):



To the best of our knowledge, it is the first time that the following processes are studied for the removal of HAs: AO using boron doped diamond (BDD) anode, EF using Platinum (Pt) anode, and EF using BDD anode. Carbon sponge (CS) was used as cathode, since it produces high amount of  $\text{H}_2\text{O}_2$  for the EF process [44]. Stainless steel (SS) and CS were also compared as cathode material for the AO process. Sorption of HAs onto the CS cathode was emphasized and the impact of this phenomenon on the electrocatalytic

oxidation of HAs was assessed. Therefore the goal of this study was (i) to show the ability of EAOPs for total removal of HAs from water (ii) to assess and compare the effectiveness of various EAOPs for the removal of HAs from aqueous solutions (iii) to understand HAs removal mechanisms during EAOPs (iv) to propose a new modeling approach to monitor TOC removal by taking into account both sorption and oxidation processes.

## 2. Material and methods

### 2.1. Chemicals

HAs were purchased from Acros Organics. A purification step was performed as described below. Iron (II) sulphate heptahydrated and sulphuric acid were of reagent grade obtained from Acros Organics. Sodium sulphate was of reagent grade purchased from Sigma Aldrich. Solutions were prepared with ultrapure water from a Millipore Milli-Q system (Molsheim, France) with a resistivity  $>18 \text{ M}\Omega \text{ cm}$ .

### 2.2. Preparation of solutions of HAs

A purification step of commercial HAs was performed, similarly to the protocol of Arai et al. [45]. The stock solution was prepared by dissolving 1 g of commercial HAs in 2 L of Milli-Q water at pH 3. This solution was filtered through Whatman GF/F filter (0.7  $\mu\text{m}$  as pore diameter). Then, HAs were precipitated by decreasing the pH at 1.2 and the solution was centrifuged at 3000 rpm during 20 min. The supernatant was then removed and precipitated HAs were dissolved in deionized water and stocked at pH 3.

### 2.3. Electrochemical treatments

All electrochemical treatments were carried out during 9 h in a 400 mL batch electrochemical cell containing 330 mL of HAs solution at initial TOC concentration of  $16.2 \text{ mg L}^{-1}$  ( $\text{TOC}_0$ ). The anode material was either a plate of Pt ( $14 \text{ cm}^2 \times 0.1 \text{ cm}$ ) from Platecxis (Noisy-le-Sec, France) or a plate made of a thin-film BDD onto a Nb substrate ( $24 \text{ cm}^2 \times 0.2 \text{ cm}$ ) purchased from Condias GmbH (Itzehoe, Germany). The cathode material was a CS ( $24 \text{ cm}^2 \times 1.2 \text{ cm}$ , 60 pores per inch) from Magneto BV Holland (The Netherlands) or a SS plate ( $24 \text{ cm}^2 \times 0.2 \text{ cm}$ ) from Goodfellow (France). Electrodes were set up with a gap of 3 cm between the anode and the cathode. The constant current intensity was provided by a power supply (HAMEG, Germany (model 7042-5)). Air was continuously bubbled inside the solution through a glass frit in order to keep enough dissolved oxygen in the solution for the hydrogen peroxide production at the cathode

(Eq. 3). A magnetic stirrer ensured the homogenization of the solution in the electrochemical cell. Similarly to optimal experimental conditions determined by Özcan et al. [44], a suitable amount of electrolyte was dissolved in the solution ( $\text{Na}_2\text{SO}_4$  at 0.05 M) and pH was adjusted at 3.0 with 1 M  $\text{H}_2\text{SO}_4$ . For the EF process, an optimal concentration of 0.1 mM  $\text{Fe}^{2+}$  (under the form of ferrous sulphate heptahydrated) was added [44]. According to the electrochemical cell configuration, processes were denoted as AO-SS (BDD anode, SS cathode), AO-CS (BDD anode, CS cathode), EF-Pt (Pt anode, CS cathode, 0.1 mM  $\text{Fe}^{2+}$ ) and EF-BDD (BDD anode, CS cathode, 0.1 mM  $\text{Fe}^{2+}$ ).

#### 2.4. Analytical procedures

Due to the complexity of the HA mixture, organic matter content concentration was determined by a global parameter, i.e. the total organic carbon (TOC) content of the solution ( $\text{TOC}_{\text{sol}}$ ), in  $\text{mg L}^{-1}$ . Samples (3.5 mL) were collected at 8 or 9 different time points during the electrolysis. TOC was measured by using a Shimadzu TOC-V analyzer. Potassium hydrogen phthalate (99.5%, Merck) was used for the calibration.

For the analytic determination of organics adsorbed onto the CS cathode ( $\text{TOC}_{\text{ads}}$ ), the treated solution was removed from the electrochemical cell. Then, 330 mL of NaOH at 0.1 M was used for desorption of HAs from the cathode, similarly to the extraction method of HAs from soil [46]. After 15 min of continuous stirring, a sample was analyzed after inorganic carbon removal from the solution by decreasing the pH at 3 and purging the sample with  $\text{O}_2$  gas. Values were given in  $\text{mg L}^{-1}$ , based on the amount of carbon adsorbed on the cathode compared to the volume of the solution treated. Therefore, the total TOC ( $\text{TOC}_{\text{tot}}$ ) in the solution was deduced as  $\text{TOC}_{\text{tot}} = \text{TOC}_{\text{sol}} + \text{TOC}_{\text{ads}}$ .

The evolution of the UV spectrum of the solution and compounds adsorbed onto the cathode was analyzed by using a Perkin Elmer Lambda 10 UV/VIS. Absorbance values were given in unit absorbance (UA).

Generated carboxylic acids were monitored by ion-exclusion HPLC, as detailed by Olvera-Vargas et al. [47].

Iron concentration was analyzed using a Perkin Elmer Optima 8300 ion coupled plasma optical emission spectrometer (ICP-OES). Some samples were analyzed after filtration through 0.7  $\mu\text{m}$  glass fiber filters, while the total iron concentration was analyzed after mineralization of samples by addition of hydrogen peroxide and nitric acid in a water bath (95°C).

## 2.5. Mathematical modeling

A model was developed in order to monitor the evolution of TOC in the solution during various EAOPs. The software Aquasim was used [48]. Both sorption and oxidation processes were considered.

First, it was assumed that organics degradation in the electrochemical cell originates only from reaction with  $\cdot\text{OH}$  (either  $\cdot\text{OH}$  from homogeneous catalysis during EF or  $\text{M}(\cdot\text{OH})$  from heterogeneous catalysis at the surface of BDD anode), a strong oxidizing agent and non-selective reagent with a standard reduction potential of  $E^\circ(\cdot\text{OH}/\text{H}_2\text{O}) = 2.8 \text{ V/SHE}$  [21].

Then, the use of the highly porous CS cathode led to the adsorption of HAs onto its surface. The kinetics of sorption from a solution onto an adsorbent was well explored by Azizian [49]. The author showed that the sorption process obeys the pseudo-second-order model, provided that the initial concentration of solute is not too high compared to the active surface area of the sorbent material (Eq. 6),

$$\frac{dq}{dt} = k(q_e - q)^2 \quad (\text{Eq. 6})$$

where  $q$  and  $q_e$  are the milligrams of HAs sorbed per gram of sorbent at any time and equilibrium, respectively, and  $k$  is the pseudo-second-order rate constant of sorption. One can also rewrite Eq. 6 as follows,

$$\frac{d[\text{HA}_{\text{ads}}]}{dt} = k'([\text{HA}_{\text{ads}}]_{\text{eq}} - [\text{HA}_{\text{ads}}])^2 \quad (\text{Eq. 7})$$

where  $k'$  is the observed pseudo-second-order rate constant ( $(\text{mg L}^{-1})^{-1} \text{h}^{-1}$ ) and  $[\text{HA}_{\text{ads}}]$  and  $[\text{HA}_{\text{ads}}]_{\text{eq}}$  are the milligrams of carbon of HAs sorbed per litre of solution ( $\text{mg L}^{-1}$ ) at any time and equilibrium, respectively; i.e.,

$$[\text{HA}_{\text{ads}}] = q \frac{m_c}{V_{\text{sol}}} \eta \quad (\text{Eq. 8})$$

where  $m_c$  is the mass of sorbent (g),  $V_{\text{sol}}$  (L) is the volume of the solution and  $\eta$  is the mass fraction of carbon in HA molecules.

Azizian [49] also reported that the pseudo-second-order rate constant of sorption is a function of the initial concentration of solute. During electrolysis, oxidation of organics modifies the total HAs concentration. Thus, it was proposed to express  $k'$  as a simple function of the total HA concentration, as follows,

$$k' = k_{\text{ads}}[\text{HA}]_{\text{tot}} \quad (\text{Eq. 9})$$

where  $[\text{HA}]_{\text{tot}}$  is the sum of  $[\text{HA}_{\text{ads}}]$  and HA concentration in the bulk ( $[\text{HA}_{\text{sol}}]$ ), and  $k_{\text{ads}}$  is the fitting parameter for the model ( $\text{h}^{-1}$ ).

Therefore, the following Eq. 10 is the general equation for the sorption process of HAs onto the CS cathode during the electrolysis,

$$\frac{d[\text{HA}_{\text{ads}}]}{dt} = k_{\text{ads}}[\text{HA}]_{\text{tot}}([\text{HA}_{\text{ads}}]_{\text{eq}} - [\text{HA}_{\text{ads}}])^2 \quad (\text{Eq. 10})$$

Additional assumptions took into consideration for the model are discussed in the 'results and discussion' part, according to the experimental results observed.

Calibration of the model was performed by adjusting unknown parameters until the model outputs adequately fit the experimental observations. Three methods were used for the comparison of model results with experimental measurements, the Root Mean Square Error (RMSE) (Eq. 11), the Modeling Efficiency (ME) (Eq. 12) and the Index of Agreement (IoA) (Eq. 13) [50–52]. Unknown parameters were determined by optimizing these three criteria.

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^K (y_i - y'_i)^2}{K}} \quad (\text{Eq. 11})$$

$$\text{ME} = 1 - \frac{\sum_{i=1}^K (y_i - y'_i)^2}{\sum_{i=1}^K (y_i - y_M)^2} \quad (\text{Eq. 12})$$

$$\text{IoA} = 1 - \frac{\sum_{i=1}^K (y_i - y'_i)^2}{\sum_{i=1}^K (|y'_i - y_M| + |y_i - y_M|)^2} \quad (\text{Eq. 13})$$

where  $K$  is the number of observed values,  $y_i$  is the single numerically simulated value,  $y'_i$  is the corresponding experimentally observed value,  $y_M$  is the average of the numerically simulated values.



## 3. Results and discussion

### 3.1. Removal of humic acids during AO-CS and AO-SS processes

#### 3.1.1. Experimental results

The TOC evolution during the AO-SS process according to the current supply intensity is reported in Figure 3.1. More than 99% of TOC removal was reached after 7 h of treatment at 1000 mA. No significant adsorption of HAs (< 2%) was observed onto the SS cathode. Mineralization kinetics were well fitted ( $R^2 > 0.99$ ) with the pseudo-first-order model (Eq. 14) (Figure 3.1). This is in accordance with Panizza et al. [25]: when the applied current is high or the concentration of the organics is low, organics electrolysis by  $\cdot\text{OH}$  formed at the surface of the anode (BDD( $\cdot\text{OH}$ )) is under mass-transport control [28,36]. Additionally, the decrease of the current intensity from 1000 to 600 and 300 mA reduced pseudo-first order constant by 2.1 and 4.1, respectively. This is attributed to the lower production of  $\cdot\text{OH}$  at the surface of the BDD anode.

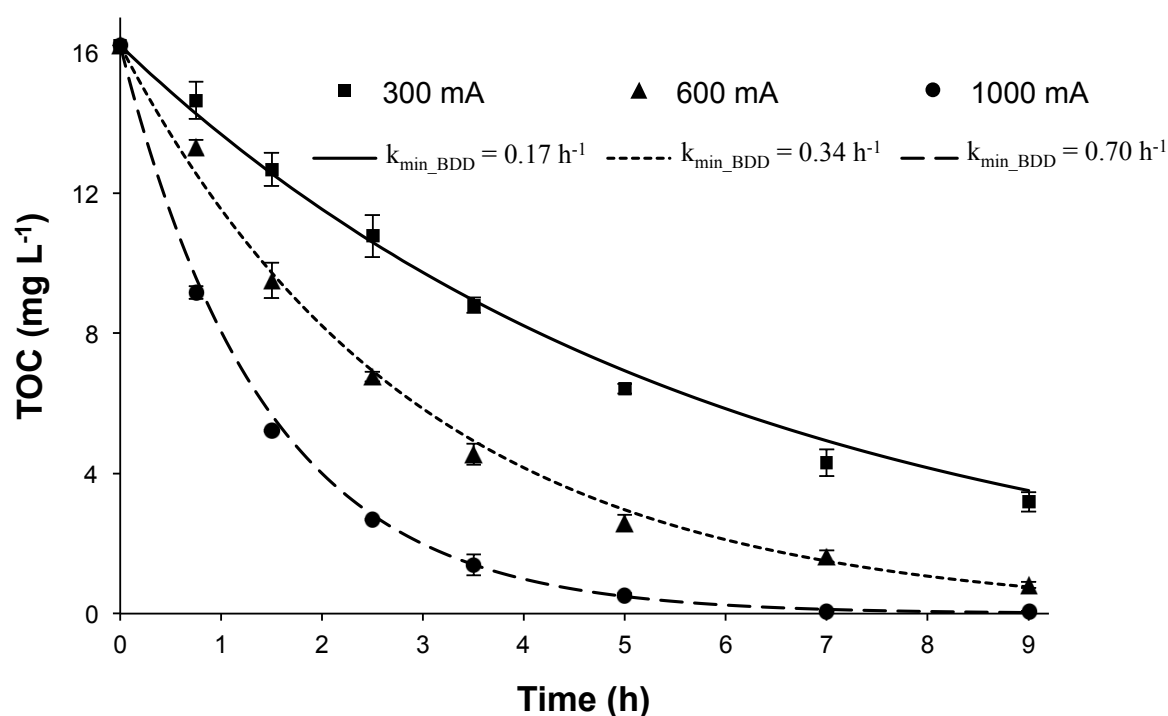
$$\frac{d[\text{TOC}]}{dt} = -k_{min\_BDD}[\text{TOC}] \quad (\text{Eq. 14})$$

$k_{min\_BDD}$  being the pseudo first-order rate constant of HAs mineralization at the surface of the BDD anode ( $\text{h}^{-1}$ ).

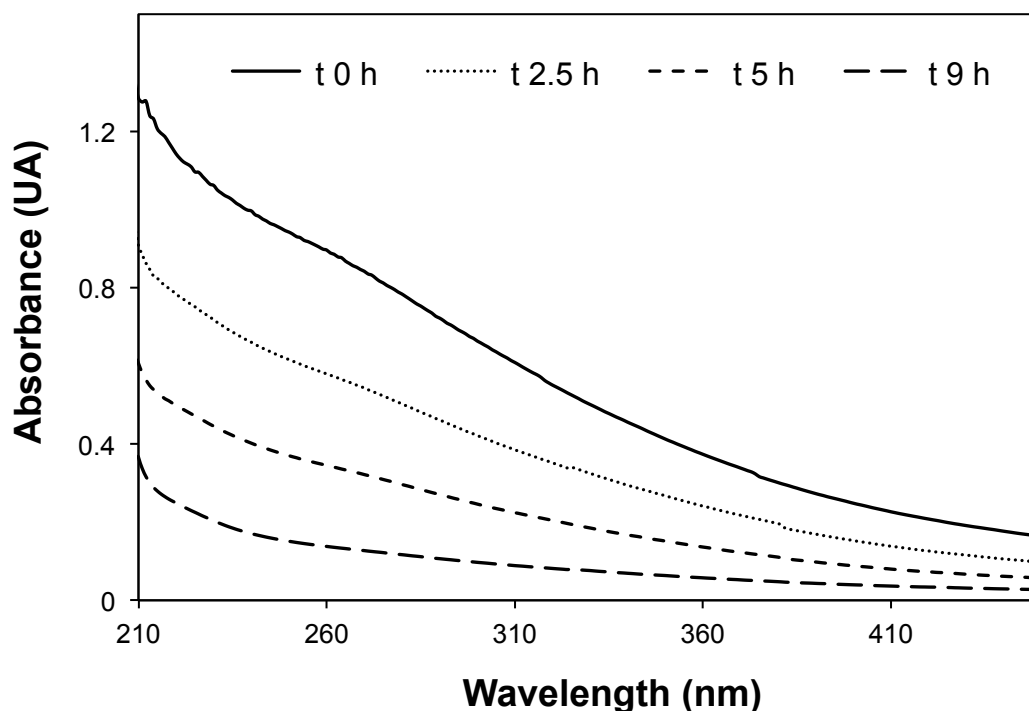
Higher TOC removal was reached with the AO-BDD process using SS cathode, compared to all other AOPs already investigated for NOM removal from water. For example, Fenton's reaction based process, ozone based process and photocatalysis achieved maximum TOC removal in the range 60–85% [53–55]. There is not any data available in the literature about removal of HAs by EAOPs to compare with.

Interestingly, no change in the UV spectrum of the solution during the treatment by AO-SS was observed (Figure 3.2). Moreover, short chain carboxylic acids were not detected by ion exclusion chromatography (*i.e.* concentrations were below 0.01 mM) during the treatment at 1000 mA. Additional analysis such as Fourier transform infrared spectroscopy would be required to verify that oxidation by-products were not accumulated in the bulk. However, this indicates complete mineralization of organics to  $\text{CO}_2$  at the anode surface without accumulation of oxidation by-products in the bulk. This

is consistent with theoretical considerations: the high oxygen overpotential of BDD allows the formation of  $\cdot\text{OH}$  or physisorbed “active oxygen” at the surface of the anode (BDD( $\cdot\text{OH}$ )). This assists the nonselective oxidation of organics and their complete combustion to  $\text{CO}_2$  [44,56,57]. Therefore, AO process appears as one of the most effective technique for the complete mineralization of HAs and production of organic free water. In this lab-scale configuration, the energy consumption used to reach 50% TOC removal was calculated as 2.7, 3.9 and 4.7  $\text{kWh (g TOC)}^{-1}$ , respectively, at 300, 600 and 1000 mA, respectively. The higher energy consumption for high current intensity comes from the increase of secondary reactions (such as  $\text{H}_2$  (cathode) and  $\text{O}_2$  (anode) evolution), resulting in the decrease of the current efficiency.

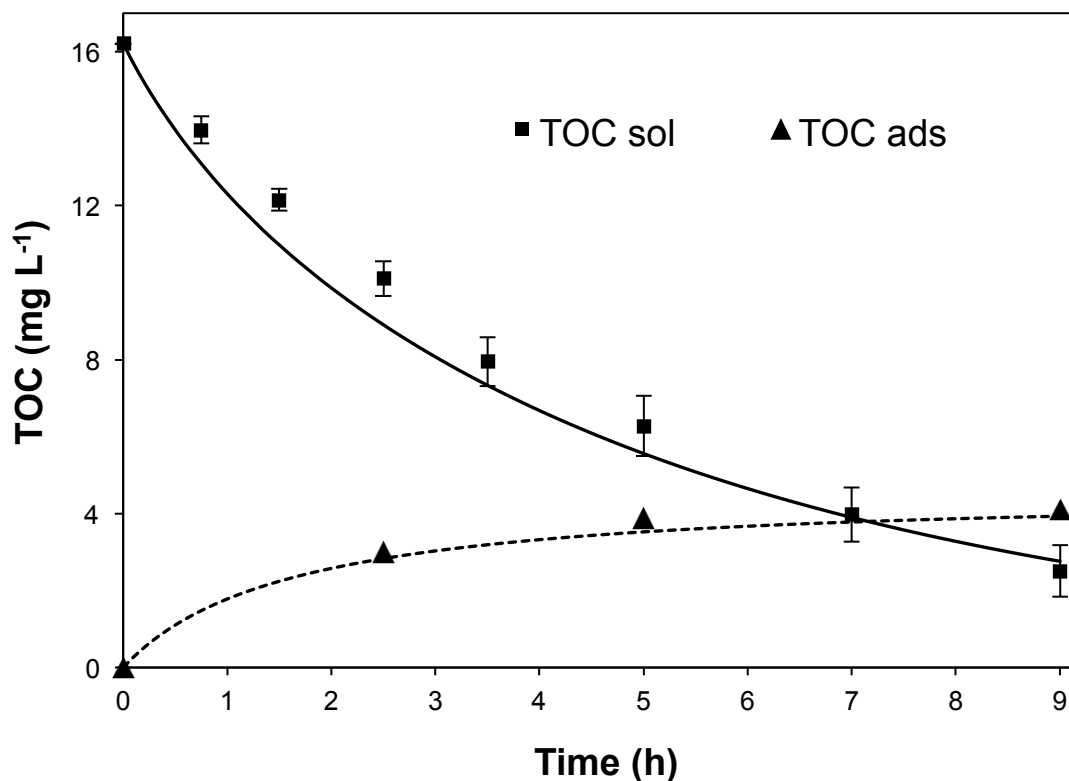


**Figure 3.1.** Evolution of  $\text{TOC}_{\text{sol}}$  during the electrolysis of HAs ( $\text{TOC}_0 = 16.2 \text{ mg L}^{-1}$ ) in  $0.05 \text{ M Na}_2\text{SO}_4$  solution by the AO-SS process according to the current intensity applied (300 – 600 – 1000 mA). Error bars refer to triplicate experiments. Lines report model results.



**Figure 3.2.** Evolution of the UV spectrum of HAs ( $TOC_0 = 16.2 \text{ mg L}^{-1}$ ) in  $0.05 \text{ M Na}_2\text{SO}_4$  solution during the treatment by the AO-SS process at  $300 \text{ mA}$ .

The evolution of  $TOC_{\text{sol}}$  and  $TOC_{\text{ads}}$  during the AO-CS process at  $300 \text{ mA}$  is reported in Figure 3.3. Much lower efficiency was observed for the AO-CS process (59%  $TOC_{\text{tot}}$  removal after 9 h of treatment), compared to the AO-SS process (80%  $TOC_{\text{tot}}$  removal after 9 h treatment). This is explained by the adsorption of organic compounds onto the porous CS cathode as it is shown by the continuous increase of  $TOC_{\text{ads}}$ . This adsorption phenomenon depends on both organic compounds and electrode material characteristics and should be always assessed in electrochemical processes using carbonaceous materials. Besides, there was not any significant decrease of  $TOC_{\text{ads}}$  during the experiment. Hydroxyl radicals produced at the surface of the BDD anode have very short lifetime, in the range of few nanoseconds. Thus, they cannot react with organics adsorbed onto the CS cathode because their lifetime is too short to reach the cathode.



**Figure 3.3.** Evolution of  $TOC_{sol}$  and  $TOC_{ads}$  during the electrolysis of HAs ( $TOC_0 = 16.2 \text{ mg L}^{-1}$ ) in  $0.05 \text{ M Na}_2\text{SO}_4$  solution by the AO-CS process at  $300 \text{ mA}$ . Symbols report experimental results. Error bars refer to triplicate experiments. Lines report model results.

### 3.1.2. Mathematical modeling

Based on these experimental observations, the proposed model considered only mineralization of HAs in the bulk (Eq. 14) and sorption of HAs onto the CS cathode (Eq. 10). Production of HA oxidation by-products (HABPs) was neglected. Therefore, it was assumed that  $[HA_{ads}] = TOC_{ads}$  and  $[HA_{tot}] = TOC_{tot}$ .

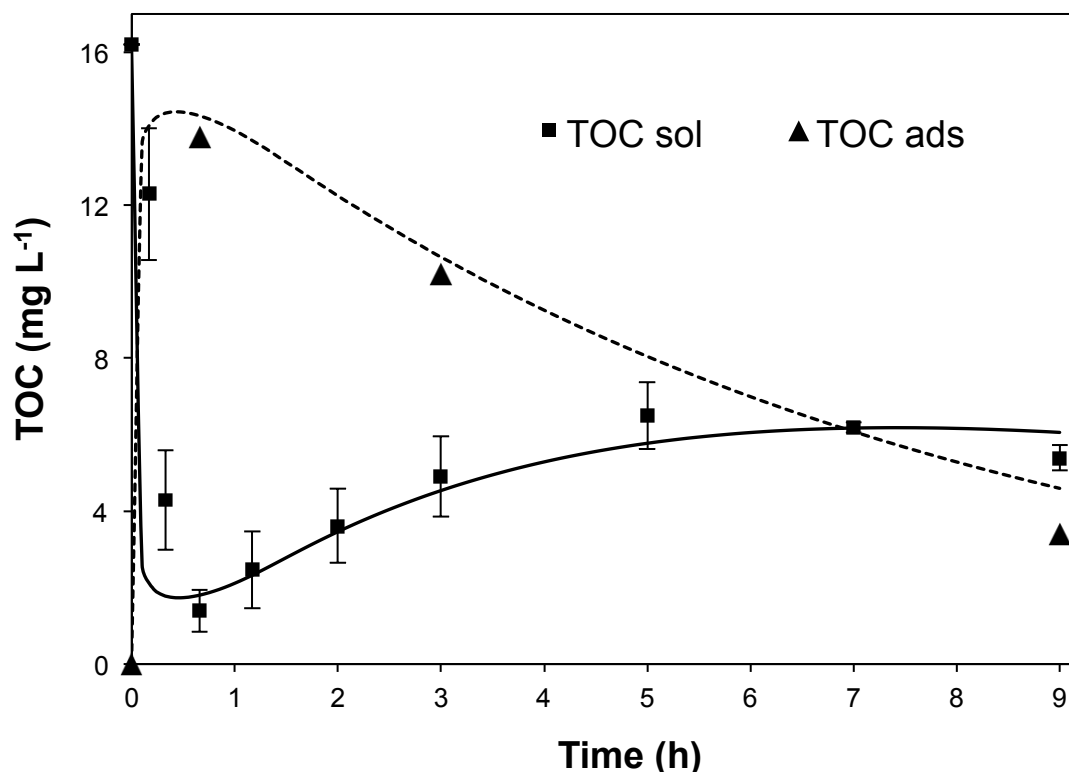
Besides, none apparent desorption of HAs was observed during the time range of these experiments, due the strong hydrophobic interactions between HAs and the surface of the CS.  $[HA_{ads}]_{eq}$  was determined by using similar experimental conditions, but without current supply in order to avoid oxidation of organics. With  $[HA]_0 = TOC_0 = 16.2 \text{ mgC L}^{-1}$ , the equilibrium was reached after 1 day with  $[HA_{ads}]_{eq} = TOC_{ads\_eq} = 6.0 \text{ mg L}^{-1}$ . Besides,

it was observed during electrolysis experiments that the adsorption kinetic (parameter  $k_{ads}$ ) was strongly increased when current intensity is supplied. This indicates that electrostatic interactions increase adsorption kinetics. Therefore, it was not possible to fit the parameter  $k_{ads}$  in a separate experiment as oxidation of HAs occurs when current intensity is supplied.

## 3.2. Removal of humic acids during EF-Pt and EF-BDD processes

### 3.2.1. Experimental results

The evolution of  $TOC_{sol}$  and  $TOC_{ads}$  during the EF-Pt process at 300 mA is depicted in Figure 3.4. A fast decrease of  $TOC_{sol}$  was observed during the first 40 min of the treatment. Simultaneously, more than 85% of the initial TOC adsorbed onto the CS cathode. The enhancement of the adsorption process could be ascribed to the formation of a complex between HAs and iron ions, leading to charge neutralization of HAs. This was confirmed by iron analysis during the EF-Pt process. After 15 min of treatment, 45% of the iron in the solution was in the fraction  $>0.7 \mu m$ . This indicates the formation of macro complex between iron and HAs. Then, this ratio continuously decreased and reached 26% after 7 h of treatment. This can be attributed to the lower affinity between HABPs and iron ions, leading to a lower formation of complex.

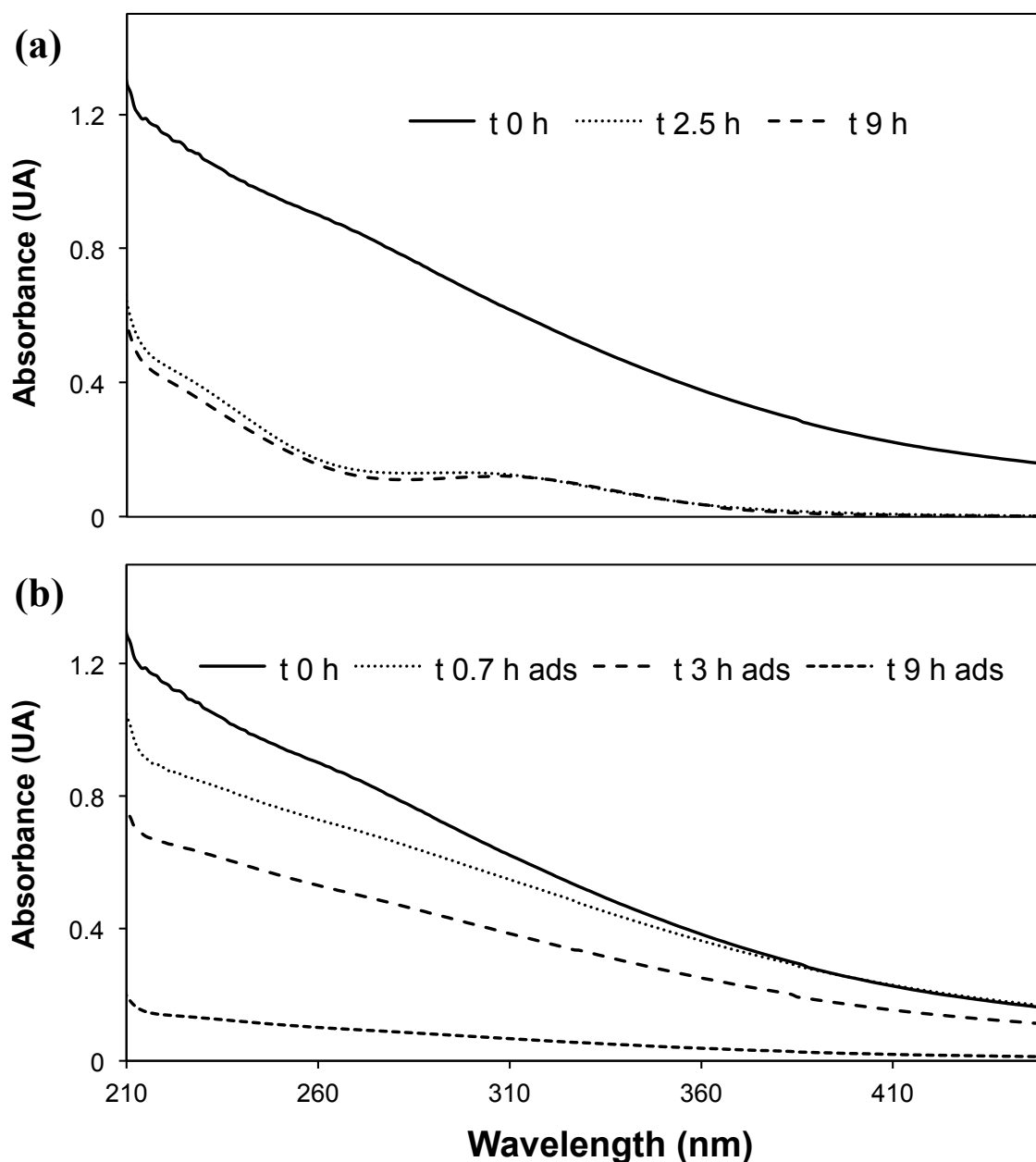


**Figure 3.4.** Evolution of  $TOC_{sol}$  and  $TOC_{ads}$  during the electrolysis of HAS ( $TOC_0 = 16.2 \text{ mg L}^{-1}$ ) in  $0.05 \text{ M Na}_2\text{SO}_4$  solution by the EF-Pt process at  $300 \text{ mA}$  ( $0.1 \text{ mM Fe}^{2+}$ ). Symbols report experimental results. Error bars refer to triplicate experiments. Lines report model results.

In contrast to the AO process,  $TOC_{ads}$  decreased from 85% to 22% of the initial TOC ( $TOC_0$ ) between 0.7 h and 9 h when performing the EF-Pt process. This is explained by the availability of adsorbed organics to oxidation by  $\cdot\text{OH}$  produced homogeneously in the bulk from Fenton's reaction (Eq. 2). The main pathway for degradation of aromatic organic compounds by  $\cdot\text{OH}$  is hydroxylation (electrophilic addition) to non-saturated bond or H atom abstraction followed by further oxidation [40,43]. This allows the conversion of HAs into more polar by-products that have low interaction with the CS cathode. Sanly et al. [58] already showed the fragmentation of the hydrophobic fraction of HAs into hydrophilic and slightly hydrophilic compounds during the Fenton process. Therefore, the increase in  $TOC_{sol}$  from 8% to 40% of the initial TOC ( $TOC_0$ ) between 0.7 and 5 h of treatment is ascribed to the accumulation of HABPs in the solution. This is in accordance with the change in the shape of the UV spectrum of the solution during the

EF treatment. Particularly, a decrease of the absorbance between 250 nm and 300 nm was observed. This is typical of breaking of aromatic rings and indicates the presence of more hydrophilic organic compounds in the solution. Similar mechanism and rebound effect was observed during the homogeneous photocatalysis ( $\text{TiO}_2/\text{UV}$ ) process, due to the initial fast adsorption of HAs onto  $\text{TiO}_2$  particles [54].

On the contrary, it was not observed any significant change in the shape of the UV spectrum of compounds adsorbed onto the CS cathode, compared to the one of the initial solution of HAs. This denotes that compounds adsorbed onto the CS cathode can be characterized as low or non-degraded HAs.



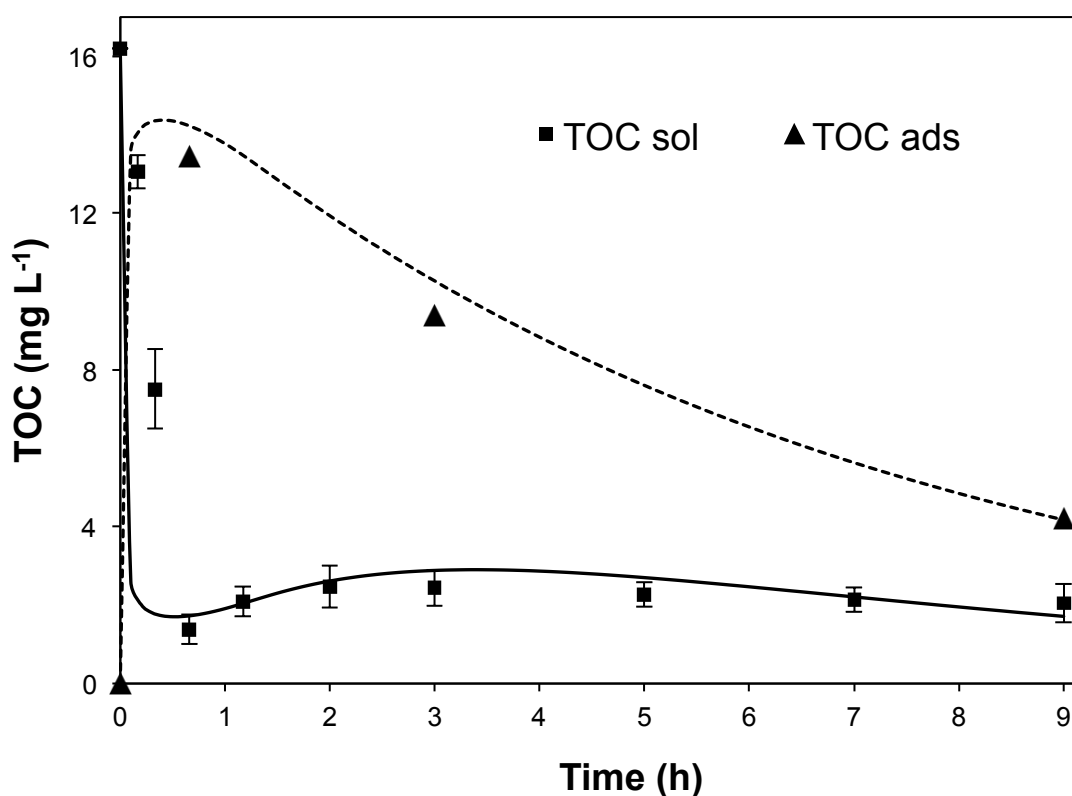
**Figure 3.5.** Evolution of the UV spectrum of organic compounds in the solution (a) and adsorbed onto the carbon sponge cathode (b) during the treatment of HAs ( $TOC_0 = 16.2 \text{ mg L}^{-1}$ ) in  $0.05 \text{ M Na}_2\text{SO}_4$  solution by the EF-BDD process at  $300 \text{ mA}$  ( $0.1 \text{ mM Fe}^{2+}$ ).

The evolution of  $TOC_{\text{ads}}$  and  $TOC_{\text{sol}}$  during the EF-BDD process is reported in Figure 3.6. Similar removal of  $TOC_{\text{ads}}$  was observed during EF-BDD and EF-Pt processes between 0.7 and 9 h of treatment. This indicates a similar bulk production of  $\cdot\text{OH}$  in both processes. This is in accordance with results observed during the AO process with CS



cathode, which showed that heterogeneous hydroxyl radicals ( $\text{BDD}(\cdot\text{OH})$ ) produced at the surface of the BDD anode cannot contribute to the oxidation of organic compounds adsorbed onto the CS cathode.

After the fast adsorption of HAs, TOC evolution in the solution depends on accumulation of HABPs in the bulk due to oxidation of adsorbed HAs, as well as mineralization of these by-products to  $\text{CO}_2$ . Thus, the rebound effect of  $\text{TOC}_{\text{sol}}$  during the EF-Pt process is ascribed to a higher oxidation rate of adsorbed HAs compared to the mineralization rate of HABPs. In contrast, the use of the BDD anode (EF-BDD process) instead of the Pt anode led to a much lower rebound effect (Figure 3.6). This is due to the accumulation of  $\text{BDD}(\cdot\text{OH})$  at the surface of the anode, thus promoting mineralization of HABPs.



**Figure 3.6.** Evolution of  $\text{TOC}_{\text{sol}}$  and  $\text{TOC}_{\text{ads}}$  during the electrolysis of HAs solution ( $\text{TOC}_0 = 16.2 \text{ mg L}^{-1}$ ) by EF-BDD process at 300 mA ( $0.05 \text{ M Na}_2\text{SO}_4$ ;  $0.1 \text{ mM Fe}^{2+}$ ). Symbols report experimental results. Error bars refer to triplicate experiments. Lines report model results.

### 3.2.2. Mathematical modeling

In contrast to the AO process, experimental observations led to take into consideration two different types of organic compounds: low or non-degraded HAs ( $HA_{Hob}$ ) that can adsorb onto the CS cathode ( $HA_{Hob\_ads}$ ) and more hydrophilic HABPs without interaction with the CS cathode. Thus, the following conclusions were drawn:

$$[HA_{ads}] = [HA_{Hob\_ads}] = TOC_{ads},$$

$$[HA_{tot}] = [HA_{Hob}] + TOC_{ads},$$

$$TOC_{sol} = [HA_{Hob}] + [HABP].$$

The fast adsorption of a large amount of humic acids during the first 45 minutes of the process led to assume that  $[HA_{Hob\_ads}]_{eq}$  is the initial concentration of HAs and  $[HA_{Hob}]_{eq}$  is  $0.0 \text{ mg L}^{-1}$ . This was coherent with the strong hydrophobic interactions between HAs and the CS cathode as well as with the following phenomenon. Charge neutralization of HAs and macro complex formation coming from the addition of iron salts increase the potential of adsorption of HAs onto the CS cathode. In fact, the porosity of the CS electrode (60 pores per inch) allows considering that the specific surface area of the sum of macro complex of HAs is much lower than the specific surface area of the CS cathode available for adsorption.

As regards to the modeling of oxidation mechanisms, pseudo-first-order reactions were considered for the kinetic model of organics degradation, in accordance with most of literature results investigating the degradation of organic compounds by the EF process [40]. It was also assumed that oxidation of  $HA_{Hob\_ads}$  led to the direct release of HABPs into the solution. Processes considered in the model are summarized in the following Petersen matrix (Table 3.1).

**Table 3.1.** Petersen matrix of processes taken into account for modeling the evolution of  $TOC_{sol}$  and  $TOC_{ads}$  during the treatment of HAs solution by EF-Pt and EF-BDD processes.

Process	$HA_{Hob}$	$HA_{Hob\_ads}$ (= $TOC_{ads}$ )	HABPs	Min. prod.*	Reaction rate ( $mg\ L^{-1}\ h^{-1}$ )
$HA_{Hob}$ adsorption onto CS cathode	-1	1			$k_{ads} ([HA_{Hob}] + TOC_{ads}) (TOC_{ads\_eq} - TOC_{ads})^2$
$HA_{Hob}$ conversion into HABPs	-1		1		$k_{HA} [HA_{Hob}]$
$HA_{Hob\_ads}$ conversion into HABPs		-1	1		$k_{HA\_ads} TOC_{ads}$
HABPs mineralization			-1	1	$k_{HABP} [HABP]$

\* Mineralization products ( $CO_2$ ,  $H_2O$ , inorganic ions)

### 3.3. Discussion about the model

Calibrated parameters were determined in order to minimize RMSE and optimize ME and IoA. Moreover, a logical approach based on experimental observations and theoretical considerations was followed for the estimation of parameters.

Mineralization rate ( $k_{min\_BDD}$ ) during AO oxidation was estimated by results observed with the SS cathode, for which adsorption did not occur. Then, a similar  $k_{min\_BDD}$  was chosen for the AO-CS process since removal of organic compounds during AO occurs mainly through heterogeneous catalysis at the surface of the BDD anode, regardless to the cathode material used. Oxidation of HAs by  $H_2O_2$  produced at the CS cathode was neglected, in accordance with its lower standard reduction potential ( $1.763\ E^\circ/V$  vs SHE) compared to  $\bullet OH$  ( $2.80\ E^\circ/V$  vs SHE). Since the adsorption kinetic of HAs depends on current intensity, the parameter  $k_{ads}$  was estimated according to experimental results obtained during electrolysis.

Oxidation parameters during the EF process were determined by taking into consideration a similar  $k_{HA\_ads} / k_{HA}$  for the EF-Pt process and  $k_{HA\_ads}$  for the EF-BDD

process since these parameters are only related to homogeneous catalysis from Fenton's reaction, with a low influence from the anode material. Moreover, higher  $k_{HABP}$  and  $k_{HA}$  were chosen for the EF-BDD process compared to the EF-Pt process due to the additional generation of BDD( $\cdot$ OH) by heterogeneous catalysis. Finally, adsorption parameters during the EF process were fitted according to experimental results obtained during electrolysis.

These values are all reported in Tables 3.2 and 3.3. Good correlation was observed between experimental results and model outputs, indicating the relevance of the modeling approach proposed in this chapter.

**Table 3.2.** Calibration of model parameters.

<b>Process</b> ( $I=300\text{mA}$ )	$k_{\text{min\_BDD}}$ ( $\text{h}^{-1}$ )	$k_{\text{ads}}$ ( $\text{h}^{-1}$ )	$k_{\text{HA}}$ ( $\text{h}^{-1}$ )	$k_{\text{HA\_ads}}$ ( $\text{h}^{-1}$ )	$k_{\text{HABP}}$ ( $\text{h}^{-1}$ )
AO-SS	0.17	0			
AO-CS	0.16	0.005			
EF-Pt		0.8	0.14	0.14	0.13
EF-BDD	-	0.8	0.24	0.15	0.50

**Table 3.3.** Comparison of model outputs with experimental measurements (Root Mean Square Error, Model Efficiency and Index of Agreement methods).

Process ( $I=300$ mA)	RMSE		ME		IoA	
	TOC sol	TOC ads	TOC sol	TOC ads	TOC sol	TOC ads
AO-SS	0.366	-	0.993	-	0.998	-
AO-CS	0.752	0.216	0.973	0.982	0.993	0.996
EF-Pt	3.69	0.345	0.336	0.996	0.847	0.999
EF-BDD	4.36	0.457	0.191	0.992	0.832	0.998

As regards to the sorption process, the predetermined value of  $[HA]_{ads,eq}$  for the AO-CS process allowed a good fitting with the evolution of  $TOC_{ads}$ . The proposed sorption model also fitted well with the low  $TOC_{sol}$  and high  $TOC_{ads}$  concentration reached after 40 min of treatment during the EF-Pt and EF-BDD processes. However, high RMSE as well as low ME and IoA values were calculated for the evolution of  $TOC_{sol}$  during EF-Pt and EF-BDD processes. This is due to the overestimation of the kinetic of  $TOC_{sol}$  decrease during the first 40 min of the treatment. Without taking into account experimental points at  $t = 0.17$  h and  $t = 0.33$  h, ME values are greatly improved for EF-Pt and EF-BDD (0.994 and 0.997, respectively). Interestingly, the use of a lower  $k_{ads}$  parameter did not improve the global model quality. It led to an underestimation of the adsorption rate of HAs, since a greater amount of HAs is degraded (formation of HABPs) before to be adsorbed. Therefore, the experimental results could only be explained by considering additional mass transfer limitations. Particularly, this could be related to a diffusion/convection mechanism corresponding to the time necessary for the solution to fully penetrate into the porous CS cathode. In fact, the real CS surface available for adsorption of HAs and  $H_2O_2$  production is progressively increasing during the beginning of the process. Further investigations and experimental results would be necessary for the calibration of this process.

Previous models were developed for EAOPs in order to monitor the degradation of single model organic compounds such as phenol [39] by following the generation of oxidation by-products until total mineralization. However, in a complex mixture of organic compounds such as HAs, alternative model based on global parameters (TOC, chemical oxygen demand) are required. Moreover, it is the first time that sorption processes are taken into consideration for the modelling of TOC removal during EAOPs. The next step would be to combine this model with previous research works modeling the generation and the role of  $\cdot\text{OH}$  according to operating conditions [25,59–61].

## 4. Conclusions

This paper reported for the first time the removal of HAs by various EAOPs. Here are the following main results and conclusions drawn from results obtained:

- More than 99% of TOC of initial solution ( $16.2 \text{ mg L}^{-1}$ ) was removed after 7 h of treatment at 1000 mA using AO process with BDD anode and SS cathode. This process generates low amount of intermediates and led to rapid mineralization of HAs to  $\text{CO}_2$ .
- The use of CS material as cathode led to significant adsorption of HAs onto its surface. This resulted in a lower amount of HAs oxidized during the AO process. Addition of iron during the EF process strongly enhanced both kinetic and capacity of HA adsorption onto the CS cathode.
- Hydroxyl radicals produced from the Fenton's reaction oxidized organic compounds adsorbed onto the cathode, as they are produced in a homogeneous way in the bulk. This resulted in the release of hydrophilic HABPs in the solution.
- The mineralization to  $\text{CO}_2$  of HABPs was much more efficient by using the BDD anode, compared to the Pt anode, due to its higher catalytic activity for heterogeneous  $\cdot\text{OH}$  production.
- The proposed model allowed monitoring  $\text{TOC}_{\text{sol}}$  and  $\text{TOC}_{\text{ads}}$  evolution during AO-SS, AO-CS, EF-Pt and EF-BDD process. It took into account both sorption and oxidation processes as well as two different types of organics (low or non-degraded HAs and hydrophilic HABPs). However, the reliability of this model should be validated with different experimental conditions, such as various initial concentrations, nature of organics, current intensity. Moreover, it was emphasized that diffusion/convection of the solution inside the CS cathode should be also considered for the assessment of the catalytic activity of this material for  $\text{H}_2\text{O}_2$  generation as well as for sorption processes.

To conclude, EAOPs are promising processes for the production of high quality organic-free water, particularly when BDD anode is used. As regards to drinking water

treatment plant issues, it would be interesting to evaluate the evolution of the potential of formation of disinfection by-products in parallel with energy consumption optimization.



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# **CHAPTER 4**

## **ANODIC OXIDATION OF SURFACTANTS AND ORGANIC COMPOUNDS ENTRAPPED IN MICELLES – SELECTIVE DEGRADATION MECHANISMS AND SOIL WASHING SOLUTION REUSE**

This chapter will be submitted soon for publication in RSC Advances as:

Trellu C., Oturan N., Pechaud Y., van Hullebusch E.D., Esposito G., Oturan M.A., Anodic oxidation of surfactants and organic compounds entrapped in micelles – Selective degradation mechanisms and soil washing solution reuse.



## Abstract

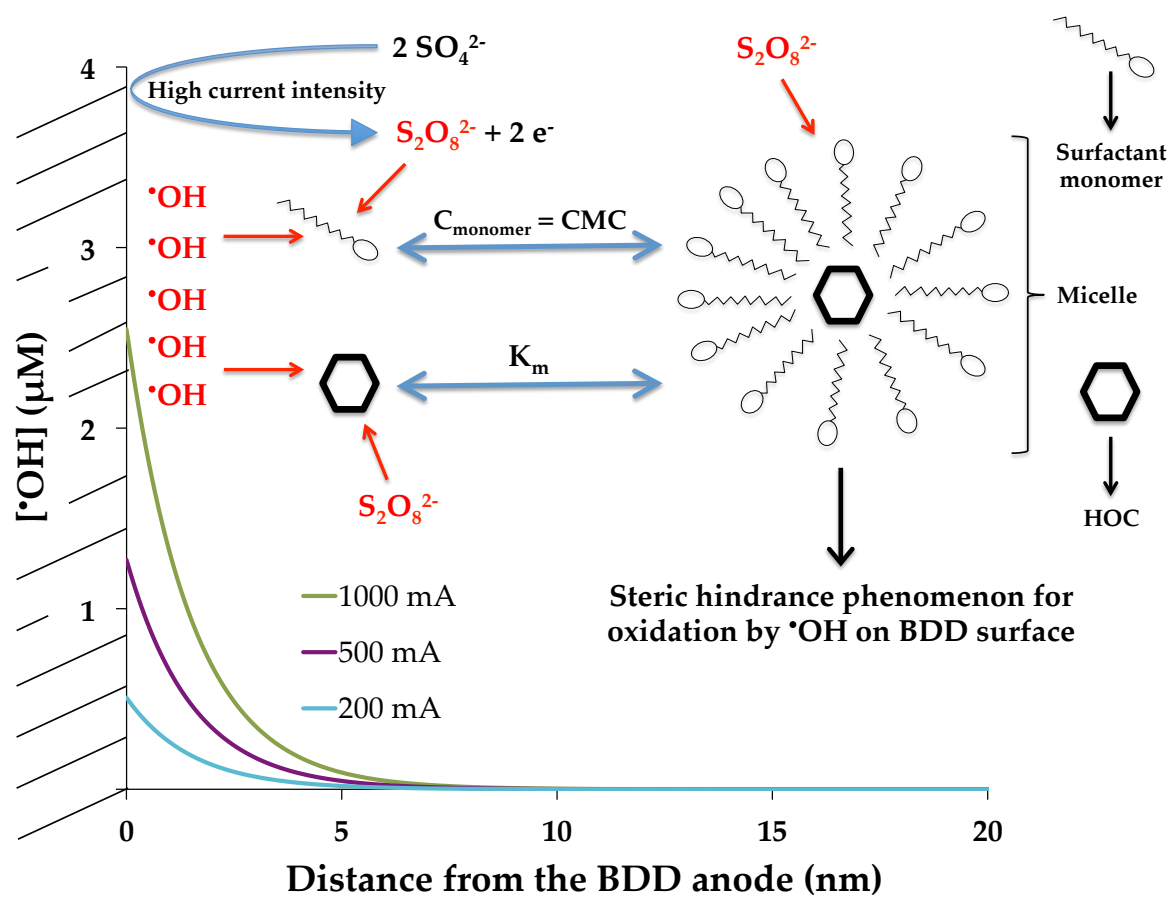
This study pointed out that the formation of micelles at high surfactant concentration strongly modifies oxidation mechanisms and kinetics of organic pollutants during anodic oxidation (AO) using boron doped diamond (BDD) anode. While the non-ionic surfactant monomers Tween<sup>®</sup> 80 (TW80) reacts quickly with BDD(<sup>•</sup>OH) ( $k_{\text{abs}}$  determined as  $(2.97 \pm 0.60) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), the ratio between the apparent (pseudo-first order) rate constant of p-hydroxybenzoic acid (used as standard competitor) and TW80 degradation ranged from 0.43 to 10, according to the current intensity and TW80 concentration. Results presented and discussed in this study emphasized the following mechanisms: (i) micelles act as a protective environment and reduce the availability of target molecules towards BDD(<sup>•</sup>OH); (ii) the use of low current intensity strongly reduces micelle degradation kinetics due to both steric hindrance phenomenon for oxidation of micelles at the BDD surface and the absence of mediated oxidation in the bulk; (iii) compounds solubilized in surfactant-containing solutions can be either oxidized after the degradation of the protective environment formed by micelles or if they are present as free extra-micellar compound. Therefore, selective degradation of organic compounds entrapped in micelles can be achieved by using low current intensity and high surfactant concentration. In fact, these operating conditions strongly hinder micelle oxidation, while free (extra-micellar) compounds can still be oxidized. Then, the remaining entrapped compounds can also be continuously released in the aqueous phase, according to the micellar / aqueous phase partitioning coefficient ( $K_m$ ). These results have been applied for the treatment of a real polycyclic aromatic hydrocarbon-containing soil washing solution. After 23 h of treatment at 50 mA, 83% of phenanthrene, 90% of anthracene, 77% of pyrene and 75% of fluoranthene were degraded and the treated SW solution was reused for an additional SW step with only 5% lower extraction capacity than a fresh TW80 solution.

**Keywords:** Anodic oxidation; Selective degradation; Tween 80 surfactant; Polycyclic aromatic hydrocarbon (PAH); Soil washing.

**Highlights:**

- Surfactant oxidation strongly depends on concentration and current intensity.
- Steric hindrance phenomenon hinders the oxidation of micelles.
- Micelles act as a protective environment for entrapped organic compounds.
- Free extra-micellar compounds are more available for oxidation.
- Low current intensity allows selective degradation and soil washing solution reuse.

## Graphical abstract



## 1. Introduction

Surfactants are amphiphilic molecules made of a hydrophilic head and hydrophobic tail mainly characterized by their critical micelle concentration (CMC) and hydrophilic-lipophilic balance (HLB) [1]. At concentration  $C < \text{CMC}$ , surfactant monomers lower the surface tension of a solution and it is only at  $C > \text{CMC}$  that surfactant aggregates called micelles are formed [2]. Micelles create a hydrophobic space in which hydrophobic organic compounds (HOCs) are entrapped, thus leading to strong HOCs solubility enhancement [3,4]. HOCs partitioning between the micellar and aqueous phase is determined by the micellar / aqueous phase partitioning coefficient  $K_m$  (Eq. 1) [3], which usually follows similar trend than the octanol / water partitioning coefficient  $K_{ow}$ . Many surfactants with different chemical structures have been developed. They are divided into four main categories, including anionic, cationic, amphoteric and non-ionic surfactants and their toxicity has been reported to be strongly dependent on their chemical structure [5,6].

$$K_m = \frac{X_m}{X_a} \quad (\text{Eq. 1})$$

whereby  $X_m$  and  $X_a$  are mole fraction of target pollutants in the micellar pseudo-phase and aqueous phase, respectively.

Surfactants are important components in the formulation of most of detergents and a large range of industrial activities (textile, paint, food, pharmaceutical and pulp-paper industries) also requires the use of these compounds because of the possibility to use them as emulsifiers, solubilizing agents, softeners, lubricants, wetting agents, dyeing agents, etc. [7]. Thus, dozens of million tons of surfactants are produced every year and they are among the most widely disseminated xenobiotic in aquatic environments [8]. Therefore, regulation authorities usually impose an effective treatment of surfactant-containing industrial wastewaters [8]. Besides, the use of environmentally friendly surfactants as extracting agent in chemically enhanced soil washing (SW) and soil flushing (SF) processes is a promising treatment strategy for the removal of HOCs from contaminated soils [1,9–11]. However, this generates SW/SF solutions containing large amounts of soil pollutants, natural soil organic matter and surfactants. The low

availability of pollutants in historically contaminated soils requires the use of high surfactant concentration and/or implementation of several successive SW steps [9,12]. Thus, the main drawback of SW/SF processes is the consumption of too much (costly) surfactant. Therefore, an optimal treatment of SW/SF solutions aims at the total removal of target HOCs together with the recovery of surfactants for reuse of the SW/SF solution in order to improve the cost-effectiveness of the whole process [9,13–15].

Aerobic biological processes are the most common treatment strategy for surfactant containing wastewaters. However, such treatment is sometimes not suitable for hardly degradable surfactants or when strong foaming issues occur [8]. Therefore, alternative remediation techniques have been developed such as coagulation processes (for anionic surfactants) [8,16,17] as well as membrane [18] and oxidation processes [19–22]. Particularly, anodic oxidation (AO) is a promising technique since it can lead to the fast and total mineralization of all organic compounds, including surfactants [23–31]. For the treatment of SW/SF solutions, air stripping [18], solvent extraction [32] or adsorption processes [33] can lead to the selective separation of target HOCs from SW solutions but only few studies reported the implementation of degradation processes for selective degradation of target pollutants [9,14]. Selective degradation is very challenging since target HOCs are entrapped in surfactant micelles, which form a protective environment around the pollutant [9,13,34].

This study focuses on the use of an electrochemical advanced oxidation process, i.e. AO process using boron doped diamond (BDD) anode for the treatment of SW solutions. It is based on the production of hydroxyl radicals  $\text{BDD}(\cdot\text{OH})$  from water oxidation on the surface of BDD anode (Eq. 2) [23,29,35,36]. The  $\cdot\text{OH}$  is the second most reactive oxidant species [37], which is also characterized by a very short lifetime. Therefore, a thin layer of  $\text{BDD}(\cdot\text{OH})$  is formed on the BDD surface; the  $\text{BDD}(\cdot\text{OH})$  concentration follows an exponential distribution from the BDD surface up to few nm/ $\mu\text{m}$ , according to operating conditions [38,39]. The amount of  $\text{BDD}(\cdot\text{OH})$  generated and the thickness of the  $\text{BDD}(\cdot\text{OH})$  layer is directly dependent on the current intensity applied and concentration / reactivity of organic compounds in the solution [38,39]. Organic pollutants react then with  $\text{BDD}(\cdot\text{OH})$  either under mass transport or current intensity control, according to the ratio between the amount of  $\text{BDD}(\cdot\text{OH})$  produced and concentration of organic compounds [35]. However, recent studies on the treatment of SW solutions by AO

process suggested that a steric hindrance phenomenon might occur for the oxidation of surfactant micelles on the surface of the BDD anode, due to the low thickness of the BDD( $\cdot$ OH) layer [34,40]. Degradation of organic pollutants during AO at high current intensity can also occur by mediated oxidation, e.g. the generation of strong oxidant species such as persulfate or ozone has been observed to promote the degradation of organic compounds in the bulk [23,34,36,41].



In the present study, Tween<sup>®</sup> 80 (TW80) was chosen as model non-ionic surfactant because several studies reported its high efficiency for the removal of HOCs from contaminated soils [42,43]. Besides, polycyclic aromatic hydrocarbons (PAHs) were studied as target pollutants (by using either phenanthrene (PHE) as model pollutant or real SW solutions) since soil contamination by PAHs is a major environmental issue. Results were also compared with the use of p-hydroxybenzoic acid (HBA), which presents a much higher solubility (36 mM) than PAHs (for example, 0.007 mM for PHE). The specific objectives of this study are to investigate for the first time (i) the mechanisms of surfactant oxidation during AO, which strongly depends on current intensity and surfactant concentration and (ii) the oxidation mechanisms of HOCs solubilized in surfactant-containing solutions in order to provide sound recommendations for the treatment of SW/SF solutions, including very promising results for surfactant recycling and SW solution reuse using a soil historically contaminated by PAHs.

## 2. Materials and methods

### 2.1. Chemicals

All solutions were prepared with ultrapure water from a Millipore Milli-Q system (Molsheim, France) with resistivity of 18.2 M $\Omega$  cm. All chemicals were purchased at analytical grade, including PHE (purity >99.5%, Sigma Aldrich), TW80 (polyoxyethylene (20) sorbitan monooleate) (Sigma Aldrich), HBA (Sigma Aldrich), TNS (6-(P-toluidino)naphthalene-2-sulphonic acid sodium) (Sigma Aldrich), Na<sub>2</sub>SO<sub>4</sub> (Sigma Aldrich), NaClO<sub>4</sub> (Fluka) and H<sub>2</sub>SO<sub>4</sub> (Sigma Aldrich). Humic acids (HAs) were purchased from Acros Organics; a purification step was performed as described in Trelu et al. [44].

### 2.2. Synthetic and real soil washing solutions

A synthetic SW solution was prepared by using 1 mM of TW80, 0.14 mM of PHE and 10 mgC L<sup>-1</sup> (mg of carbon per liter) of HA. The solution was continuously stirred during 3 days in order to ensure the total dissolution of PHE before to perform the experiments.

The treatment of a real SW solution was also investigated. The soil used during all experiments originates from a historically contaminated site (polluted by industrial activities of bituminous production). SW experiments were performed on the sand fraction (>63  $\mu$ m), which was previously identified as the most contaminated and less treatable fraction, due to the presence of large amount of solid particles of weathered and resinified tar oil [45–47]. Four PAHs were monitored including PHE, anthracene (ANT), pyrene (PYR) and fluoranthene (FLUO). The total amount of these PAHs in the soil fraction used during SW experiments was determined by the extraction method developed by Eschenbach et al. [48]. It contained 78 mg PHE kg<sup>-1</sup>, 36 mg ANT kg<sup>-1</sup>, 117 mg PYR kg<sup>-1</sup> and 75 mg FLUO kg<sup>-1</sup>. The protocol used for SW experiments was similar to the protocol described by Mousset et al. [12]. SW was performed in bottles of 2 L filled with 1.5 L of fresh SW solution containing 5 mM of TW80. The ratio soil/liquid was 10%. The contact time in the rotary shaker (20 rpm) was 24 h. At the end of the experiment, the SW solution was allowed to settle during 2 h and then, centrifuged at 3500 rpm during 15 min. The same procedure was performed for investigation of the

extraction capacity of the treated SW solution. SW was performed in bottles of 500 mL filled with 330 mL of reused washing solution and a ratio soil/liquid of 10%.

### 2.3. Anodic oxidation

AO experiments were performed in batch mode in a 400 mL undivided, open and cylindrical electrochemical cell containing 330 mL ( $V_0$ ) of solution under continuous agitation, similarly to the setup previously described by Trelu et al. [49]. A thin film of BDD onto a Nb substrate ( $24 \text{ cm}^2 \times 0.2 \text{ cm}$ , Condias GmbH, Itzehoe, Germany) and stainless steel ( $24 \text{ cm}^2 \times 0.2 \text{ cm}$ , Goodfellow, France) were used as anode and cathode, respectively. Electrodes were placed face to face with a gap of 3 cm. Most of experiments were performed with  $\text{Na}_2\text{SO}_4$  at 0.05 M as supporting electrolyte. Results were also compared with the use of  $\text{NaClO}_4$  at 0.1 M. A power supply (HAMEG, model 7042-5, Germany) ensured constant current supply in the range 50 – 1000 mA. All experiments with single compounds and binary mixtures (HBA/TW80 or PHE/TW80) were performed at pH 3 by using  $\text{H}_2\text{SO}_4$  for pH adjustment. The treatment of SW solutions was performed at the natural pH (synthetic SW solution: 5.5; real SW solution: 7.2), however the pH rapidly decreased between 3-4 during the treatment due to the formation of degradation by-products such as carboxylic acids [49]. It has been reported that the efficiency of the AO process does not depend on the pH of the solution [27]; contradictory results have also been reported in the literature [50].

### 2.4. Adsorption experiments

The adsorption material used during all experiments was activated carbon fibers from Dacarb (France) with a specific surface area of  $1200 \text{ m}^2 \text{ g}^{-1}$ . Glass bottles (500 mL) containing 350 mL of SW solution and various amount of activated carbon (in the range  $0.1 - 3.5 \text{ g L}^{-1}$ ) were shaken at 20 rpm in a rotary shaker for 72 h (preliminary experiments showed that the equilibrium is reached after 72 h). Control tests without activated carbon confirmed that PAH loss by volatilization or degradation was lower than 5%. Analyses were performed on the liquid phase.



## 2.5. Analysis of PAHs and p-hydroxybenzoic acid (HBA)

All PAHs and HBA were analyzed by high performance liquid chromatography (HPLC), using an Elite LaChrom<sup>®</sup> system. A reverse phase C-18 end-capped column was placed in an oven set at 40.0 °C and combined to a UV (Merck Hitachi, L-2400) or fluorescence detector (Merck Hitachi L-2480). A 20 µL injection loop was used.

For PAHs analyses, the mobile phase was a mixture of methanol/water (80:20 v/v) with a flow rate of 1.0 mL min<sup>-1</sup> in isocratic mode. The fluorescence detector was set at the following excitation/emission wavelengths: 275/350 for PHE, 220/405 for ANT, 270/440 for PYR and FLUO. For HBA analysis, the mobile phase was a mixture of methanol/water (with 1% acetic acid) (30:70 v/v) with a flow rate of 0.8 mL min<sup>-1</sup> in isocratic mode. The UV detector was set at 254 nm.

## 2.6. Tween<sup>®</sup> 80 analysis

TW80 analysis was performed according to the method developed by Mousset et al. [51]. It is based on the measurement of the fluorescence (excitation: 318 nm, emission: 428 nm) of the complex formed between Tween 80 and TNS. A Kontron SFM 25 spectrofluorimeter was used. Due to the high sensitivity of this method, there was not any significant interference originating from the fluorescence of PHE and HAs during the analysis of synthetic SW solutions.

## 2.7. Total organic carbon (TOC) analysis

TOC analyses were performed for the determination of mineralization rates of HAs and SW solutions. A Shimadzu TOC-V analyzer using catalytic combustion method was used. Calibration was achieved with potassium hydrogen phthalate (99.5%, Merck).

## 2.8. Competition kinetics method

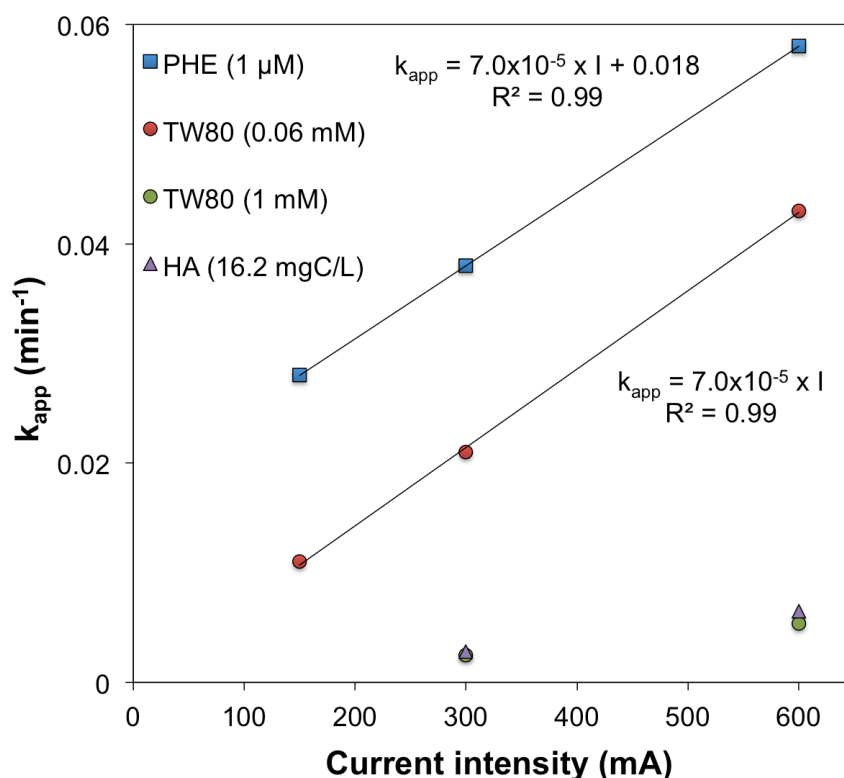
The absolute rate constant of TW80 degradation by BDD( $\cdot$ OH) during AO was determined by the competition kinetics method using HBA as standard competitor (with absolute rate constant of  $1.63 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [52]). BDD( $\cdot$ OH) cannot be accumulated in the electrochemical cell due to their very short lifetime. Therefore, a quasi-stationary state approximation can be made for its concentration [53]. This allows considering pseudo-first order reaction kinetics for the oxidation of TW80 and HBA by BDD( $\cdot$ OH). Thus, kinetic analysis allows the determination of the apparent rate constants ( $k_{\text{app}}$ ) and then the absolute rate constant ( $k_{\text{abs}}$ ) by means of the Eq. 3 [13,54].

$$k_{\text{abs(TW80)}} = k_{\text{abs(HBA)}} \times \frac{k_{\text{app(TW80)}}}{k_{\text{app(HBA)}}} \quad (\text{Eq. 3})$$

### 3. Results and discussion

#### 3.1. Degradation kinetics of single compounds

The first experiments were performed to study separately the oxidation kinetics of the main components of a synthetic SW solution, according to the current intensity supplied during AO (PHE as model target pollutants, TW80 as extracting agent and HA as model soil organic matter). Degradation kinetics of PHE and TW80 as well as mineralization kinetics of HA proceeded according to a pseudo-first order kinetic; apparent (pseudo-first order) rate constants ( $k_{app}$ ) are reported in Figure 4.1. The degradation of PHE was studied at a concentration below its solubility limit, while the degradation of TW80 and HAs was studied using concentrations relevant with respect to the issue of SW solutions.



**Figure 4.1.** Apparent (pseudo-first order) rate constant ( $k_{app}$ ) obtained for the degradation of Tween<sup>®</sup>80 (TW80) and phenanthrene (PHE) and mineralization of humic acids (HA), as a function of current intensity ( $I$ ) during anodic oxidation ( $[Na_2SO_4] = 0.05 M$ ;  $V_0 = 330 mL$ ).

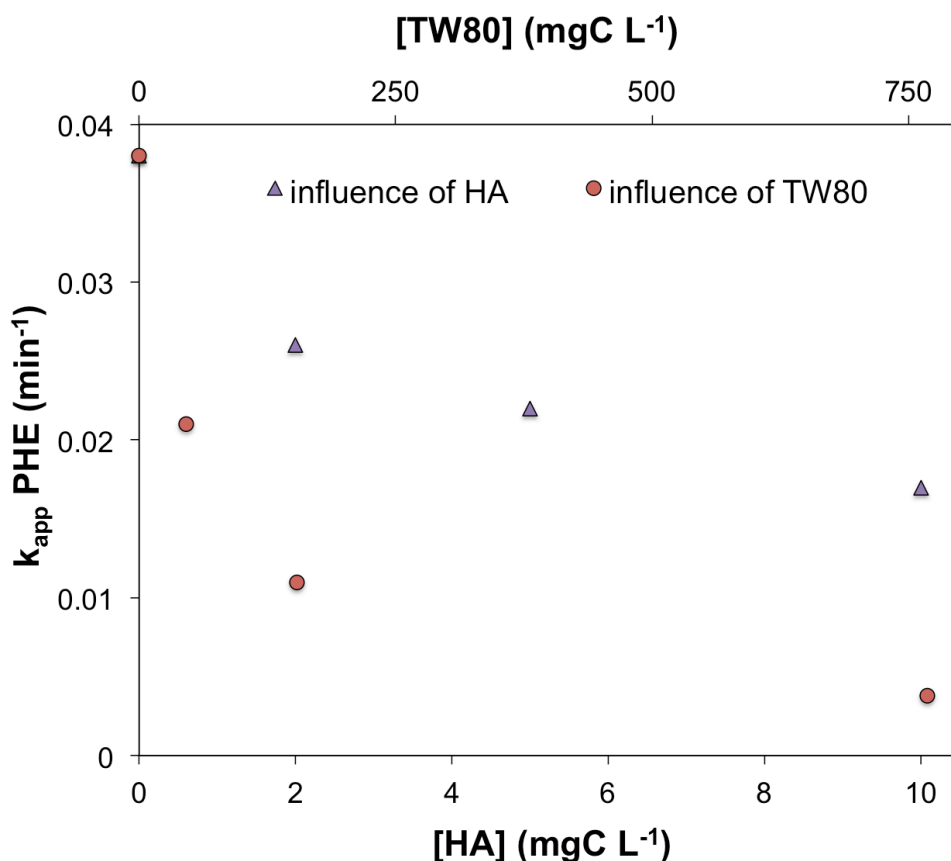
The highest degradation kinetics were obtained with 1  $\mu\text{M}$  PHE, due to its aromatic structure, which react very quickly with  $\text{BDD}(\cdot\text{OH})$  [55]. Interestingly, a linear relation was observed between the current intensity supplied and the apparent degradation kinetics of 0.06 mM TW80 and 1 mM PHE.

The increase of the TW80 concentration from 0.06 mM to 1 mM strongly reduced the degradation kinetics of TW80 by a factor 8.4 and 8.0 at 300 and 600 mA, respectively. This is mainly ascribed to an increase of the amount of organic compounds oxidized with the same amount of  $\text{BDD}(\cdot\text{OH})$ . Thus, the degradation kinetic of 1 mM of TW80 was decreased as low as the mineralization kinetic of 16.2  $\text{mgC L}^{-1}$  of HAs. Besides, the decrease of the current intensity from 600 to 150 mA led to the reduction of the apparent rate constant of 0.06 mM TW80 and 1  $\mu\text{M}$  PHE by a factor 3.9 and 2.1, respectively. This indicates that the decrease of the current intensity has higher adverse effects on the degradation kinetic of TW80.

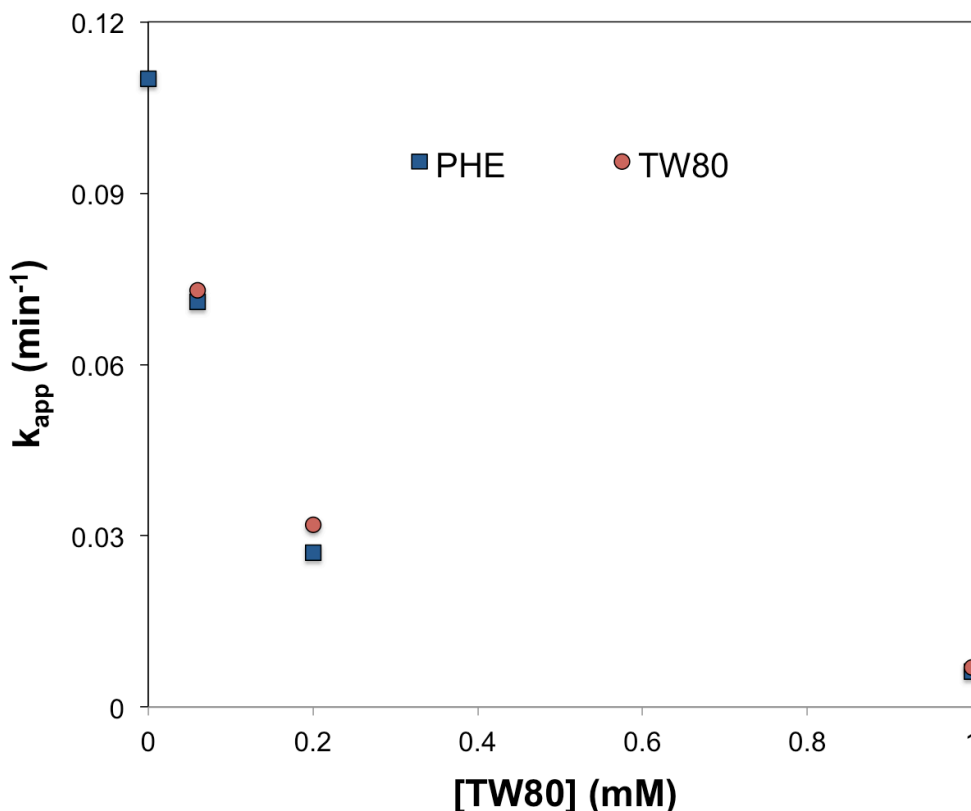
### **3.2. Inhibitory effect of Tween® 80 and humic acids on phenanthrene degradation kinetics**

The influence of TW80 and HAs on PHE degradation kinetics was investigated (Figure 4.2). In both cases, the evolution of the apparent rate constant of PHE degradation according to the initial TW80 and HA concentration followed a reverse exponential trend. The addition of 10  $\text{mgC L}^{-1}$  of HAs or 46  $\text{mgC L}^{-1}$  of TW80 (0.06 mM) decreased the apparent rate constant of PHE degradation by a factor 2.2 and 1.8, respectively, indicating a higher inhibitory effect from HAs. This is ascribed to the aromatic structure of HAs, which reacts very quickly with  $\text{BDD}(\cdot\text{OH})$  [55]. Thus, HAs act as strong  $\text{BDD}(\cdot\text{OH})$  scavengers [56,57]. However, in the case of a SW solution containing high TW80 concentration, the large amount of surfactant led to the higher inhibitory effect; 768  $\text{mgC L}^{-1}$  (1 mM) decreased the apparent rate constant of PHE degradation by a factor 10. In addition to the  $\text{BDD}(\cdot\text{OH})$  scavenging effect, TW80 micelles form a protective environment for PHE and reduce the availability of PHE towards  $\text{BDD}(\cdot\text{OH})$  [9,13]. This latter phenomenon was further emphasized in Figure 4.3. By using high current intensity and various concentrations of TW80 above the CMC, it was observed that the apparent rate constant of PHE degradation was always similar to the apparent

rate constant of TW80 degradation, whereas it was observed that the degradation of PHE in single compound-containing solutions was much faster than the degradation of TW80. These results indicate that micelle degradation is required for allowing the oxidation of a PHE molecule entrapped in a TW80 micelle. The locus of solubilization of target molecules in micelles depends on the hydrophobicity of the target organic compounds [58]. Highly hydrophobic compounds are entrapped in the very hydrophobic space formed at the middle of micelles, while the locus of solubilization of less hydrophobic compounds is closer to the external shape of the micelle (hydrophilic head of surfactants). Therefore, a higher protective effect of micelles might be expected for the most hydrophobic compounds.



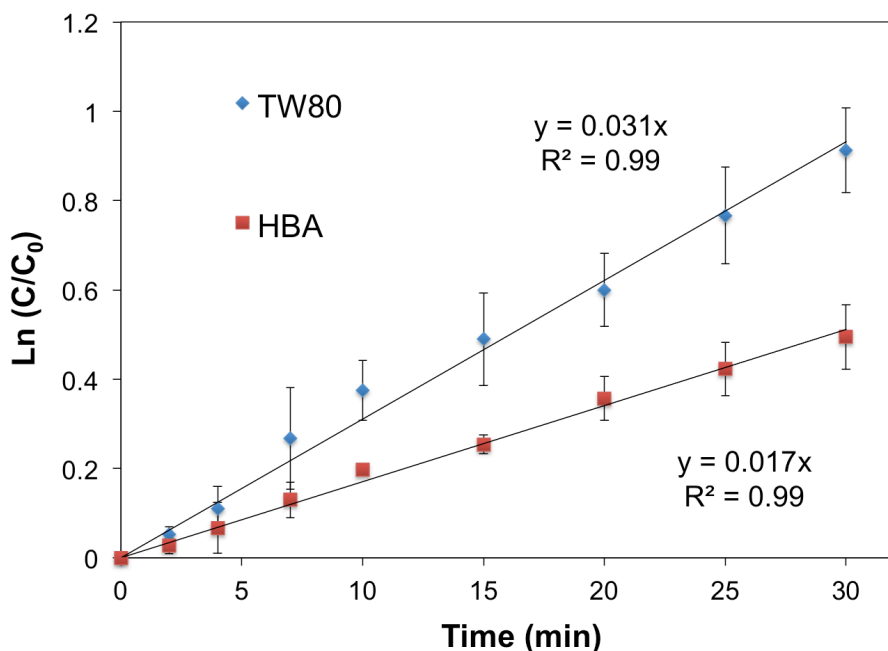
**Figure 4.2.** Effect of initial HA and TW80 concentration (in mgC L<sup>-1</sup>) on the apparent (pseudo-first order) degradation kinetics ( $k_{app}$ ) of phenanthrene ( $[PHE]_0 = 0.1 \mu\text{M}$ ) in a binary mixture phenanthrene-humic acid or phenanthrene-Tween<sup>®</sup> 80 treated by AO at 300 mA ( $[Na_2SO_4] = 0.05 \text{ M}$ ;  $V_0 = 330 \text{ mL}$ ) (1 mM TW80 = 768 mgC L<sup>-1</sup>).



**Figure 4.3.** Effect of initial Tween<sup>®</sup> 80 concentration on the apparent (pseudo-first order) degradation kinetics ( $k_{app}$ ) of phenanthrene ( $[PHE]_0 = 0.1 \mu M$ ) and Tween<sup>®</sup> 80 (TW80) in a binary mixture treated by anodic oxidation at 1000 mA ( $[Na_2SO_4] = 0.05 M$ ;  $V_0 = 330 mL$ ).

### 3.3. Tween<sup>®</sup> 80 degradation kinetic and mechanism during the AO process

Due to the crucial role of surfactants during the treatment of SW solutions, the mechanisms of TW80 oxidation during AO was further investigated in this study. First, the absolute rate constant of TW80 monomer oxidation by BDD( $\cdot OH$ ) was assessed at  $C < CMC$  condition, using the competition kinetics method with HBA as standard competitor (Figure 4.4). The value determined as  $(2.97 \pm 0.60) \times 10^9 M^{-1} s^{-1}$  showed that BDD( $\cdot OH$ ) react quickly with TW80 monomers. The value obtained was much higher than the one reported by Mousset et al. [13]. The reason might be that this previous study used TW80 at a concentration of 0.6 mM (above the CMC), while the formation of micelles strongly changes the oxidation mechanism and kinetics.



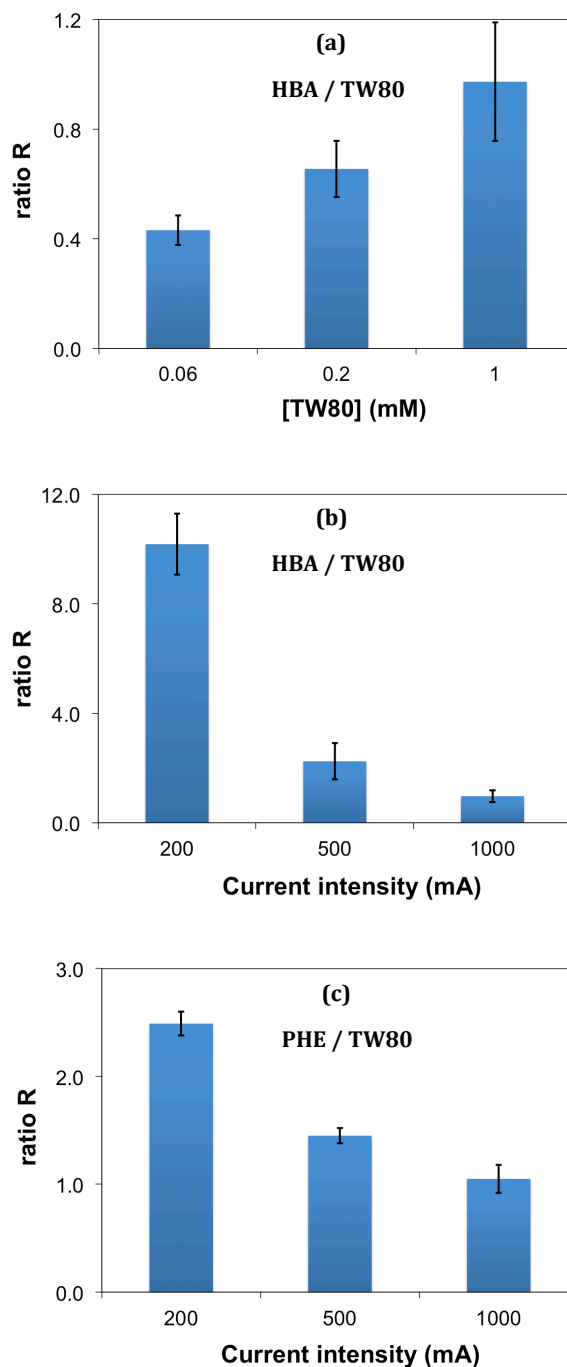
**Figure 4.4.** Determination of the absolute (second-order) rate constant for oxidation of Tween® 80 by BDD( $\bullet$ OH) at  $C < CMC$  condition ( $C = 7.5 \mu\text{M}$ ) by competition kinetics method using HBA (0.1 mM) as standard competitor, during treatment by AO under the following operating conditions: BDD anode, SS cathode,  $[\text{Na}_2\text{SO}_4] = 0.05 \text{ M}$ ;  $V_0 = 330 \text{ mL}$ ;  $I = 200 \text{ mA}$ ; pH 3. Error bars refer to triplicate experiments.

Therefore, this study also investigated the evolution of the degradation of organic compounds in a binary mixture target molecule / TW80 for TW80 concentrations above the CMC. Particularly, the selective (or preferential) degradation of target molecules was assessed by using the ratio  $R$  (Eq. 4), defined as follows:

$$R = \frac{k_{app_X}}{k_{app_{TW80}}} \quad (\text{Eq. 4})$$

where  $k_{app_X}$  is the apparent (pseudo-first order) rate constant of the degradation of a target molecule X (HBA or PHE) and  $k_{app_{TW80}}$  is the apparent rate constant of TW80 degradation.

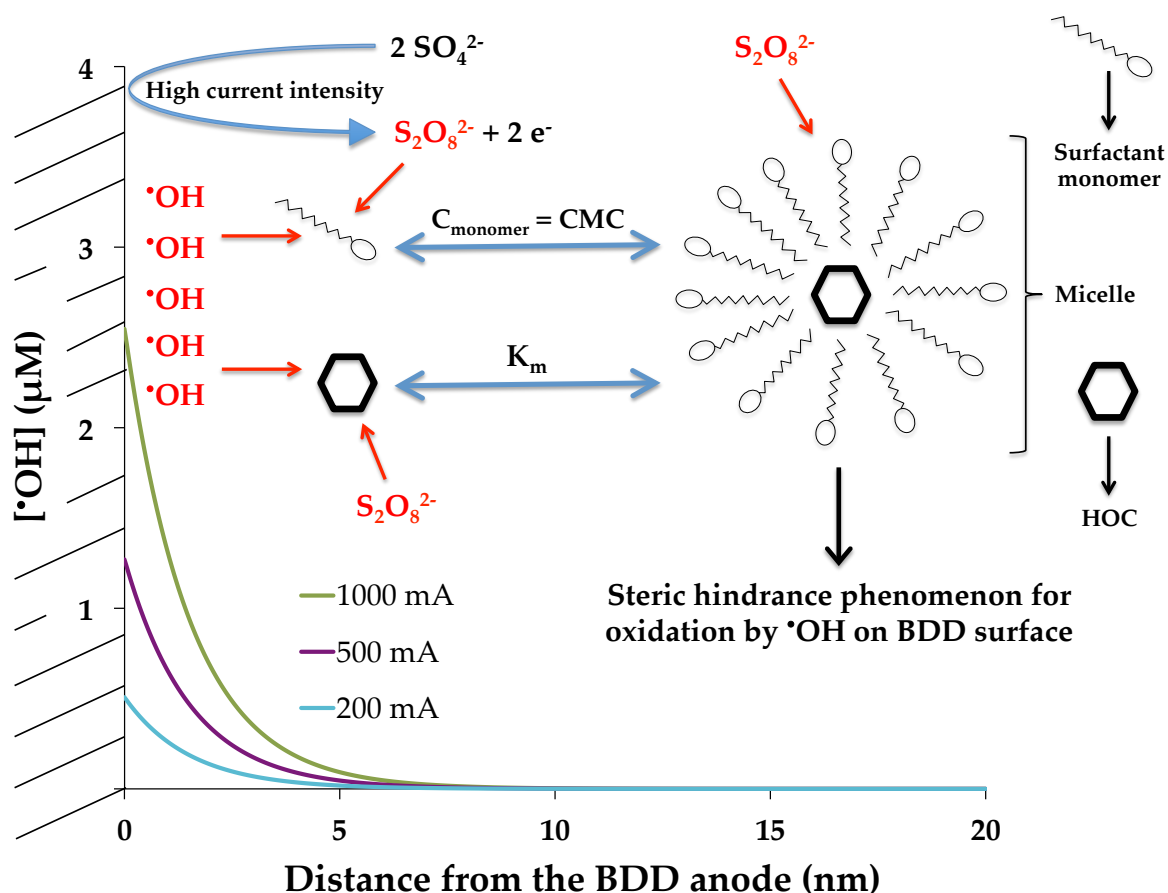
Interestingly, the ratio  $R$  varied between 0.43 and 10 by using HBA as target molecule, according to current intensity and TW80 concentration (Figures 4.5a and 4.5b).



**Figure 4.5.** Treatment of a binary mixture (HBA / TW80 (a and b) or PHE / TW80 (c)) by AO ( $[\text{Na}_2\text{SO}_4] = 0.05 \text{ M}$ ;  $V_0 = 330 \text{ mL}$ ). (a): ratio R between the apparent (pseudo-first order) degradation kinetics ( $k_{app}$ ) of HBA ( $[\text{HBA}]_0 = 0.2 \text{ mM}$ ) and TW80, as a function of TW80 concentration (AO at  $I = 1000 \text{ mA}$ ). (b): ratio R between  $k_{app}$  of HBA ( $[\text{HBA}]_0 = 0.2 \text{ mM}$ ) and TW80 ( $[\text{TW80}]_0 = 1 \text{ mM}$ ), as a function of current intensity. (c): ratio R between  $k_{app}$  of PHE ( $[\text{PHE}]_0 = 0.14 \text{ mM}$ ) and TW80 ( $[\text{TW80}]_0 = 1 \text{ mM}$ ), as a function of current intensity. Error bars refer to triplicate experiments.

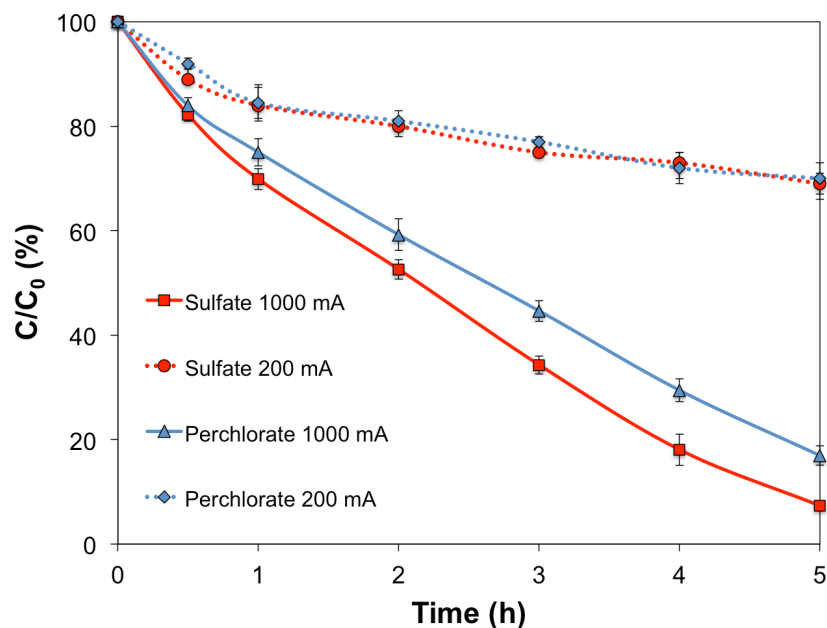


At high TW80 concentration (1 mM) and whatever the pollutant used (HBA or PHE), it was observed that the lower the current intensity, the higher the ratio R (Figures 4.5b and 4.5c). This came from the low decrease of the degradation kinetic of target molecules (almost not significant in the case of HBA) combined to the strong reduction of the TW80 degradation kinetic at low current intensity. This interesting behavior is explained by differences in terms of availability of organic compounds towards BDD( $\cdot$ OH). AO is based on the formation of BDD( $\cdot$ OH) on the surface of the BDD anode (*i.e.* in a heterogeneous way in the electrochemical cell). By using the theoretical model developed by Kapalka et al. [39], the profile of BDD( $\cdot$ OH) concentration according to the distance from the surface of the BDD anode can be calculated (results presented in Figure 4.6). Interestingly, at high concentration of TW80 (1 mM) and in the range of current intensity used in this study, the thickness of the BDD( $\cdot$ OH) layer was calculated to be lower than 5 nm. Therefore, a steric hindrance phenomenon could occur for the degradation of TW80 micelles during AO, since the diameter of TW80 micelles reported in the literature is in the range 3-10 nm [59]. This phenomenon might be enhanced in real SW solutions by the aggregation of soil particles with surfactant molecules. For example, Dos Santos et al. [34,40] reported particle size diameters in real SW solutions in the range 250 – 2000  $\mu$ m. Besides, the profile of BDD( $\cdot$ OH) concentration on the surface of the BDD anode strongly depends on current intensity (Figure 4.6) [39]. Thus, low current intensity may increase this steric hindrance phenomenon.



**Figure 4.6.** Schematic view of mechanisms occurring during anodic oxidation of a binary mixture HOC – Tween<sup>®</sup> 80. Profiles of BDD( $\cdot\text{OH}$ ) concentration are calculated from the model of Kapalka et al. [39] with  $[\text{TW80}] = 1 \text{ mM}$  and different current intensities.

Also, one should consider that mediated oxidation in the bulk can occur during AO. Particularly, at high current intensity (1000 mA), it was observed a significant higher degradation kinetic of TW80 by using  $\text{Na}_2\text{SO}_4$  as supporting electrolyte, compared to  $\text{NaClO}_4$  (Figure 4.7). This might be related to the generation of highly oxidant species such as persulfates, which promoted the oxidation of TW80 micelles in the bulk [23,60]. This phenomenon was not observed at 200 mA because low current intensity does not allow the production of such oxidant species at a sufficient concentration. Overall, the absence of mediated oxidation combined to the steric hindrance phenomenon can explain the strong decrease of degradation kinetics of TW80 micelles at low current intensity.



**Figure 4.7.** Influence of the supporting electrolyte (either 0.05 M  $\text{Na}_2\text{SO}_4$  or 0.1 M  $\text{NaClO}_4$ ) on the degradation of Tween® 80 ( $[\text{TW80}]_0 = 1 \text{ M}$ ) during treatment by AO at 200 mA and 1000 mA. Error bars refer to triplicate experiments.

Besides, it was also observed that the ratio  $R$  depends on the TW80 concentration. At 1000 mA, experimental results showed that the lower the TW80 concentration, the lower the ratio  $R$  (Figure 4.5a). However, the decrease of the TW80 concentration led to the increase of the apparent rate constant of HBA degradation, due to a lower BDD( $\cdot\text{OH}$ ) scavenging effect and to a higher concentration of free extra-micellar HBA. But, overall, the decrease of the ratio  $R$  was ascribed to the strong increase of TW80 degradation kinetic at low concentration. At  $C > \text{CMC}$ , the concentration of surfactant monomer is  $C_{\text{monomer}} = \text{CMC}$  and  $C_{\text{micelle}} = [\text{TW80}]_{\text{total}} - \text{CMC}$  [3]. Besides, the availability towards oxidant species of surfactant monomers is expected to be much higher than the one of surfactant micelles, due to (i) the steric hindrance phenomenon described previously for micelles, (ii) the spatial configuration of micelles, which reduces the availability of the hydrophobic tail of surfactant towards oxidant species. This is why the increase of the ratio  $C_{\text{monomer}} / C_{\text{micelle}}$  at low TW80 concentration strongly promoted the oxidation of TW80. Lower current intensity is expected to enhance this trend due to the lower availability of TW80 micelles for oxidation by BDD( $\cdot\text{OH}$ ) and absence of mediated oxidation.

### 3.4. Degradation mechanism of organic compounds solubilized in Tween® 80-containing solutions

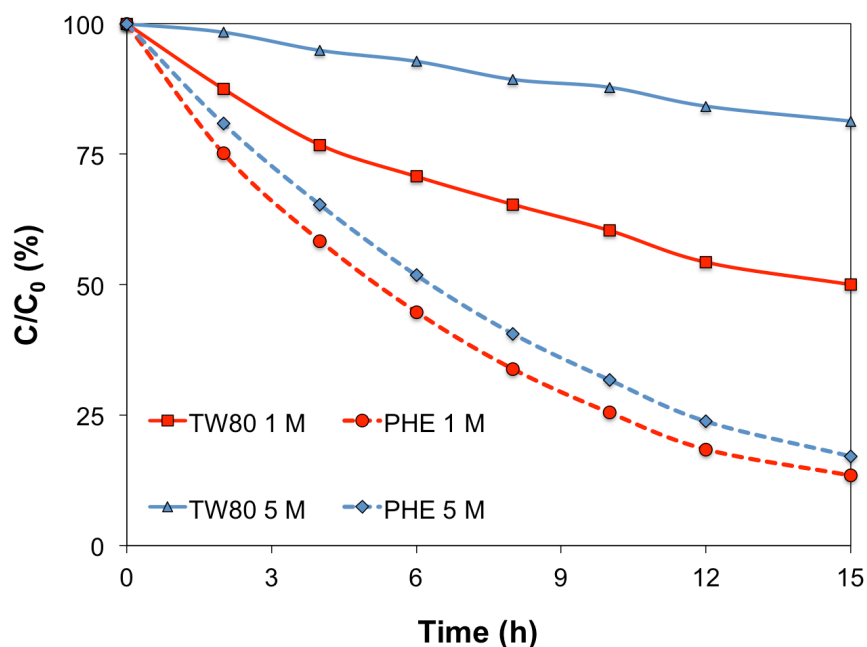
In contrast to experiments performed at 1000 mA, low current intensity (200 mA) allowed reaching higher apparent rate constants for target molecules (HBA or PHE) degradation than for TW80 degradation ( $R > 1$ ) (Figure 4.5b and 4.5c). This does not mean that surfactant does not act anymore as a protective environment for target molecules entrapped inside micelles. It can be explained by considering the micellar / aqueous phase partitioning coefficient  $K_m$ . A significant amount of target molecules are not entrapped inside micelles and are directly available for oxidation by BDD( $\cdot\text{OH}$ ). After oxidation of free extra-micellar target molecules, other molecules can be continuously released in the aqueous phase according to  $K_m$ . This transfer process is not a kinetic limiting step, since the relaxation time of micelles is in the range of milliseconds to few seconds, according to surfactant concentration and nature [61,62]. At low current intensity, the increase of the availability of target molecules entrapped in TW80 micelles is more controlled by this pathway than by the degradation of micelles (because of the inhibition of micelle oxidation as explained previously). This phenomenon is consistent with the higher ratio  $R$  observed by using HBA as target molecule since this latter has a much lower  $K_m$  than PHE (having a higher hydrophobicity), leading to the presence of a larger amount of free extra-micellar compounds.

The phenomena observed in this study are schematically explained in Figure 4.7.

### 3.5. Application – Reuse of soil washing solutions by selective degradation of target pollutants during AO at low current intensity

These experiments showed that high TW80 concentration and low current intensity favor the selective degradation of target molecules solubilized in a TW80-containing solution, due to the strong decrease of the oxidation rate of TW80 micelles. These results have interesting applications for the treatment of SW solutions. In the case of high sequestration of pollutants in an aged contaminated soil, large amounts of costly extracting agents (such as TW80) is required for the effective removal of pollutants from soil [63,64]. Then, extracting agents must be recovered and reused for further SW steps

in order to ensure the cost-effectiveness of the process [9]. Therefore, treatment of synthetic and real SW solutions by AO at low current intensity was investigated in order to assess the degradation of target pollutants and the extraction capacity of the treated SW solution. Using a synthetic SW solution (containing PHE, TW80 and HAs), it was observed that after 15 h of AO at 50 mA, 87% of PHE and 50% of TW80 was removed from a solution containing 1 mM TW80, while 83% of PHE and only 19% of TW80 was removed from a solution containing 5 mM TW80 (Figure 4.8). This confirmed that the treatment at low current intensity of SW solutions containing high surfactant concentrations is a promising process for selective degradation of target pollutants. Particularly, this is consistent with results from the Figure 4.5a; the increase of the TW80 concentration has a stronger adverse effect on TW80 degradation kinetics than on target pollutant degradation kinetics, due to the decrease of the ratio  $C_{\text{monomer}} / C_{\text{micelle}}$  that strongly hinders the oxidation of TW80. Besides, the decrease of the TOC was very low, 11% at 1 mM TW80 and 3% at 5 mM TW80, indicating a low mineralization rate of organic compounds due to the low current intensity.

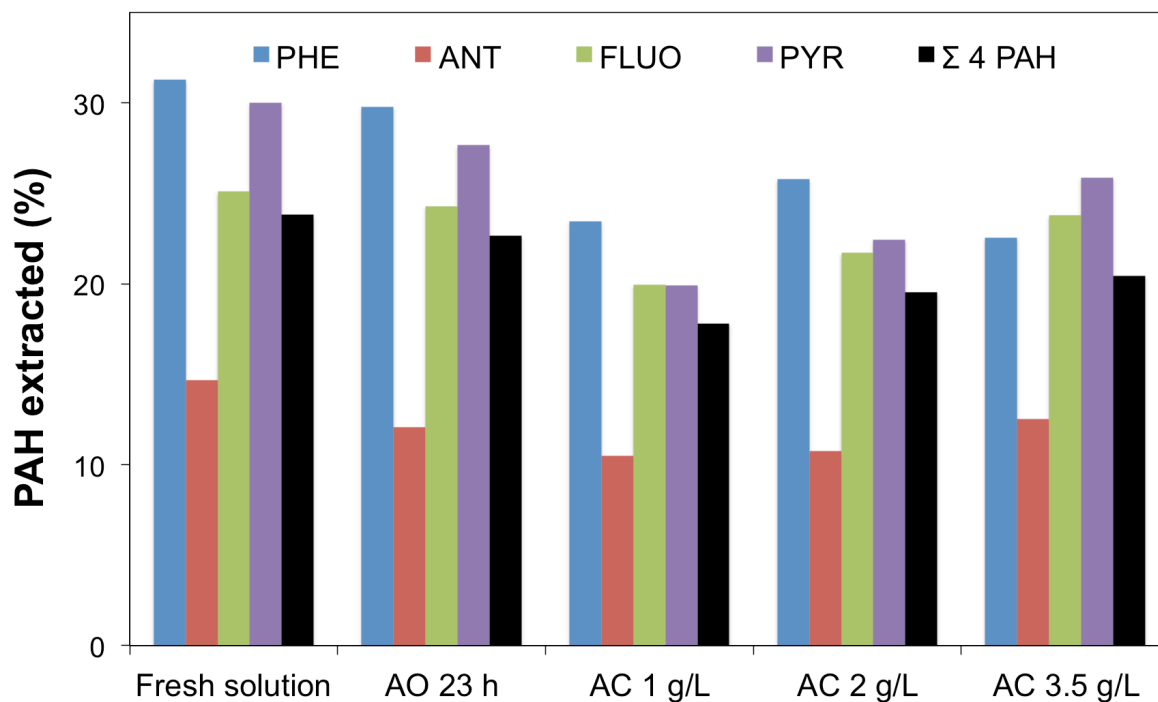


**Figure 4.8.** Time course of phenanthrene ( $[PHE]_0 = 0.14 \text{ mM}$ ) and Tween<sup>®</sup> 80 ( $[TW80]_0 = 1 \text{ M}$  or  $5 \text{ M}$ ) concentrations during treatment of the synthetic SW solution by AO at 50 mA ( $[Na_2SO_4] = 0.05 \text{ M}$ ;  $V_0 = 330 \text{ mL}$ ).

For the treatment of the real SW solution, lower degradation kinetics of target PAHs were observed compared to the synthetic SW solution, due to the competition of a large range of dissolved organic compounds as well as fine particles from the clay-humus complex. After 23 h of treatment, 83%, 90%, 77% and 75% of 0.014 mM PHE, 0.0031 mM ANT, 0.015 mM PYR and 0.011 mM FLUO was degraded, respectively. Furthermore, the extraction capacity of the SW solution after 23 h of treatment was only 5% lower than a fresh SW solution (Figure 4.9). This is ascribed to the low degradation of TW80 as well as possible formation of TW80 oxidation by-products with extracting properties.

A decrease of the pH around 3.8 was observed after a treatment time of 23 h, due to the production of oxidation by-products such as carboxylic acids. However, the reuse of the treated SW solution may not affect the pH of the soil since a real soil has a much higher buffer capacity than the reused SW solution [12]. Moreover, Trellu et al. [49] observed that the treatment of a SW solution by AO leads to the production of more hydrophilic and more biodegradable by-products, therefore, intermediates are not expected to affect the soil microbial activity [12].

In this study, one SW step using 5 mM of TW80 only removed from soil 24% of the total of the 4 PAHs analyzed (Figure 4.9). This is due to the strong sequestration of PAHs in solid particles of weathered and resinified tar oil [45–47]. Thus, either additional SW solution steps or a higher TW80 concentration would be required to reach the regulation discharge for contaminated soils. This is the reason why selective oxidation of target pollutants at low current intensity is an attractive treatment strategy for recycling the SW solution for required additional SW steps. Moreover, it has been widely reported in the literature that low current intensity increases treatment times but reduces energy consumption [49,65]; 23 h of treatment at 50 mA led to the consumption of only 13.2 kWh m<sup>-3</sup>. By comparison, a previous study reported that 5 h of treatment by AO at 1000 mA of the same synthetic SW solution than the one used in this study (with 1 mM TW80) led to the consumption of 127 kWh m<sup>-3</sup> [49].



**Figure 4.9.** PAHs (PHE, ANT, FLUO, PYR) extraction efficacy from a historically contaminated soil of a fresh SW solution containing 5 mM of Tween® 80, a SW solution reused after treatment by anodic oxidation (AO) at 50 mA during 23 h and a SW solution reused after treatment by activated carbon (AC) at 1 g L<sup>-1</sup>, 2 g L<sup>-1</sup> or 3.5 g L<sup>-1</sup>.

### 3.6. Comparison with selective adsorption on activated carbon for soil washing solution treatment and reuse

A comparison was made with the use of activated carbon for selective adsorption of target pollutants, which has been recently proposed for extracting agent recovery from SW solutions [33,66–69]. Very promising results were obtained for the selective adsorption of 0.14 mM of PHE in a binary mixture with 5 mM of TW80. For example, 0.5 g L<sup>-1</sup> of activated carbon allowed the removal of 96% of PHE, while 97% of TW80 was still in the solution. However, the efficiency of PAHs adsorption in the real SW solution was much lower. By using 1, 2 and 3.5 g L<sup>-1</sup> of activated carbon, the removal rate of the sum of the 4 PAHs analyzed reached 46%, 72% and 95%, respectively, while the decrease of the extraction capacity of the treated SW solution was 25%, 18% and 14%, respectively. The decrease of the extraction capacity is ascribed to both the

insufficient removal of organic compounds entrapped in micelles (mainly at low activated carbon dose) and the loss of TW80 by adsorption onto the activated carbon (mainly at high activated carbon dose). Thus, it was observed a lower extraction capacity from SW solutions treated by activated carbon, by comparison to the use of AO at low current intensity. Moreover, the use of the adsorption process requires a post-treatment step of the contaminated sorbent material, while the use of AO at low current intensity allows both target pollutant degradation and SW solution recirculation.



## 4. Conclusions

Solubilization of organic compounds in surfactant-containing solutions strongly reduces their availability towards oxidant species because micelles act as a protective environment. Moreover, it was found that the formation of micelles has strong adverse effects on surfactant degradation kinetics during AO, due to a lower availability of surfactant molecules towards  $\bullet\text{OH}$ . This is mainly ascribed to a steric hindrance phenomenon; the BDD( $\bullet\text{OH}$ ) layer generated at the surface of the BDD anode is too thin compared to the size of micelles. This is the reason why current intensity and surfactant concentration are two critical parameters to consider. Low current intensity strongly reduces micelle degradation kinetics due to the steric hindrance phenomenon combined to the absence of mediated oxidation in the bulk. The decrease of the ratio  $C_{\text{monomer}} / C_{\text{micelle}}$  at high surfactant concentration is also unfavorable for surfactant degradation, since monomers have a higher availability towards oxidant species than micelles. Besides, the degradation of target molecules entrapped in micelles occurs either through the degradation of micelles followed by their degradation or by oxidation of free extramicellar compounds. Therefore, selective degradation of target molecules can be observed by implementing low current intensity and high surfactant concentration. These operating conditions strongly hinder TW80 degradation, while free (extramicellar) can be oxidized and continuously released from micelles according to the partitioning coefficient  $K_m$ . Particularly, this study reported that the treatment by AO at 50 mA of a real SW solution containing PAHs and 5 mM of TW80 allows the selective degradation of PAHs and the reuse of the treated SW solution with similar extraction capacity than a fresh TW80 solution.

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## **CHAPTER 5**

### **COMBINATION OF ANODIC OXIDATION AND BIOLOGICAL TREATMENT FOR THE REMOVAL OF PHENANTHRENE AND TWEEN® 80 FROM SOIL WASHING SOLUTIONS**

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## Abstract

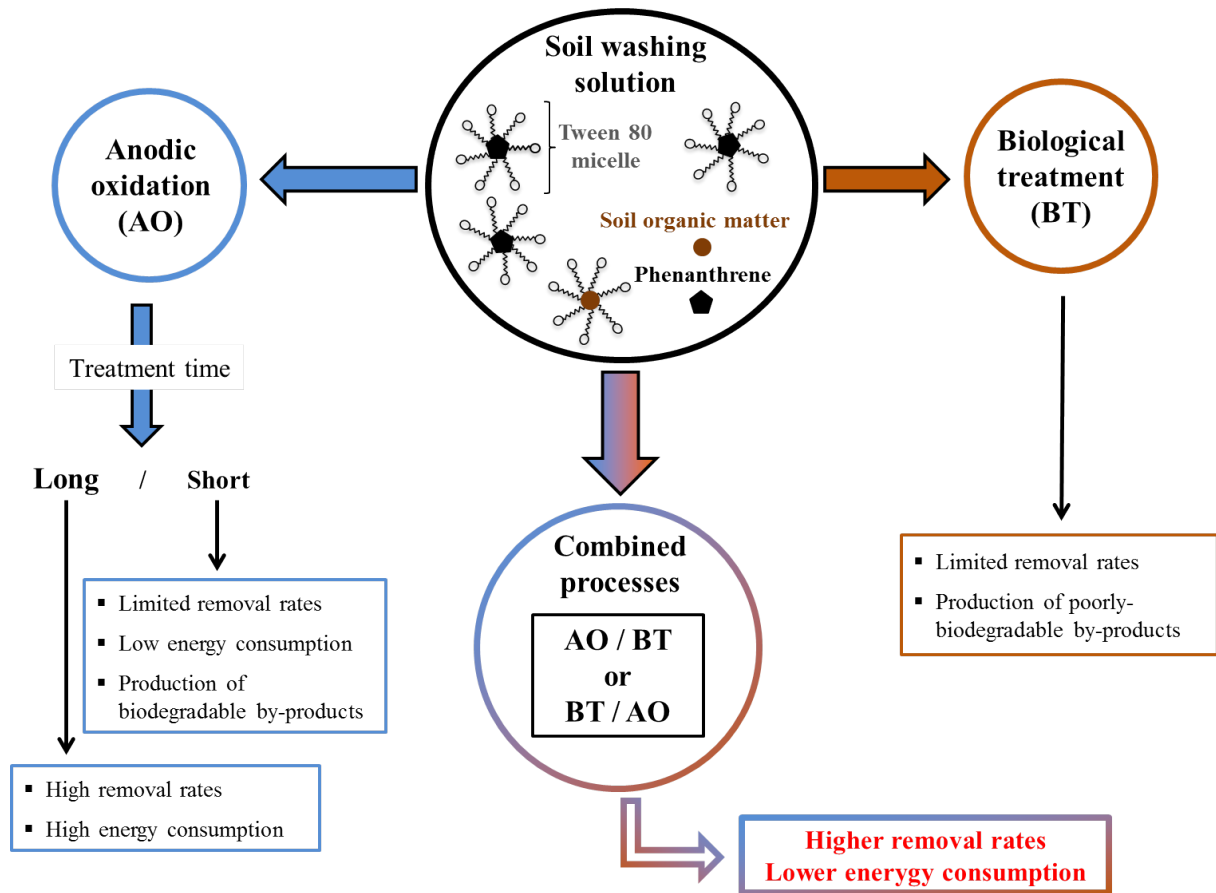
Surfactant enhanced soil washing (SW) and soil flushing are efficient processes for polycyclic aromatic hydrocarbons removal from contaminated soils. However, management of soil washing solutions is a complex challenge for environmental engineering. This study investigated the implementation of a combined process coupling anodic oxidation (AO) – an electrochemical advanced oxidation process – and aerobic biological treatment (BT) for proper handling of a synthetic SW solution containing phenanthrene, Tween® 80 and humic acids. As a sole process, AO required a treatment duration of 5 h and a current intensity of 1 A to remove 95% of phenanthrene and Tween® 80 as well as 71% of COD. Such operating conditions resulted in high electrical energy consumption (67 kWh (kg COD)<sup>-1</sup>). In contrast, BT alone allowed a total degradation of both phenanthrene and Tween® 80, but an insufficient removal of COD (44%) was observed due to the production of non-biodegradable by-products. In order to promote synergistic effects, AO and BT were combined and two different treatment strategies were investigated depending on whether AO was used as pre- or post-treatment. The production of more biodegradable by-products was observed after short AO pre-treatment (3 h, 500 mA), resulting in 80% COD removal after BT. The opposite combination (with AO post-treatment) led to 76% and 93% COD removal after the AO post-treatment at 500 mA for 3 h and 5 h, respectively. Therefore, such combined process appears as a sustainable way to enhance both quality of treated effluent and process cost-effectiveness.

**Keywords:** Soil washing solution; Phenanthrene; Tween® 80 surfactant; anodic oxidation; biological treatment; combined process.

### Highlights:

- A synthetic SW solution containing PHE, TW80 and humic acids was treated.
- BT resulted in 44% COD removal and generation of poorly-biodegradable by-products.
- AO resulted in higher removal rates and production of more biodegradable by-products.
- AO/BT combination gave synergistic effects, leading to 80% COD removal.
- AO post-treatment removed poorly-biodegradable BT by-products.

## Graphical abstract



## 1. Introduction

Anthropogenic release of polycyclic aromatic hydrocarbons (PAH) in the environment is associated with domestic (heating, cooking), transport (exhaust fumes of vehicles) or industrial (coke, cement, asphalt production, petrochemical industries, waste incineration, wood preservation, manufactured gas plant) sources. The latter lead to significant toxic contamination of soils making industrial sites unsuitable for human activities [1]. The remediation of contaminated lands is nowadays an important matter of concern, particularly due to the increase of the urban pressure. Therefore, cost-effective technologies have to be implemented for a proper handling of polluted sites. During the two last decades, soil washing (SW) (*ex situ*) and soil flushing (SF) (*in situ*) processes enhanced by the use of extracting agents have shown great efficiencies for PAH removal from soils [2–4]. However, these processes generate effluents containing large amounts of extracting agents, PAHs and soil organic matter that require further treatment. The management of SW solutions is an important challenge for environmental engineering [5,6].

Anodic oxidation (AO) is an efficient electrochemical advanced oxidation process (EAOP) for the removal of organic compounds from aqueous solutions [7–11]. It is an environmentally friendly process, which only involves a power supply and the use of a sufficient amount of supporting electrolyte [12,13]. This process is based on the production of physisorbed hydroxyl radicals ( $\bullet\text{OH}$ ) on the surface of “non-active” anodes (Eq. 1) [13–16].



with M denoting the anode material. The process is particularly efficient in the case of boron-doped diamond (BDD) anode [17,18]. BDD( $\bullet\text{OH}$ ) radicals thus generated from water oxidation are strong oxidant species ( $E^\circ(\bullet\text{OH}/\text{H}_2\text{O}) = 2.8 \text{ V/SHE}$ ) [19] and have an averaged lifetime in water of few nanoseconds. They react in a non-selective way with organic compounds by dehydrogenation, hydroxylation or redox reaction [20,21]. Particularly,  $\bullet\text{OH}$  has very quick reaction kinetics with aromatic compounds [20]. Then, further reactions lead to mineralization of organic compounds, i.e. conversion into carbon dioxide ( $\text{CO}_2$ ), water and inorganic ions [13,22]. BDD is a very promising

material when used as anode, as it leads to the production of large amounts of  $\cdot\text{OH}$  on its surface [23,24]. The production of other electrochemically generated redox reagents can simultaneously occur with the generation of BDD( $\cdot\text{OH}$ ), particularly from the oxidation of anions from the salt used as electrolyte (mediated oxidation) [25–27]. The use of stainless steel as counter-electrode is suitable because of its cheapness and robustness [28].

Besides, aerobic biodegradation is the most widespread technique for the treatment of biodegradable compounds from wastewaters. A sufficient concentration of oxygen and nutrients is supplemented for promoting the growth of aerobic microorganisms and the metabolism of organic compounds.

However, effective degradation of PAH requires the use of costly treatment technologies such as advanced oxidation processes (AOPs) [9,29–34]. Biological treatment (BT) is a more cost-effective alternative [35], but it usually results in low removal efficiencies due to the large amount of poorly-biodegradable compounds and inhibiting extracting agents at high concentrations [36]. A promising alternative for the clean up of SW solutions is to combine an AOP to a BT. By using AOPs as pre-treatment, an increase of the effluent biodegradability is expected [37,38]. On the contrary, post-treatment by AOPs can be used as a polishing step to improve the effluent quality from a BT [39,40]. The potential of BT as post-treatment of an EAOP has been previously demonstrated for pharmaceuticals [41–43], dyes [44] and herbicides [45,46] removal as well as treatment of sanitary leachates [47].

This study investigated the use of two different configurations for the treatment of a synthetic SW solution containing phenanthrene (PHE), Tween<sup>®</sup>80 (TW80) and humic acids. AO was first used as a pre-treatment coupled to an aerobic BT. Subsequently, AO was performed as a post-treatment to polish the residual concentration of contaminants from BT. The efficiency of both treatment strategies was compared to each single process in terms of degradation and mineralization yields of organic compounds. To the best of our knowledge, this is the first study investigating a combined EAOP/BT process for the treatment of SW solutions. Moreover, the use of a BDD anode and a stainless steel cathode has recently shown promising results [48–52]. The combination with a BT is assessed for the first time in this study.

## 2. Materials and methods

### 2.1. Preparation of the synthetic soil washing solution

The synthetic SW solution containing 1.31 g TW80 L<sup>-1</sup>, 25 mg PHE L<sup>-1</sup> and 10 mg C L<sup>-1</sup> of humic acids (HAs) was prepared in a 2 L glass volumetric flask with ultrapure water from a Millipore Milli-Q system (Molsheim, France) (resistivity >18 MΩ cm). The initial COD was 2.7 g L<sup>-1</sup>. A purification step of commercial HAs (Acros Organics) was performed, similarly to the protocol of [53]. The stock solution was prepared by dissolving 0.5 g L<sup>-1</sup> of commercial HAs in milli-Q water at pH 3. This solution was filtered through Whatman GF/F filter (0.7 μm as pore diameter). Then, HAs were precipitated by decreasing pH at 1.2 and the solution was centrifuged at 3000 rpm for 20 min. The supernatant was then removed and the precipitated HAs were dissolved in deionized water and stocked at pH 3. PHE (purity >99.5%) and TW80 (polyoxyethylene (20) sorbitan monooleate) were of reagent grade provided by Sigma Aldrich. All the other chemicals used (nutrients, Na<sub>2</sub>SO<sub>4</sub>, NaOH, H<sub>2</sub>SO<sub>4</sub>) were of reagent grade.

### 2.2. Anodic oxidation

AO process was carried out in an undivided, cylindrical and open batch electrochemical glass cell containing 330 mL of solution to be treated. The anode (working electrode) material was a thin-film BDD deposited onto a Nb substrate (28 cm<sup>2</sup> × 0.2 cm) purchased from Condias GmbH (Itzehoe, Germany) and the cathode material was stainless steel (28 cm<sup>2</sup> × 0.2 cm) from Goodfellow (France). The anode and the cathode were set up face to face with a gap of 3 cm. The constant current intensity was managed by a power supply (HAMEG, model 7042-5, Germany) in the range 200 – 1000 mA. A magnetic stirrer ensured continuous agitation in the electrochemical cell. A larger glass reactor was also used, with a working volume of 800 mL. A similar ratio between the immersed area of electrodes and total volume of the solution was ensured. The distance between the electrodes was fixed in order to reach a similar electric potential during both experiments. Na<sub>2</sub>SO<sub>4</sub> was added as electrolyte at a concentration of 0.05 M, according to the optimal experimental conditions reported by [12]. The solution pH was

initially maintained at 5.5 and 7.0 when AO was used as pre- and post-treatment, respectively.

When BT was used as pre-treatment, the biomass was settled and the supernatant was mixed with  $\text{Na}_2\text{SO}_4$  and transferred to the AO reactor prior performing AO.

### 2.3. Biological treatment

An aerobic biological reactor was operated in batch mode in a 2 L cylindrical open beaker with a working volume of 1 L. The reactor was inoculated with activated sludge from a municipal wastewater plant (Cassino, Italy). Before each experiment, microbial cultures were acclimated to the feed solution (initial or pre-treated SW solution) for 2 weeks. In particular, during the first 3 d of acclimation, microbial activity was stimulated by adding nutrients and sucrose at a concentration of approximately  $2.7 \text{ g COD L}^{-1}$ . Subsequently, sucrose was gradually replaced each 3 or 4 days by the feed solution, in order to decrease the sucrose contribution to total COD from 50 to 0%.

The biological reactor was operated as follows: continuous aeration with air in order to maintain oxygen concentration  $> 2.5 \text{ mg O}_2 \text{ L}^{-1}$ ; regular pH adjustment with NaOH in order to keep the pH in the range 6.5 – 7.5; continuous stirring at 300 rpm by means of a rod stirrer. Temperature was naturally maintained at  $23 \pm 2 \text{ }^\circ\text{C}$ .  $\text{NH}_4\text{Cl}$  and  $\text{K}_2\text{HPO}_4$  were added as sources of N and P, respectively, in order to keep a ratio COD:N:P  $> 100:5:1$  during the experiments.  $\text{CaCl}_2$  ( $27.5 \text{ mg L}^{-1}$ ),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  ( $0.25 \text{ mg L}^{-1}$ ),  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  ( $22.5 \text{ mg L}^{-1}$ ),  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  ( $0.21 \text{ mg L}^{-1}$ ),  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  ( $0.34 \text{ mg L}^{-1}$ ),  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  ( $0.084 \text{ mg L}^{-1}$ ) were also added in order to ensure sufficient mineral nutrients for microbial activity.

The initial volatile suspended solid (VSS) concentration was  $0.35 \pm 0.05 \text{ g VSS L}^{-1}$  in each experiment. VSS were analyzed according to the method from Rodier et al. [54].

COD, TW80 and PHE concentrations were monitored for a total duration of 15 d. Then, the biomass settled for 2 h and the supernatant was subsequently used for electrochemical treatment or final analysis.



When AO was performed as pre-treatment, pH adjustment at pH 7 with NaOH (1 M) was the only intermediate step required before the BT. The addition of the biomass led to a dilution of the pre-treated solution by approximately 10%.

## 2.4. Analytical procedures

During BT, the soluble fraction of the chemical oxygen demand ( $\text{COD}_{\text{sol}}$ ) and TW80 were analyzed after filtration of samples at  $0.45 \mu\text{m}$  on Millex cellulose membranes. Non-filtered samples were analyzed for the total COD ( $\text{COD}_{\text{tot}}$ ). Thus, the particulate fraction of COD ( $\text{COD}_{\text{part}}$ ) was calculated as the difference between  $\text{COD}_{\text{tot}}$  and  $\text{COD}_{\text{sol}}$ . Two different fractions of PHE were analyzed ( $<1.5 \mu\text{m}$  and  $>1.5 \mu\text{m}$ ) in order to evaluate eventual sorption mechanisms between PHE and the biomass. Whatman 934-AH glass microfiber filters ( $>1.5 \mu\text{m}$ ) were used and microwave extraction was subsequently applied to the filter, according to the USEPA method 3546 [55], prior to analysis of the  $>1.5 \mu\text{m}$  fraction.

### 2.4.1. Phenanthrene

Liquid-phase PHE was determined by a reversed phase liquid chromatography (HPLC) Elite LaChrom<sup>®</sup> coupled with a UV detector (Elite LaChrome, L-2400) set at a wavelength of 245 nm. The column (RP C-18, Purospher<sup>®</sup>, Merck) was placed in an oven set at  $40.0 \text{ }^\circ\text{C}$  and the mobile phase was a mixture of methanol/water (78:22 v/v) with a flow rate of  $0.8 \text{ mL min}^{-1}$  in isocratic mode. A  $20 \mu\text{L}$  injection loop was used.

### 2.4.2. Tween<sup>®</sup> 80

TW80 was quantified by a spectrofluorimetric technique as reported by [56]. Fluorescence analyses were performed with a Kontron SFM 25 spectrofluorimeter set at 318 nm for excitation and 428 nm for emission. TW80 was determined in the range of 1 – 35 mg TW80  $\text{L}^{-1}$ . Preliminary experiments showed the absence of significant interference coming from PHE and humic acids under these conditions.

### 2.4.3. Chemical oxygen demand

COD was determined following the photometric method from [57] (100 – 1000 mg O<sub>2</sub> L<sup>-1</sup> range). Samples were added to the COD tubes containing a mixture of digestion solution and acidic reagent and further incubated at 148 °C for 2 h in a Spectroquant® TR 420 (Merck, Germany) digester. Samples were analyzed at 605 nm using a Spectroquant® NOVA 60 (Merck, Germany) photometer.

### 2.4.4. Biodegradability

The biodegradability of the SW solution and AO pre-treated samples was assessed respirometrically (OECD 301F, ISO 9048) by monitoring the evolution of the biological oxygen demand (BOD) during the incubation time. An OxiTop® IS 6 system (WTW, Germany) was used for both initial solution and pre-treated samples. The saline solution was prepared as reported by Rodier et al. [54]. The phosphate buffer solution was adapted from Rodier et al. [54]. NH<sub>4</sub>Cl was added in order to reach a ratio of 100:5 between the initial COD of the synthetic soil washing solution and the nitrogen concentration. Thus, a circum-neutral pH was used and enough nutrients were provided for bacterial growth. N-allylthiourea was added in order to inhibit nitrification. Sludge from a conventional activated sludge plant operated under extended aeration was used as inoculum. All pre-treated samples were diluted 1.3 times in the bottles used for BOD measurements. A control of the endogenous respiration was performed by replacing the samples with ultrapure water. All the bottles were incubated at (20.0±0.1) °C in dark for 45 d. The oxygen consumption (BOD<sub>t</sub>) was followed every day using the OxiTop® IS 6 system. Then, the effluent biodegradability was assessed after 5 d, by the ratio between BOD<sub>5</sub> and initial COD (COD<sub>0</sub>), and when BOD reached a final plateau (ultimate BOD, BOD<sub>u</sub>), by the ratio BOD<sub>u</sub>/COD<sub>0</sub>.

### 2.4.5. Carboxylic acids

Generated carboxylic acids were quantified by ion-exclusion HPLC using an Altech LC fitted with a Supelcogel H column (9 µm, 25 cm × 4.6 mm) from Supelco at room

temperature. The chromatograph was coupled with an AD20 UV detector from Dionex set at  $\lambda = 220$  nm. The mobile phase was 1%  $\text{H}_2\text{SO}_4$  at  $0.2 \text{ mL min}^{-1}$ . The identification of each carboxylic acid was performed by comparing the retention times obtained with samples and pure standard compounds.

#### 2.4.6. Acute toxicity

Acute toxicity of the solution was assessed through *Vibrio fischeri* (from LUMIstock LCK-487, Hach Lange) bioluminescence inhibition assay using Microtox® standard method (ISO 11348-3). Prior to the analysis, all samples were adjusted to circum-neutral pH (with NaOH) and 22% of NaCl was added to insure an osmotic protection for bacteria. Then, the bioluminescence inhibition percentage was measured using the M500 equipment (Modern Water, United Kingdom), based on 5 min of exposure.

### 2.5. Energy consumption

One of the main costs of the AO process is associated to the use of electrical energy. Therefore, it is important to assess energy consumption (EC). EC was calculated according to the equation (2) [20], as follows:

$$EC (kWh (kg COD)^{-1}) = \frac{E_{cell}It}{(\Delta COD)_t V_s} * 1000 \quad (2)$$

where  $E_{cell}$  is the average cell voltage (V),  $I$  is the applied current (A),  $t$  is the electrolysis time (h),  $V_s$  is the solution volume (L) and  $(\Delta COD)_t$  is the COD decay ( $\text{g O}_2 \text{ L}^{-1}$ ).

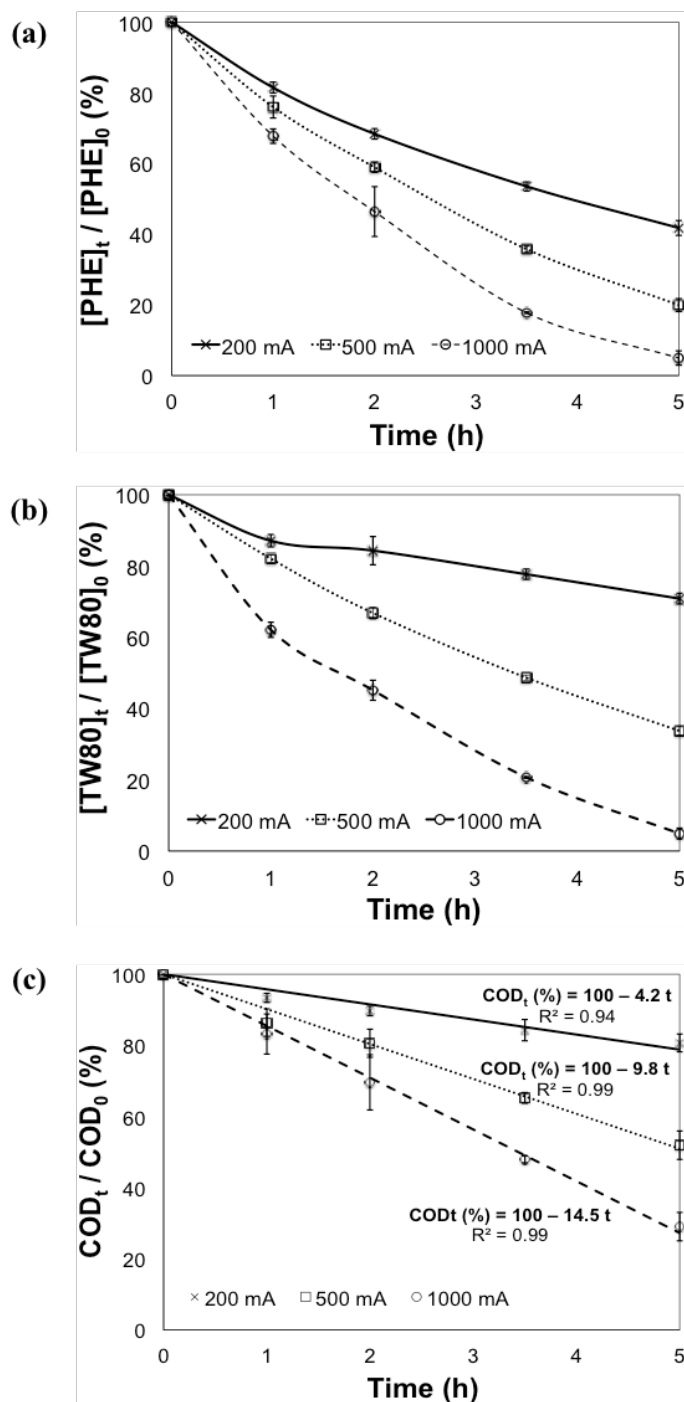
### 3. Results and discussion

#### 3.1. Treatment of the soil washing solution by anodic oxidation

The evolution of COD, PHE and TW80 concentrations during AO was as reported in Figure 5.1. At increasing current intensity, the degradation of organic compounds was faster. More than 95% removal of PHE was observed after 5 h of treatment at 1 A constant current electrolysis. However, faster degradation kinetics had already been reported by using AO with a similar setup. Complete degradation of 0.1 mM atrazine in pure aqueous solution had been observed in 20 min of treatment by AO at 500 mA [24], while the absolute degradation rate of atrazine by hydroxyl radicals was 5 times lower than that obtained for PHE [58,59]. In this study, a slower degradation rate was mainly attributed to the presence of high amount of additional organic compounds (TW80, HAs) acting as hydroxyl radical scavengers [60]. The partition of PHE inside TW80 micelles may also reduce the availability of PHE towards hydroxyl radicals [33,61].

PHE degradation is not the only requirement to fulfill in order to respect the regulation limits of discharge. A significant reduction of the organic load is also required. When AO was used as sole process, more than 70% COD removal was reached after 5 h of treatment at 1 A. Such high mineralization rate is attributed to the generation of large amount of BDD( $\cdot\text{OH}$ ) generated on the surface of the BDD anode [13]. However, COD removal was strongly dependent on current intensity. At 1000 mA, electrolysis led to a 3.7 times higher mineralization rate than at 200 mA. This was due to the production of a greater quantity of BDD( $\cdot\text{OH}$ ) on the anode surface by increasing current intensity. Besides, COD removal was observed to follow a pseudo-zero order kinetic for all the current intensities studied. This linear decrease is consistent with the model developed by Panizza et al. [62], who observed that COD removal occurs under conditions of current control when the concentration of organics is enough high compared to current intensity. These operating conditions allow the reduction of concomitant undesired reactions (such as oxygen evolution at the anode and hydrogen evolution at the cathode), which lead to the decrease of current efficiency. Nevertheless, in the present study AO resulted in high EC values (calculated according to Eq. (2)), *i.e.* 33, 39 and 67 kWh (kg COD)<sup>-1</sup> in the experiments performed at 200, 500 and 1000 mA,

respectively, demonstrating one of the main drawbacks of AO. Moreover, more than 5 h of treatment would be required to reach almost complete COD removal from the SW solution.



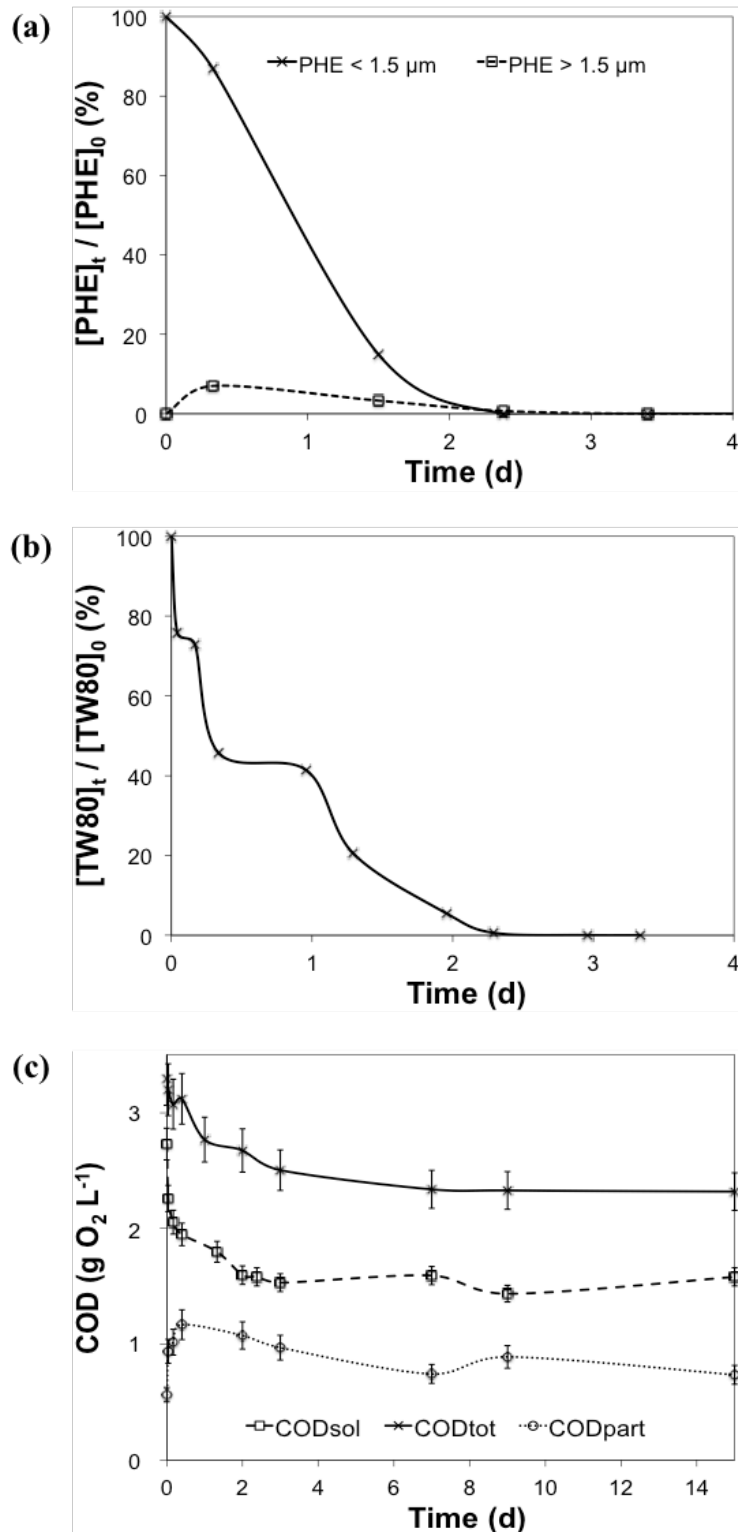
**Figure 5.1.** Evolution of (a) phenanthrene ( $[PHE]_0 = 25 \text{ mg L}^{-1}$ ), (b) Tween® 80 ( $[TW80]_0 = 1.31 \text{ g L}^{-1}$ ) and (c) COD content ( $[COD]_0 = 2.7 \text{ g L}^{-1}$ ) of the SW solution during treatment by AO ( $[Na_2SO_4] = 0.05 \text{ M}$ ;  $V_T = 330 \text{ mL}$ ), in dependence on current intensity. Error bars refer to triplicate experiments.

### 3.2. Biological treatment of the soil washing solution

The effectiveness of the BT for the synthetic SW solution was initially evaluated by monitoring the evolution of BOD in the OxiTop system. The BOD<sub>5</sub>/COD ratio of the initial SW solution was 0.32. According to Rodier et al. [54], this BOD<sub>5</sub>/COD ratio corresponds to a moderately biodegradable effluent. After 15 d of incubation, the ultimate BOD (BOD<sub>u</sub>) was 49% of COD, indicating that the residual organic matter was poorly biodegradable.

Based on these results, the biological treatability of the effluent was further assessed in a batch reactor. The evolution of PHE, TW80, COD<sub>sol</sub> and COD<sub>tot</sub> were as reported in Figure 5.2. PHE and TW80 reached a concentration below the detection limits after 2.4 d of treatment. Biosorption onto microbial cells was not a significant pathway for PHE removal since limited amount of PHE was observed in the fraction >1.5 μm. This was due to the moderate hydrophobicity of PHE as well as PHE partition inside TW80 micelles. A similar behavior has been reported by Sponza et al. [63] during the BT of a petrochemical wastewater by using an activated sludge process. Similarly, phenanthrene volatilization was also strongly reduced by partition into Tween 80 micelles [64,65].

During BT, COD<sub>sol</sub> gradually decreased until reaching a plateau at approximately 56% of the initial concentration (1.2 g O<sub>2</sub> L<sup>-1</sup> removed) after 3 d of treatment. 0.79 g COD<sub>tot</sub> L<sup>-1</sup> was removed whereas COD<sub>part</sub> increased of 0.41 g O<sub>2</sub> L<sup>-1</sup>. The overall COD decrease confirmed that the organic compounds contained in the SW solution were used as carbon source for microbial metabolism. The high residual COD<sub>sol</sub> was due to the production of poorly-biodegradable by-products, which mainly originated from the TW80 biodegradation, as TW80 contributed to 95% of the initial COD. This might be attributed to very different biodegradability of the hydrophobic tail and hydrophilic head of TW80. At the end of the treatment, BOD test performed with fresh activated sludge confirmed the low biodegradability of the effluent solution. The BOD<sub>5</sub>/COD ratio was <0.03 at the end of the BT.

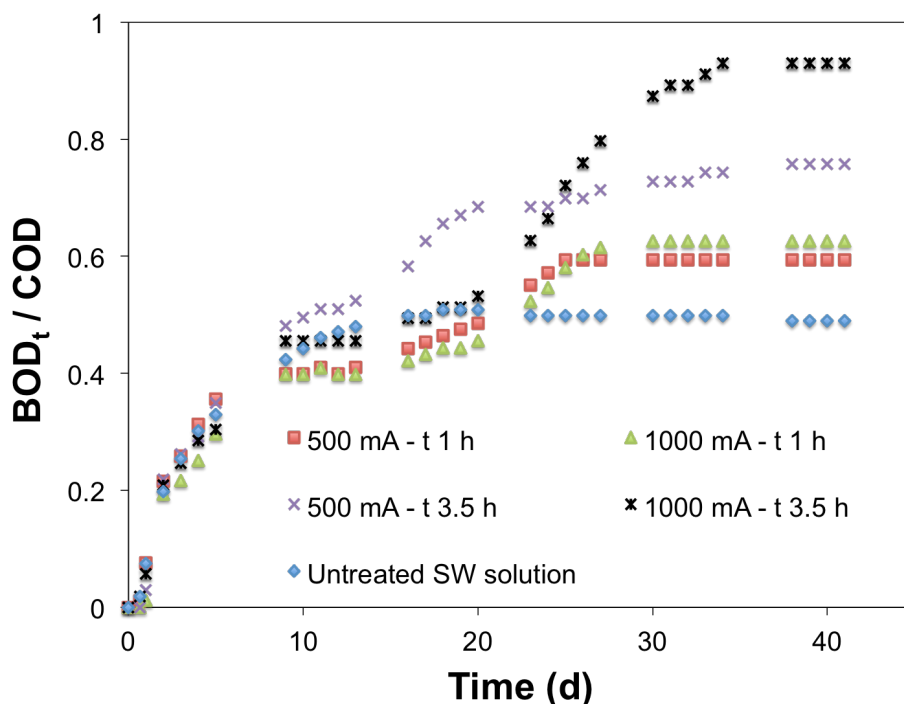


**Figure 5.2.** Evolution of (a) PHE ( $[PHE]_0 = 25 \text{ mg L}^{-1}$ ), (b) TW80 ( $[TW80]_0 = 1.31 \text{ g L}^{-1}$ ) and (c) COD of the SW solution during the biological treatment. Error bars refer to the uncertainty on COD measurements.

### 3.3. Anodic oxidation pre-treatment combined with a biological treatment

In order to increase COD removal efficiencies by BT, an AO pre-treatment was performed to enhance the biodegradability of the effluent. While BOD evolution of the initial SW solution followed an exponential trend, a different behavior was observed for BOD evolution of all the AO pre-treated solutions (Figure 5.3). Two distinct stages were observed. First, BOD evolution followed an exponential trend until it reached a plateau around day 10, corresponding to the removal of the most easily biodegradable compounds. Then, starting from day 15, another increase of the BOD was observed until BOD reached a definitive plateau around day 30 ( $BOD_u$ ). This behavior can be explained by the different nature of the organic compounds in the pre-treated solution, which involved different microorganisms or metabolic pathways for their biodegradation. Therefore, after the consumption of the most easily biodegradable fraction, an additional time was necessary in order to allow biomass adaptation and the biodegradation of slowly degradable organic compounds. This phenomenon is coherent with the study of Mason et al. [66] who observed that a multi-species model involving rapidly and slowly degradable material was more accurate for the description of BOD patterns.





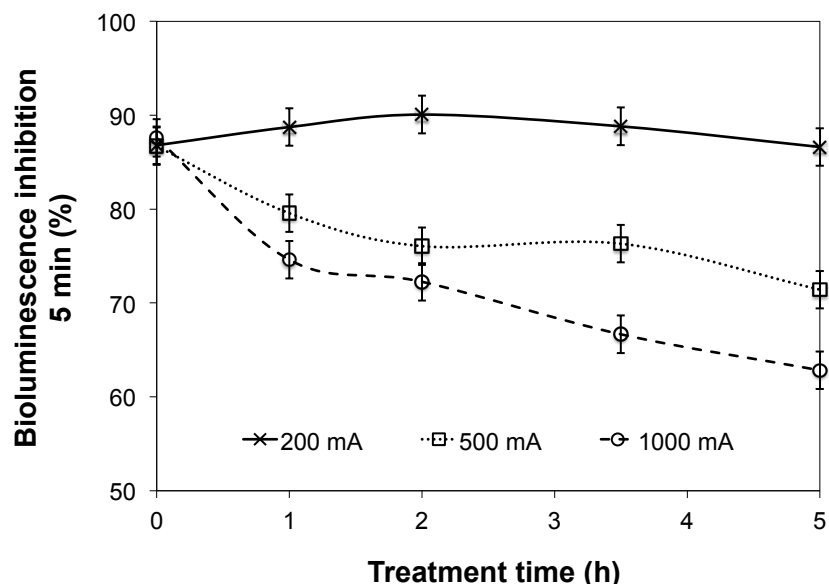
**Figure 5.3.** Evolution of the  $BOD_t/COD$  ratio of the SW solutions pre-treated with AO ( $[Na_2SO_4] = 0.05\text{ M}$ ;  $V_T = 330\text{ mL}$ ) under different current intensity and treatment time conditions.  $BOD_t$  is the biological oxygen consumption after 't' days of incubation of a solution. Uncertainty related to the measurement of each data point is estimated to be  $\pm 0.015$ .

Short AO treatment times resulted in a significant increase of the  $BOD_u/COD$  ratio (Figure 5.3). A higher biodegradability enhancement in terms of  $BOD_u/COD$  ratio was achieved with higher current intensities. After 3.5 h of treatment at 1 A, the  $BOD_u$  of the pre-treated solution reached 95% of the remaining COD, indicating that almost all the compounds in the pre-treated solution were biodegradable. Therefore, the optimal operating conditions for the AO pre-treatment are a compromise between low EC (shorter treatment time and lower current intensity) and high biodegradability enhancement (longer treatment time and higher current intensity).

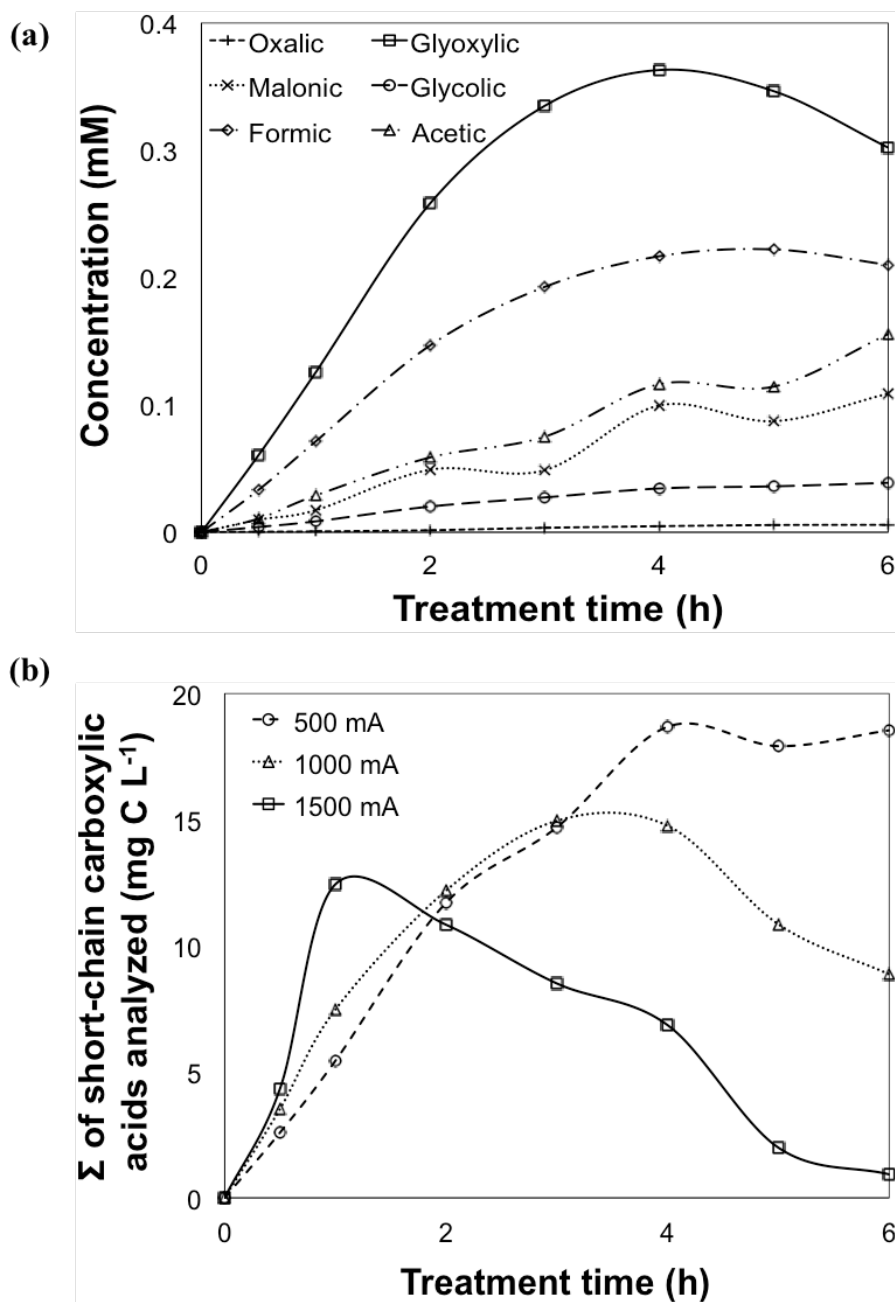
Additional investigations were carried out in order to assess the acute toxicity of the untreated and treated solutions (Figure 5.4) through the Microtox standard test. The initial SW solution displayed high bioluminescence inhibition of *Vibrio fischeri*, indicating high acute toxicity towards this microorganism. While the treatment at

200 mA did not lead to any decrease of the acute toxicity of the effluent during the first 5 h, a significant decrease of the acute toxicity was observed at 500 and 1000 mA. Thus, at higher current intensities, the degradation of the initial toxic compounds was faster with a lower production of potential toxic intermediates due to the faster mineralization of the initial compounds to  $\text{CO}_2$ .

Various degradation by-products are produced during the AO process. For example, short-chain carboxylic acids, including glyoxylic, formic, acetic and malonic acids, were detected in the pre-treated solutions (Figure 5.5a). These are non-toxic and easily biodegradable by-products, which can be removed in a cost-effective way during a biological post-treatment. However, they have lower affinity for  $\cdot\text{OH}$  [67]. The amount and the time-course of the short-chain carboxylic acids produced during AO significantly depended on the current intensity applied (Figure 5.5b). A higher production of carboxylic acids was achieved with lower current intensities because of the lower amount of BDD( $\cdot\text{OH}$ ) generated, leading to their slower mineralization. Besides, slower degradation rates of initial compounds at low current intensity resulted in increasing time necessary to reach the maximum concentration of carboxylic acids.



**Figure 5.4.** *Vibrio fischeri* bioluminescence inhibition by the solution (based on 5 min of exposure time), in dependence on current intensity and treatment time by the AO process ( $[\text{Na}_2\text{SO}_4] = 0.05 \text{ M}$ ;  $V_T = 330 \text{ mL}$ ). Error bars refer to the uncertainty on the measurements.

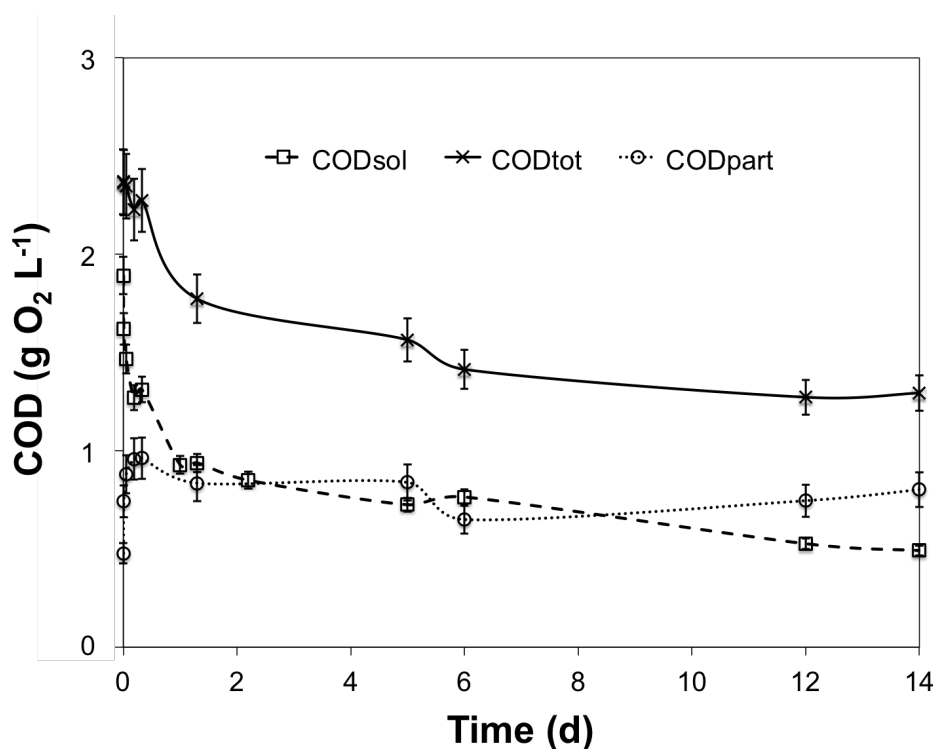


**Figure 5.5** (a) Time-course of the concentration of the main short-chain carboxylic acids produced during the AO of the SW solution ( $I = 500$  mA;  $[Na_2SO_4] = 0.05$  M;  $V_T = 330$  mL); (b) Time-course of the sum of the short-chain carboxylic acids detected during the AO of the SW solution, in dependence on the current intensity.

Finally, it is worth to notice the pH evolution during the AO pre-treatment. AO was performed with the initial natural pH of the SW solution (5.5) as pH was demonstrated not to affect significantly AO efficiency [22]. After 1 h of treatment, pH decreased to a value in the range 3.4 – 3.8 depending on the current intensity used. Then, pH stabilized within the range 3.1 – 3.5. This was attributed to the production of carboxylic acids and the low-acid buffering capacity of the synthetic treated solution. Therefore, a pH adjustment step was necessary prior to performing BT.

Based on these results, the combined process coupling the larger AO reactor (800 mL) and a batch bioreactor was carried out. A pre-treatment time of 3 h and a current intensity of 500 mA were used as a reasonable compromise between biodegradability enhancement, decrease of acute toxicity, maximum short-chain carboxylic acids production and EC. Slightly lower degradation and mineralization kinetics were obtained during AO in the larger reactor ( $\text{COD}_t(\%) = 100 - 7.4 t (\text{h})$ ), compared to the 330 mL reactor ( $\text{COD}_t(\%) = 100 - 9.8 t (\text{h})$ ). Subsequent to AO, BT was performed for 14 d (Figure 5.6). In contrast to previous BOD experiments, the two-stage biodegradation kinetics was not observed. This was most likely attributed to the better acclimation of the microorganisms that resulted in a rapid consumption of the  $\text{COD}_{\text{sol}}$  in the first 3 d of treatment. Then, the degradation of  $\text{COD}_{\text{sol}}$  slowed down between days 3 and 14 because of the recalcitrance of some oxidation by-products.

In conclusion, the application of standalone AO and BT processes allowed reaching 27 and 44% of COD removal, respectively, while the combination of both processes led to 80% of COD removal, significantly higher than the addition of COD removal obtained with the two “stand-alone” processes. This indicates a synergistic effect between both processes, due to the formation of more easily biodegradable by-products during AO. At the end of the combined AO/BT, the residual COD was mainly due to the incomplete biodegradation of the initial compounds remained after the AO pre-treatment (52 and 33% for TW80 and PHE, respectively).

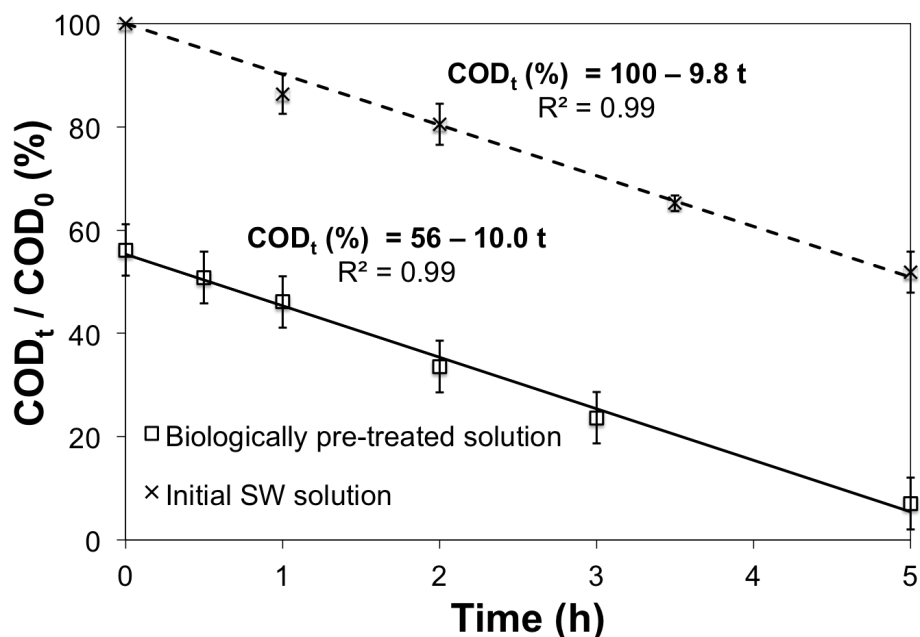


**Figure 5.6.** Evolution of the COD content during the biological treatment of the pre-treated SW solution by AO ( $t = 3$  h;  $I = 500$  mA;  $[Na_2SO_4] = 0.05$  M;  $V_T = 800$  mL). Error bars refer to the uncertainty on COD measurements.

### 3.4. Anodic oxidation post-treatment following biological treatment

The opposite configuration, with AO as post-treatment following BT, was then evaluated with the main purpose to apply AO only for the residual poorly-biodegradable fraction of the effluent after BT.

Results of AO performed at 500 mA as post-treatment of the effluent biologically treated beforehand are presented in Figure 5.7 and compared to results obtained during the treatment of the initial SW solution with similar operating conditions. 58% and 88% of the COD remained after BT was removed after 3 h and 5 h of AO, respectively, resulting in 24% and 7% residual COD compared to the initial COD of the SW solution. This clearly indicates the effectiveness of the use of AO for removing poorly-biodegradable compounds and increasing the quality of a biologically treated SW effluent.



**Figure 5.7.** COD evolution during treatment of the initial SW solution ( $COD_0 = 2.7 \text{ g L}^{-1}$ ) and biologically pre-treated solution ( $COD_0 = 1.5 \text{ g L}^{-1}$ ) by the AO process ( $I = 500 \text{ mA}$ ;  $[Na_2SO_4] = 0.05 \text{ M}$ ;  $V_T = 330 \text{ mL}$ ).

COD abatement of the biologically pre-treated solution followed a linear trend during the first 5 h of AO treatment indicating that the amount of soluble organic compounds was still high enough to perform COD removal under conditions of current control. Based on the pseudo-zero order model, COD removal rate was similar during the treatment of both initial and biologically pre-treated SW solution (Figure 5.7). Moreover, similar EC was also observed during the treatment of the biologically pre-treated effluent ( $33 \text{ kWh (kg COD)}^{-1}$ ) and treatment of the initial solution ( $39 \text{ kWh (kg COD)}^{-1}$ ), which contained a higher organic load. However, Olvera-Vargas et al. [68] reported an increase of the EC (in terms of  $\text{kWh (kg TOC)}^{-1}$ ) when the organic load was lower during the treatment by EAOP of ranitidine (in the range  $30\text{--}120 \text{ mg L}^{-1}$ ). This was explained by the deceleration of the parasitic reactions such as oxygen evolution because of the greater amount of hydroxyl radicals that reacted with a larger amount of organic compounds. The different behavior observed in the present study can be attributed to the fact that COD removal occurred under current control for both experiments due to high initial organic load, therefore, parasitic reactions such as oxygen evolution only played a minor role in both cases. Moreover, biodegradation by-products in the

biologically pre-treated effluent could be more available towards hydroxyl radicals due to micelle breakdown during the BT. This is coherent with the recent study from Dos Santos et al. [61,69] showing that steric hindrance of large micelles seems to prevent direct oxidation of micelles on the anode surface.

However, the BT/AO did not give an overall significant synergistic effect since the combined process with 5 h of AO post-treatment led to 93% COD removal, while the addition of COD removal obtained with two “stand-alone” processes was 92%.

Interestingly, it was also observed that AO short treatment time increased the biodegradability of the biologically pre-treated effluent. While the BOD<sub>5</sub>/COD ratio was <0.03 after BT, it increased to 0.44 after 2 h of treatment at 500 mA. Similarly to what observed when AO was used as pre-treatment, this was due to the degradation of poorly-biodegradable compounds into more easily biodegradable by-products.

## 4. Conclusions and perspectives

This study showed that the combination of AO and BT is a promising treatment strategy for high strength SW solutions. Following conclusions can be listed from the obtained results:

- AO led to 95, 95 and 71% removal of TW80, PHE and COD, respectively, after 5 h of treatment at 1 A but resulted in high electrical EC, i.e. 67 kWh (kg COD)<sup>-1</sup>.
- A complete biodegradation of PHE and TW80 was observed during 2.4 d of BT. However the COD removal only reached a plateau at 44% after 3 d due to the production of poorly-biodegradable by-products.
- When the combined AO/BT system was used, short AO pre-treatment times (1 h, 3 h) increased the final biodegradability of the effluent. This was due to the degradation of hardly biodegradable initial compounds into more easily biodegradable oxidation by-products such as short-chain carboxylic acids. Therefore, a synergistic effect was observed when coupling BT with a 3 h pre-treatment by AO at 500 mA, leading to 80% COD removal.
- The use of AO as post-treatment following BT allowed reaching high quality effluent. COD abatement rate was similar during the treatment of both biologically pre-treated and initial SW solutions. Interestingly, short AO treatment times (2 h) increased the biodegradability of the biologically pre-treated effluent.

Synergistic effect obtained with the combined approach gave very promising results for the development of a combined process with high effectiveness, optimized operating conditions and lower costs. In the view of an application at industrial scale, the logical perspective of this work is the scale-up of a pilot plant operated in continuous or sequential batch mode. Particularly, it would be very interesting to investigate the influence of recirculation loops between both processes in order to perform AO as both pre- and post-treatment and enhance the final quality of the effluent.



This study also emphasized that biological and AO processes lead to the production of different degradation by-products. Large amount of poorly-biodegradable by-products were produced during BT, while the biodegradability of the solution was improved after AO treatment. Therefore, a detailed comparative study of degradation pathways would be necessary for a better understanding of the degradation mechanisms.

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# **CHAPTER 6**

## **CONCLUSIONS AND PERSPECTIVES**

## **1. General overview and conclusion**

This research project focused on the treatment of polycyclic aromatic hydrocarbon (PAH) contaminated soils by soil washing processes (SW) using Tween<sup>®</sup> 80 (TW80) as extracting agent. Particularly, the results presented and discussed in this thesis emphasized new improvements for the treatment of SW solutions, with a direct impact on the effectiveness and cost efficiency of SW processes.

### **1.1. Characteristics of contaminated soils are a critical parameter**

The choice and the effectiveness of remediation processes depend on the nature and level of contamination and sequestration of pollutants [1]. Experiments with artificially contaminated soils overestimate the effectiveness of remediation processes. Thus, the first experiments were dedicated to a better understanding of characteristics of real tar oil-contaminated soils (Chapter 2). The sand fraction of historically tar oil-contaminated soils appeared to contain a large amount of PAHs associated to various coal/coke/wood particles as well as solid particles of resinified and weathered tar oil, with a widely recognized low (bio)availability. This behavior of PAH partitioning strongly reduces SW effectiveness and only several SW steps at high surfactant concentration may lead to sufficient removal rates (Chapter 4). This is why the reuse of SW solutions is a critical issue for SW processes. Moreover, at the highest levels of tar oil resinification and pollutant sequestration, both bioremediation and surfactant enhanced SW processes may lead to insufficient removal rates. In this case, the selective separation of the most contaminated and less (bio)available fraction is a promising technique, as presented in Chapter 2.

### **1.2. Anodic oxidation is a promising process for the treatment of soil washing solutions**

The main part of this thesis aimed at the development of a suitable and effective treatment strategy for the management of soil washing solutions. The literature review

(Chapter 1) identified electrochemical advanced oxidation processes (EAOPs) as an effective technology for the treatment of SW solutions because of their ability to degrade and mineralize a large range of recalcitrant organic pollutants [2,3]. EAOPs have also several technical benefits such as the absence of storage and handling of chemicals, an easily automated operation as well as a compact and modular reactor design [4]. This is why they are attractive for decentralized wastewater treatment. Particularly, this may allow the treatment of SW solutions on-site in order to decrease costs associated to the transport of contaminated effluents.

Among the different EAOPs, anodic oxidation (AO) has been selected for the treatment of SW solutions. Chapter 3 presents results obtained for the removal of humic acids during electro-Fenton and AO processes. It was observed that the possibility to use non-carbonaceous materials as cathode during AO avoid adsorption phenomenon occurring during electro-Fenton [5]. Since SW solutions contain a large range of hydrophobic compounds, the absence of adsorption during AO can facilitate the monitoring of removal of organic compounds, avoid the fouling of electrode materials and improve the robustness of the process. Moreover, AO does not require acidification of the solution and oxygen supply compared to the electro-Fenton process. This latter is a critical parameter since foaming during oxygen supply might be an important drawback at industrial scale. Furthermore, additional operating costs are avoided.

AO is based on the use of “non-active” anodes with high  $O_2$  evolution overpotential [3]. Particularly, the use of boron doped diamond (BDD) has shown very interesting results because this material combines the ability to generate large amount of hydroxyl radicals ( $\cdot OH$ ) with various other very interesting properties such as an inert surface (low adsorption and high deactivation resistance) as well as a high mechanical and corrosion resistance [3]. The cathode is the non-working electrode during AO; therefore, stainless steel cathode met the main requirements expected from the material used as cathode, which are high conductivity, mechanical resistance and robustness.

By comparison to conventional wastewater treatment processes, the AO process presents also some drawbacks, including a high energy consumption, the required addition of a sufficient amount of electrolyte (even if it is the only chemical required during AO) and the cost of BDD electrodes. This is why the objective of this research

project was also to assess whether and how the advantages and benefits arising from the use of AO for the treatment of SW solutions can surpass the actual drawbacks of this process (mainly operating costs).

### **1.3. Soil washing solution reuse vs removal of the organic load: main results and recommendations**

This thesis aimed at the investigation of the best way to implement the AO process for the treatment of PAH and TW80-containing SW solutions. Both synthetic and real SW solutions (by using the sand fraction of a historically contaminated soils) were studied. Based on the results obtained, two different treatment strategies have been identified (Chapters 4 and 5).

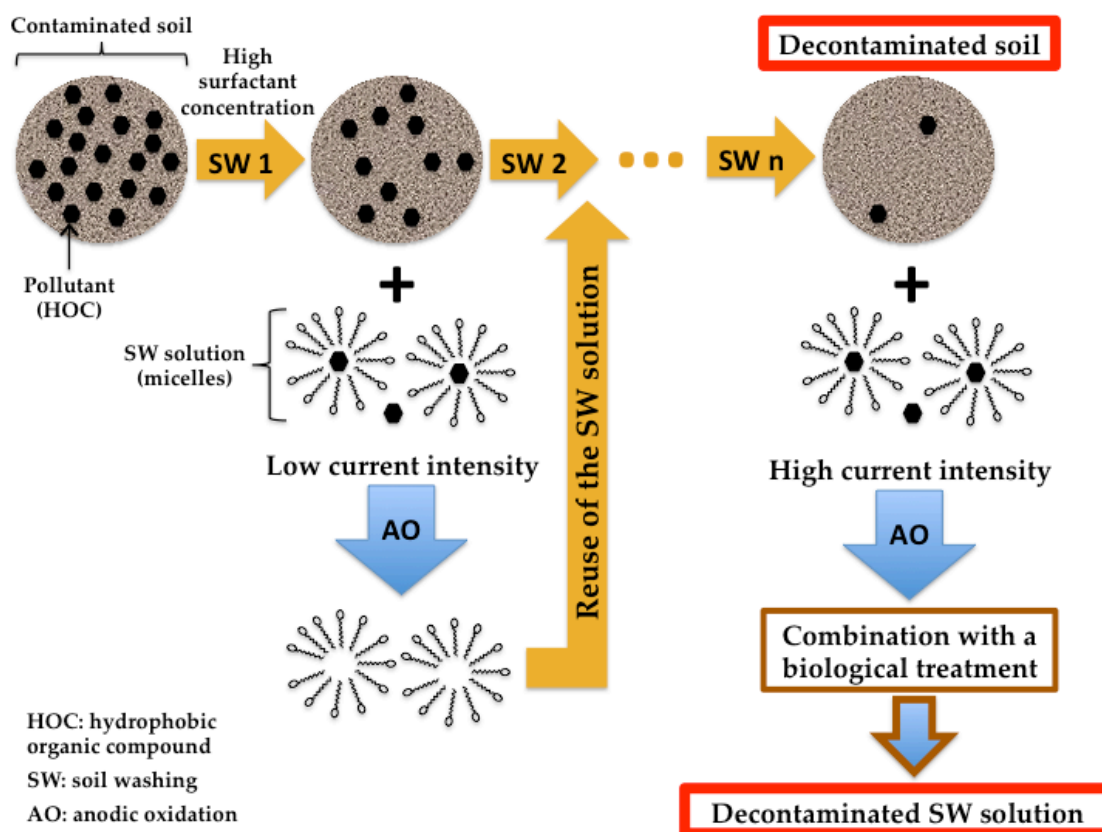
First, the treatment of a real SW solution by AO at low current intensity (50 mA) during a long treatment time (23 h) leads to the selective degradation of target pollutants (PAHs) (Chapter 4). Thus, the treated SW solution can be reused for additional SW steps. This strongly improves the cost-effectiveness of the SW process. The challenge relied on the fact that PAHs are entrapped inside surfactant micelles, which form a protective environment. However, the detailed understanding of degradation mechanisms during AO emphasized that low current intensity strongly hinders micelle oxidation (steric hindrance phenomenon for oxidation on the surface of the BDD anode), while free (extra-micellar) compounds can still be oxidized. Then, the remaining entrapped target pollutants can also be released in the aqueous phase, according to the micellar / aqueous phase partitioning coefficient ( $K_m$ ) (Figure 5.7). This study also emphasized that a high surfactant concentration increases the selective degradation of target pollutants and decrease only slightly the degradation kinetics of PAHs (at low current intensity). These results have two major implications for the treatment of the historically contaminated soil studied, which contains large amount of highly sequestered pollutants:

- Several SW cycles can be implemented for increasing removal rates of PAHs from the contaminated soil without additional consumption of surfactant, due to the reuse of the SW solution;

- High concentration of surfactant can be used in order to increase the transfer of PAHs from the soil-sorbed fraction to the washing solution, because the additional amount of surfactant used might be compensated by the higher selective degradation of PAHs during AO at low current intensity.

The other treatment strategy aimed at improving the cost-effectiveness of the removal of the organic load during the treatment of a synthetic SW solution (Chapter 5). Biological treatments are widely considered as cost-effective processes for the removal of organic compounds from the aqueous phase; however, insufficient mineralization rates were observed during the treatment of the synthetic SW solution due to the recalcitrance of some degradation by-products (Chapter 5). This is the reason why we investigated the use of AO in combination with a pre- or post-biological treatment. It was observed that high current intensity (500 mA) during AO leads to the fast degradation of organic compounds as well as to the production of more biodegradable by-products. Thus, synergistic effects were observed for the combination of AO with a post-biological treatment and only short treatment times by AO were required (3 h). Moreover, after a biological treatment, AO can also act as a polishing step for the removal of non-biodegraded compounds.

These two treatment strategies can be used in a complementary way. One important advantage of AO is the possibility to manage easily the operating conditions [4]. Thus, one can imagine an AO treatment unit, initially treating the SW solution at low current intensity in order to reuse the solution, and when sufficient pollutant removal rate from soil is reached, treating the SW solution at high current intensity in order to remove the organic load with a possible combination with a biological treatment. This is schematically explained in Figure 6.1.



**Figure 6.1.** Treatment strategy for the decontamination by a soil washing process of the historically contaminated soil studied during the thesis. The implementation of the anodic oxidation process for the treatment of soil washing solutions allows the reuse of SW solution for  $n$  soil washing steps. The organic load of the final soil washing solution can be removed in a cost-effective way by combining anodic oxidation and a biological treatment.

A critical parameter during AO operation is the energy consumption. The lower the current intensity, the lower the energy consumption. This is the reason why SW solution reuse by using AO at low current intensity only required  $13.2 \text{ kWh m}^{-3}$  (Chapter 4). By considering the price of the electricity as  $0.12 \text{ € kWh}^{-1}$ , this corresponds to an energy consumption cost of  $1.6 \text{ € m}^{-3}$ . The cost of TW80 can be estimated at  $4 \text{ € kg}^{-1}$ . Therefore,  $1 \text{ m}^3$  of a solution at  $5.0 \text{ mM}$  of TW80 ( $6.6 \text{ g L}^{-1}$ ) costs  $26.2 \text{ €}$ . Thus, savings arising from SW solution reuse may largely compensate treatment costs. By comparison, the higher current intensity required during the second treatment strategy used for organic pollutant removal leads to a strong increase of the energy consumption (Chapter 5). This latter was assessed to be  $39 \text{ kWh (kgCOD)}^{-1}$  and  $33 \text{ kWh (kgCOD)}^{-1}$  during AO pre-

treatment at 500 mA and AO post-treatment at 500 mA, respectively. By considering 3 h of AO pre-treatment (29% COD removal of an initial solution at  $2.7 \text{ gO}_2 \text{ L}^{-1}$ ) or 3 h of AO post-treatment (54% removal of the COD remaining after the biological treatment ( $1.5 \text{ gO}_2 \text{ L}^{-1}$ ), this corresponds to the consumption of  $30.5 \text{ kWh m}^{-3}$  ( $3.7 \text{ € m}^{-3}$ ) or  $26.7 \text{ kWh m}^{-3}$  ( $3.2 \text{ € m}^{-3}$ ), respectively. This is much higher than the energy consumption involved for SW solution reuse. Moreover, the costs of biological treatment (mainly energy consumption of air compressors for  $\text{O}_2$  supply) are not considered and it might be necessary to use AO as both pre- and post-treatment. However, a final step for the removal of the organic load from SW solutions is always required prior SW solution discharge in order to avoid contamination of the aquatic environment.

This short cost-benefit analysis confirms the necessity to reuse SW solutions and, thus, the suitability of the treatment strategy proposed in this thesis (Figure 6.1); Table 6.1 recapitulates the most suitable operating conditions emphasized in this research work. Future works should now focus on the scale-up of the process in order to assess the suitability of the approach for field scale applications.



**Table 6.1.** Recapitulative table of the most suitable operating conditions determined during this research project for the treatment of soil washing solutions by electrochemical advanced oxidation processes. \* Costs of the pre- or post-biological treatment are not considered.

Parameter	SW <sup>1</sup> solution reuse		Organic load removal	
	AO <sup>2</sup>	AO pre-treatment *	AO post-treatment *	
Effluent	Real SW <sup>1</sup> solution	Synthetic SW solution (2.7 gO <sub>2</sub> L <sup>-1</sup> )		
Anode	BDD <sup>3</sup> (28 cm <sup>2</sup> )	BDD <sup>3</sup> (28 cm <sup>2</sup> )	BDD <sup>3</sup> (28 cm <sup>2</sup> )	
Cathode	SS <sup>4</sup> (28 cm <sup>2</sup> )	SS <sup>4</sup> (28 cm <sup>2</sup> )	SS <sup>4</sup> (28 cm <sup>2</sup> )	
Volume	330 mL	330 mL	330 mL	
Electrolyte	Na <sub>2</sub> SO <sub>4</sub> (0.05 M)	Na <sub>2</sub> SO <sub>4</sub> (0.05 M)	Na <sub>2</sub> SO <sub>4</sub> (0.05 M)	
Current intensity	Low (50 mA)	High (500 mA)	High (500 mA)	
Treatment time	23 h	3 h	3 h	
Energy consumption	13.2 kWh m <sup>-3</sup>	30.5 kWh m <sup>-3</sup>	26.7 kWh m <sup>-3</sup>	
Benefits	<ul style="list-style-type: none"> <li>- 80% removal of Σ PHE<sup>5</sup>, ANT<sup>6</sup>, FLUO<sup>7</sup>, PYR<sup>8</sup></li> <li>- Reuse of the SW solution with 5% lower extraction capacity than a fresh SW solution</li> </ul>	<ul style="list-style-type: none"> <li>- 29% COD removal</li> <li>- Increase of the biodegradability</li> </ul>	<ul style="list-style-type: none"> <li>- 54% removal of the COD remaining after the biological treatment</li> <li>- Re-increase of the biodegradability</li> </ul>	

<sup>1</sup> soil washing; <sup>2</sup> anodic oxidation; <sup>3</sup> boron-doped diamond; <sup>4</sup> stainless steel; <sup>5</sup> phenanthrene; <sup>6</sup> anthracene; <sup>7</sup> fluoranthene; <sup>8</sup> pyrene

## **2. From laboratory scale to field scale application: perspectives and scientific challenges**

This subsection focuses on perspectives related to the development and scale-up of SW solution treatment by AO. However, other scientific challenges related to this thesis are still under investigation or would deserve further studies. For example:

- The development and scale-up of the selective separation of the most contaminated fraction in tar oil-contaminated soils.
- The development of the model presented in Chapter 3 (application to other organic compounds, influence of current intensity, consideration of degradation by-products and oxidation pathways, better understanding of sorption mechanisms during electrolysis etc.).
- The development of a mathematical and mechanistic model for the oxidation of surfactants and organic compounds entrapped in micelles.
- The influence of successive SW steps on total PAH removal from soils (does a plateau is reached?)
- Additional studies on the biological treatment (respirometric data, implementation of a reactor in a continuous-flow mode, modeling).
- The treatment of SW solutions by a selective adsorption step on activated carbon, combined with the regeneration of the activated carbon by the electro-Fenton process.

The development of electrochemical advanced oxidation processes (EAOPs) also offers a variety of research challenges and perspectives for the scientific community. For example, the combination of electrochemical processes with adsorption or membrane processes are promising treatment strategies. In fact, these integrated processes aims at the separation and concentration of micro-pollutants in order to allow their destruction by EAOPs in a cost-effective way. These topics would also deserve a lot of discussion and additional researches.

## 2.1. Application to other contaminated soils: what is the influence of soil characteristics?

It is worth to consider that the results obtained in Chapter 4 on SW solution reuse have been obtained with a specific soil. The process was applied to the sand fraction (63 – 2000  $\mu\text{m}$ ) of a real historically tar oil-contaminated soil, in which it was observed a lot of solid particles of resinified and weathered tar oil containing a large amount of PAHs with a widely recognized low (bio)availability. Thus, the treatment of such contaminated fraction is challenging from the viewpoint of environmental engineering.

However, the success of soil remediation processes tightly relies on characteristics of contaminated soils. Soil is a complex matrix, which can present very different characteristics. First, the soil organic matter content may affect the efficiency of both SW (soil organic matter could as competitor with target pollutants for solubilization in micelles) and SW solution treatment ( $\cdot\text{OH}$  scavenging effect). The influence of the presence of large amount of fine clay materials should be also further investigated. The higher specific surface of the fine fraction can increase surfactant adsorption on soil particles. This would lead to the loss of large amounts of surfactant during SW and would have adverse effects on the possibility to reuse SW solutions. Surfactant sorption depends on surfactant nature as well as amount and nature of clays [6,7]. Therefore, preliminary tests should be always performed in order to choose a surfactant allowing the lowest possible adsorption on the treated soil. Moreover, fine clay particles might also affect the treatment of SW solutions by AO. Particularly, their influence on sorption mechanisms and micelles formation [8] may change the partitioning of target pollutants and surfactant and thus, oxidation mechanisms and kinetics.

Soil contamination by both organic and inorganic (such as heavy metals) pollutants can also often occur. This issue would require further investigations. For example, toxic concentrations of heavy metals may inhibit the biological treatment during the combined approach. Moreover, an additional treatment step would be required in order to remove heavy metals from SW solutions.

Finally, soil characteristics also influence the conductivity of SW solutions, and thus, the amount of additional electrolyte required. Further investigations are required for the optimization of electrolyte consumption during AO in order to decrease operating costs.

An optimum has to be defined since the increase of the solution conductivity also decreases the resistance to current flow and the energy consumption. Moreover, some ions such as sulfates also increase mediated oxidation during AO at high current intensity [3,9]. Besides, it has to be considered that addition of too high concentration of  $\text{Na}_2\text{SO}_4$  might require an additional treatment (ion-exchange resin, biological reduction) in order to avoid contamination of the aquatic environment and to respect specific guidelines from public authorities. The mobilization of chlorides and bromides from soil can also lead during AO to the production of toxic AOX (adsorbable organic halogen), chlorate and perchlorate, which may compromise the quality of the final effluent [4].

## 2.2. Which electrochemical reactor design and configuration?

Successful scale-up of AO is based on a proper configuration of the electrochemical reactor [10,11]. This latter has to be designed in order to reduce mass transfer limitations (because  $\cdot\text{OH}$  are formed in an heterogeneous way in the electrochemical cell, on the surface of the anode) and to optimize current efficiency by minimizing waste reactions. Therefore, the following promising reactor configurations should be further investigated:

- The use of a flow-through electrochemical reactor, which promotes the convective transport of pollutants from the bulk to the anode surface [4]; however this requires the development of porous non-active three-dimensional anodes.
- The reduction of the inter electrode distance, which can reduce the electrical resistance between anode and cathode and the mass transfer limitations [4]; however this may also involves an increase of the ratio electrode surface / reactor volume, and thus, of the capital costs of treatment.
- The operation of current supply in a modulation mode in order to ensure a value of current intensity the closest possible to the limiting current of organic compounds oxidation throughout the treatment [12] (concerning this thesis, this can be applied only for the cost effective removal of the organic of the SW

solution). This aims at optimizing the current efficiency and the energy consumption [12].

The implementation of tests at pilot-scale is required in order to assess which configuration would be the most suitable for industrial scale applications.

The other critical parameter is the development of cost effective electrodes. BDD electrodes present very attractive properties, however their application at large scale is still hindered by their high cost (currently more than 10,000 € m<sup>-2</sup>) and by the limitation to small-scale production of chemical vapor deposition for synthetic diamond manufacturing [4]. Currently, BDD film can be only deposited on costly substrates such as metals (Nb, W or Ta) or silicon; future advances in BDD manufacturing may focus on the use of titanium as substrate, which possesses very interesting characteristics for electrochemical applications [4]. Radjenovic and Sedlak [4] reported that the price of BDD electrodes is expected to drop by approximately half in the next decade. Finally, further investigations would be required on the lifetime of these electrodes.

Aside from advances in BDD manufacturing, it would be also interesting to investigate the combination of different electrodes in order to decrease the capital costs of treatment by AO. For example, mixed metal oxide anodes (dimensionnaly stable anodes (DSA), consisting for example of titanium coated with a layer of metal oxides such as RuO<sub>2</sub>, IrO<sub>2</sub>, PbO<sub>2</sub>, SnO<sub>2</sub>) can also be used for the removal of organic compounds from water [3,4]. Their price is currently about ten times lower than the one of BDD electrodes [4]. However, these materials lead to the production of a higher amount of oxidation by-products and have a lower ability than BDD to achieve total mineralization of organic compounds [4]. Therefore, a suitable configuration might be the combination of DSA and BDD anodes, in order to reduce the surface of BDD used in the electrochemical reactor. DSA anodes would allow the removal of the less recalcitrant organic compounds with similar efficiency than BDD anodes, while these latter would be used for the degradation of the most recalcitrant organic compounds. This might be applied to the treatment strategy studied in Chapter 5, for the cost-effective removal of the organic load. This idea is based on similar conceptual considerations than the combination of AO with a biological treatment.

Finally, sub-stoichiometric titanium oxides are very promising anode materials. They can exhibit performances similar than BDD anodes for removal of organic compounds from water and offer the possibility to produce porous anodes, which can be used in flow-through electrochemical cell and as ultra or nanofiltration membranes [13].

### **2.3. Which configuration for the biological pre- or post-treatment?**

One aspect of particular interest of the combined approach investigated in Chapter 5 is the use of activated sludges from a real wastewater plant as inoculum for the biological treatment. This means that a conventional wastewater treatment plant might be able to treat a SW solution pre-treated by AO. Therefore, in agreement with wastewater treatment plant operators, pre-treated SW solutions might be discharged into the municipal wastewater plant.

Interestingly, it was also observed that AO allows the increase of the biodegradability of both initial solution and biologically pre-treated solution. Therefore, it would be very interesting to assess various configurations for the combined approach such as the implementation of several electrochemical / biological reactors placed in series or a process in continuous mode with recirculation loops between the electrochemical and biological reactors. This would aim at increasing the cost-effectiveness of the process by reducing the treatment time by AO. Ideally, AO should be used only for the degradation of non-biodegradable organic compounds.

It could be also tested various biological reactors, including sequential batch reactors (SBRs), membrane bioreactors (MBs) or moving bed biofilm reactors (MBBRs). They potentially present all some promising advantages. First, the adaptability and easy operation of SBRs might be suitable in a combined approach with an electrochemical reactor operated in batch or for the implementation of a decentralized water treatment system. Then, MBs have higher operating costs but the step of biomass separation from the aqueous phase is very effective. Thus, this would allow the optimization of a post-treatment by AO by reducing the  $\cdot\text{OH}$  scavenging effect, which could arise from insufficient biomass separation effectiveness during the settling step. Moreover, MBs avoid the use of an additional settling tank. Finally, MBBRs present also a very

promising configuration because high removal rates are usually reported when it is correctly operated [14]. Furthermore, it would be interesting to investigate the use of an integrated process based on the combination in a single reactor of this technology with AO at low current intensity. The absence of mediated oxidation in the bulk at low current intensity and the steric hindrance phenomenon emphasized in Chapter 4 may avoid the oxidation of the biomass attached to the solid supports and could make feasible such integrated approach. Thus, AO could enhance removal rates of the most recalcitrant organic compounds in MBBRs.

## 2.4. Environmental and economical analysis

The application of AO at industrial scale also requires further environmental and economical analyses in order to answer to the following questions:

- What is the cost of AO per unit of service (for example, per volume of water treated, per mass of pollutants removed or per amount of surfactant saved)? This should include capital costs (reactor, electrodes and other devices), energy consumption, electrolyte consumption, eventual transport costs and costs of human resources.
- Does AO is more cost-effective than the other processes currently used for SW solution treatment (for example air stripping, selective adsorption, liquid-liquid extraction, other advanced oxidation processes)? The answer to this question might also depend on contamination characteristics. For example, air stripping will be often preferred in case of volatile organic compounds as target pollutants. Besides, it is worth to mention that most of current processes used for SW solution reuse are based only on a selective separation step; an additional treatment step is then required for the degradation of pollutants. In contrast, AO at low current intensity allows both SW the reuse of the SW solution and the degradation of target pollutants.

Life-cycle assessments as well as cost-effectiveness and cost-benefits analyses are usually the most suitable studies for allowing decision-makers and stakeholders to

compare different alternatives and to select the most appropriate treatment strategy [15]. The application of AO at industrial scale is still often impaired by its high cost. However, such studies would allow the assessment of the balance between this drawback and the important benefits obtained from the use of AO for the treatment of SW solutions (SW solution reuse, high degradation/mineralization rates of recalcitrant organic compounds, compact and modular design giving the possibility to use AO as a decentralized wastewater treatment system).



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## CURRICULUM VITAE

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### EDUCATION AND TRAINING

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- 2013-2016**     **PhD fellow in Environmental Sciences and Technologies**, Erasmus Mundus Joint Doctorate, University of Paris-Est (France) – University of Cassino (Italy) – UNESCO-IHE (The Netherlands).  
“Implementation of electrochemical advanced oxidation processes for the treatment of soil washing solutions from polycyclic aromatic hydrocarbon contaminated soils”.  
Supervisor: Prof. Mehmet A. Oturan.  
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Defended on December 2<sup>nd</sup>, 2016. Reviewers: Prof. Manuel A. Rodrigo (University of Castilla-La Mancha, Spain) and Prof. Marie-Odile Simmonot (University of Lorraine, France).
- 2013**             **Master’s Degree – Quality and Water Treatment**, University of Poitiers (France)
- 2010-2013**     **Engineer’s Degree – Water and Civil Engineering**, Ecole Nationale Supérieure d’Ingénieurs de Poitiers: Graduate School of Engineering, Poitiers (France).
- 2008-2010**     **Preparatory Class for Engineering Schools**, University of Poitiers (France).

### WORK EXPERIENCE

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- Since**             Laboratory of Geomaterials and Environment, University of Paris-Est (France)
- 01/10/2013**     *Doctoral Researcher*  
Micropollutants (polycyclic aromatic hydrocarbons); physics and chemistry of interfaces; catalytic oxidation (electro-Fenton, anodic oxidation, kinetics); reactivity of hydroxyl radicals; solid-liquid interactions and transfers (soil washing, activated carbon, sorption, kinetics, partition equilibrium); process engineering; dynamic modeling.
- 2015**             Helmholtz Centre – UFZ, Leipzig (Germany)
- (6 months)**     *Doctoral Researcher*  
Micropollutants (PAH); physics and chemistry of interfaces; solid-liquid interactions; sequestration of pollutants in real soils; (bio)disponibility; transfer and diffusion of pollutants in soils; biodegradation.
- 2015**             University of Cassino (Italy)
- (6 months)**     *Doctoral Researcher*  
Micropollutants (PAH, pharmaceuticals); oxidation by-products; effluent biodegradability; combined processes (advanced oxidation / biological treatment).

- 2013 AREVA and Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), France  
(6 months) *Master's thesis – Supervisor: Prof. Hervé Gallard*  
“Treatment of uranium mine water”. On-site sampling protocols; chemical equilibrium; speciation; sorption and precipitation mechanisms.
- 2012 UNESCO-IHE, Delft (The Netherlands)  
(4 months) *Research assistant – Supervisor: Dr. Assiyeh Tabatabai and Prof. Maria Kennedy*  
“Ultrafiltration systems for seawater reverse osmosis pretreatment during periods of severe algal blooms”. Solid-liquid interactions; membrane fouling; process engineering.

## **EXPERTISE**

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### **SCIENTIFIC SKILLS**

#### *Process engineering, water and soil analysis*

- Laboratory skills: implementation and monitoring of electrochemical, biological and membrane reactors; extraction of pollutants from soil; sampling protocols.
- Metrology and analysis: liquid chromatography (detector: DAD, Fluo); gas chromatography-mass spectrometry; ionic chromatography, ICP-OES, TOC analyzer; spectroscopy (UV-vis, Fluo, Raman); standardized methods for analysis of wastewater effluents and sludge, respirometry.
- Modeling: development and calibration of dynamic models 1-D; chemical equilibrium and speciation (Minteq software).
- Imaging: stereomicroscope.

#### *Computer skills*

- Programming: Matlab, Aquasim.
- Operating systems: Microsoft Windows, MAC OS.

### **LANGUAGES**

- French: mother tongue.
- English: proficient user (oral and written).
- German: basic user.

### **PROJECT MANAGEMENT**

- Design and planning of experimental procedures in collaboration with various research groups and private partners (AREVA).
- Integration into 3 different international research teams during the doctoral thesis.
- Supervision of 2 research assistants (bachelor level, 3 months) and a Master's thesis (5 months).

## **TEACHING**

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- Practicum – Industrial regulation (52 h) – University of Paris-Est (France).
- Lecture courses – Industrial regulation (12 h) – University of Paris-Est (France).

## **SCIENTIFIC COMMUNICATIONS**

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### **PUBLICATIONS IN INTERNATIONAL PEER-REVIEWED SCIENTIFIC JOURNALS**

Trellu C., Mousset E., Pechaud Y., Huguenot D., van Hullebusch E.D., Esposito G., Oturan M.A., 2016. Removal of hydrophobic organic pollutants from soil washing/flushing solutions: A critical review. **Journal of Hazardous Materials**, 306, 149–174.

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#### BOOK CHAPTERS

**Trellu C.**, van Hullebusch E.D., Huguenot D., Pechaud Y., Esposito G., Oturan M.A. Remediation of soil contaminated by HOCs: How to recover extracting agents from soil washing solutions? In Contaminated soils : from characterization to remediation, **Springer** (Applied Environmental Science and Engineering for a Sustainable Future) (submitted soon).

#### COMMUNICATIONS AT INTERNATIONAL (4) AND NATIONAL (1) CONFERENCES

**Trellu C.**, Ganzenko O., Papirio S., Oturan N., Huguenot D., van Hullebusch E.D., Esposito G., Oturan M.A., 2016. Treatment of soil washing solution by combined processes coupling anodic oxidation and biological treatment. **67<sup>th</sup> Annual Meeting of the International Society of Electrochemistry**, The Hague, The Netherlands (oral).

**Trellu C.**, Pechaud Y., Oturan N., Huguenot D., van Hullebusch E.D., Esposito G., Oturan M.A., 2016. Treatment of soil washing solutions by electro-oxidation with BDD anode: selective removal of target pollutants and biodegradability enhancement, **256<sup>th</sup> ACS National Meeting**, Boston, Etats-Unis (oral).

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#### SEMINARS AND SUMMER SCHOOLS

- Summer schools on contaminated Sediments (Unesco-IHE, 2016), contaminated soils (University of Paris-Est, France, 2015) and biological treatment of solid waste (University of Cassino, Italy, 2014).
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## **HONORS AND AWARDS**

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- Best oral presentation (2015) - Indo-French bilateral meeting on sustainable water purification technologies, Karaikudi, Inde.
- Mobility fellowship from the Mediterranean Office for Youth (2015).
- Mobility fellowship from the Doctoral School “Science, Engineering and Environment” (2015).
- Erasmus Mundus Joint Doctorate fellowship (2013-2016).
- First rank in the class for results obtained at the Graduate School of Engineering (ENSIP, 2013).
- Master’s Degree with honors.

## **REFERENCES**

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