Ministero dell'Istruzione,
dell'Università e della Ricerca

UNIVERSITÀ DEGLI STUDI DI SALERNO

Dipartimento di Ingegneria Civile

Dottorato di Ricerca
in
Rischio e sostenibilità
nei sistemi dell'ingegneria civile, edile ed ambientale

XXX Ciclo (2014-2017)

Advanced processes for remediation of contaminated sediments

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In copertina: immagine presa da "Sonofusion returns to mainstream science"- www. http://atom-ecology.russgeorge.net

ADVANCED PROCESSES FOR REMEDIATION OF CONTAMINATED SEDIMENTS.

Finito di stampare maggio 2018

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Abstract

Sediments play a fundamental role in the aquatic environment, especially for their interaction with the aquatic life. However, in the last decades, due to the increasing anthropic activities, a large amount of contaminants were released into the environment, as well as in the water bodies. The sediments, due to their characteristics, tend to adsorb the polluting compounds becoming a potential sink of contaminants.

Among the several hazardous compounds, polycyclic aromatic hydrocarbon (PAHs) and heavy metals represent the contaminants most frequently detected onto sediments. These compounds are classified as “known” or “probable” human carcinogen by U.S. Environmental Protection Agency (US EPA) and the International Agency for Research on Cancer (IARC).

The presence of hazardous compounds in the sediments constitutes a concern, not only for the possible negative effects on the environment and human health, but also for the technical-economical aspects related to their management. Indeed, contaminated sediments need a proper management and their free disposal in the aquatic system is not allowed. It was estimated that in Europe about 200 million cubic meters of sediments are dredged every year. These dredging activities are necessary not only for remediation purposes, but also to maintain adequate depth of navigation in the water bodies. Once removed, the traditional management options for the sediments include landfill and confined aquatic disposal, which are among the most used solutions. Nevertheless, these options are not sustainable under both an economic and an environmental point of view. The sediment reuse could be an effective alternative, but their adequate treatment is fundamental in order to avoid the possible release of hazardous compounds into the environment and the resulting adverse effects.

In scientific literature different remediation technologies were proposed for treatment of contaminated soil. Few attempts have been also

provide to adapt some of these techniques to polluted sediments. However, due to the specific characteristics of the sediments, including the prevalent fine grain size fraction, the technologies used for soil remediation are not always suitable for sediment treatment.

Advanced Oxidation Processes (AOPs), which are widely used for the wastewater treatment, were also applied for the treatment of other environmental matrices thanks to their technology flexibility.

Among AOPs, ultrasound (US) has raised growing interest in the scientific community, as an environmental friendly technology holding several advantages over conventional treatment solutions.

In the field of wastewater treatment, US has been studied in order to promote either the partial degradation of organic compounds before biological process or the mineralization of the same kind of contaminants. Few research experiences also focused on US application to solid matrices, with the main aim of desorbing inorganic compounds.

In polluted sediments, both organic and inorganic contaminants are simultaneously present and this aspect represents a major challenge in the choice of a remediation technology that could be effective for each kind of polluting compound. In this regard, the application of US can promote both the contaminant desorption from the solid particles and the degradation of the dissolved organic compounds.

Therefore, aim of this work was in the study of the advanced technology effectiveness for the remediation of contaminated sediments. For this purpose, the experimental activity was divided in two main parts:

- the first one focused on the study of US treatment effectiveness in promoting the reduction of both organic and inorganic contamination in a single stage;

- the second part, performed on the basis of the results of the previous phase, was devoted to the assessment of the US effectiveness as treatment prior to another main remediation technique. In particular, US was implemented as pretreatment for electrokinetic (EK) processes.

The first step was conducted at the laboratory of the Sanitary Environmental Engineering Division (SEED) of Salerno University. During this step both sonication frequency and treatment time were varied to investigate their effect on the removal yields of organic (B[α]A and B[α]P) as well as inorganic (Cd, Pb and Zn) contaminants.

Experimental results demonstrated that the application of ultrasonic waves led to an overall reduction of the contaminant concentration. The best performances were achieved for the organic compounds, with high removal efficiencies reached after few minutes of treatment. Heavy metals showed removal yields almost constant in all experiments, despite the sonication frequency as well as the treatment time. The desorption of inorganic compounds was variable for each compound and the best results were obtained for Cd and Zn compared to Pb.

In order to improve the heavy metal desorption by US, two different processing solutions, namely citric acid and ethylenediaminetetraacetic acid (EDTA), were tested as sonication medium. Both solutions determined an improvement in the desorption yields. However, the best performances were achieved with the citric acid, at a sonication frequency of 130 kHz. As previously noted, the variation of the treatment time was observed to be not significant, thus a long US treatment is not justified. In this regard, the process optimisation was pursued by reducing the treatment time. To this end, further tests were performed using a citric acid solution at 130 kHz and 2,5 min of sonication.

An slight decrease in desorption percentage, was observed for each metal. Nevertheless, the desorption yields were satisfactory, with percentages always more than 75%.

The second part of the work was performed at the laboratory of the Bioengineering and Sustainable Processes (BIOSUV) group at the University of Vigo (Spain). In order to evaluate the effectiveness of US as pre-treatment, this technology was applied before the electrokinetic process (EK). To this end, the combined process (US+EK) was compared with the remediation performances provided by the EK alone. Referring to the Cd and Zn, the results demonstrated a comparable desorption efficiency, close to the complete removal, for both EK process alone and US+EK. For Pb, instead, the use of US pre-treatment was able to improve the its desorption promoted a synergetic effect.

The results obtained from the experimental activity proved that US technology could be a promising alternative for the reduction of both organic compounds and heavy metals from contaminated sediments.

The studied process was observed to be very versatile, providing interesting performances as either stand-alone treatment or in combination with other remediation technologies.

Sommario

All'interno dell'ambiente acquatico i sedimenti rivestono un ruolo fondamentale, in particolare per via della loro interazione con gli organismi acquatici. Tuttavia, negli ultimi decenni, a causa delle crescenti attività antropiche, una grande quantità di contaminanti è stata rilasciata nell'ambiente così come nei corpi idrici. I sedimenti, per via delle loro caratteristiche, tendono ad assorbire i composti inquinanti diventando un potenziale serbatoio di tali sostanze.

Tra i numerosi composti pericolosi vi sono gli Idrocarburi Policiclici Aromatici (IPA) ed i metalli pesanti, che rappresentano i contaminanti più frequentemente ritrovati nei sedimenti. Questi composti sono stati classificati, dall'Agenzia Statunitense per la Protezione dell'Ambiente (US EPA) e dall'Agenzia Internazionale per la Ricerca sul Cancro (IARC), come "probabilmente" o "possibilmente" cancerogeni per l'uomo.

La presenza di composti pericolosi nei sedimenti costituisce una preoccupazione, non solo per i possibili effetti negativi sull'ambiente e sulla salute umana, ma anche in riferimento agli aspetti tecnico-economici relativi alla loro gestione. Infatti, i sedimenti contaminati necessitano di una corretta gestione in quanto il loro smaltimento diretto nell'ambiente acquatico non è consentito. È stato stimato che in Europa circa 200 milioni di metri cubi di sedimenti vengono dragati ogni anno. Le attività di dragaggio sono necessarie non solo al fine delle operazioni di bonifica, ma anche per mantenere un'adeguata profondità di navigazione nei corpi idrici. I sedimenti vengono quindi rimossi, le opzioni tradizionali di gestione dei sedimenti includono lo smaltimento in discarica ed il confinamento, che sono tra le soluzioni più utilizzate. Tuttavia, queste opzioni non sono sostenibili né da un punto di vista economico né ambientale. Il riutilizzo dei sedimenti, invece, potrebbe essere un'alternativa efficace, ma al fine di evitare il possibile rilascio di composti pericolosi nell'ambiente nonché i

possibili effetti negativi che ne derivano, un adeguato trattamento risulta fondamentale.

Nella letteratura scientifica diverse tecnologie di bonifica sono state proposte per il trattamento del suolo contaminato ed in pochi casi si è cercato di adattare tali tecnologie anche per il trattamento di sedimenti contaminati. Tuttavia, a causa delle caratteristiche specifiche dei sedimenti, come la prevalenza di frazione a grana fine, le tecnologie utilizzate per la bonifica del terreno non sempre risultano essere adatte per il trattamento dei sedimenti.

I processi di ossidazione avanzata (AOP), sono ampiamente utilizzati per il trattamento delle acque reflue e, grazie alla loro flessibilità, hanno trovato impiego anche per il trattamento di altre matrici ambientali.

Tra gli AOP, gli ultrasuoni (US) hanno suscitato un crescente interesse nella comunità scientifica, essendo considerati una tecnologia rispettosa dell'ambiente e che presenta numerosi vantaggi rispetto alle soluzioni di trattamento convenzionali.

Nel campo del trattamento delle acque reflue gli US sono stati studiati al fine di promuovere la mineralizzazione dei composti organici o la parziale degradazione di tali composti prima del processo biologico. Limitate esperienze di ricerca si sono concentrate anche sull'applicazione degli US alle matrici solide, con l'obiettivo principale di desorbire i composti inorganici.

La presenza contemporanea di contaminanti sia organici che inorganici nei sedimenti, rappresenta una sfida importante nella scelta di una tecnologia di bonifica che possa essere efficace per ogni tipo inquinante. A tal proposito, invece, l'applicazione degli US può promuovere sia il desorbimento dei contaminanti dalle particelle solide che la degradazione dei composti organici nella matrice liquida.

Pertanto, lo scopo di questo lavoro è stato lo studio dell'efficacia di tecnologie avanzate per la bonifica dei sedimenti contaminati. A tal fine, l'attività sperimentale è stata divisa in due parti principali:

- la prima parte è stata focalizzata sullo studio dell'efficacia del trattamento ad US nel promuovere la riduzione, in un'unica fase, della contaminazione organica ed inorganica;
- la seconda parte, eseguita sulla base dei risultati della fase precedente, è stata dedicata alla valutazione dell'efficacia degli US

come pretrattamento di un'altra nota tecnica di bonifica. In particolare, gli US sono stati implementati come pretrattamento al processo elettrocinetico (EK).

La prima parte dell’attività è stata condotta presso il laboratorio della Divisione di Ingegneria Sanitaria Ambientale (SEED) dell'Università di Salerno. Durante questa fase la frequenza di sonicazione ed il tempo di trattamento sono stati variati per analizzare il loro effetto sulle rese di rimozione dei contaminanti organici (B [α] A e B [α] P) ed inorganici (Cd, Pb e Zn).

I risultati sperimentali hanno dimostrato che l'applicazione delle onde ultrasoniche ha portato a una riduzione complessiva della concentrazione di contaminanti. Le migliori prestazioni sono state ottenute per i composti organici, con elevate efficienze di rimozione raggiunte dopo pochi minuti di trattamento. I metalli pesanti hanno mostrato, invece, rese di rimozione poco variabili durante tutti gli esperimenti, nonostante la variazione della frequenza di sonicazione e del tempo di trattamento. Inoltre, il desorbimento dei composti inorganici ha mostrato risultati variabili per ciascuno dei composti considerati e percentuali più elevate per Cd e Zn rispetto al Pb.

Al fine di migliorare il desorbimento dei metalli pesanti tramite il trattamento ad US, due diverse soluzioni di trattamento, ovvero, acido citrico ed acido etilendiamminotetraacetico (EDTA), sono state testate durante il processo di sonicazione. Entrambe le soluzioni hanno apportato un miglioramento dei rendimenti di desorbimento, tuttavia, i migliori risultati sono stati raggiunti con l’impiego dell'acido citrico ed una frequenza di sonicazione di 130 kHz. Come notato in precedenza, la variazione del tempo di trattamento non ha mostrato un contributo significativo nel processo di desorbimento, tale risultato evidenza come un lungo trattamento ad US non risulta giustificato. Pertanto, per l'ottimizzazione del processo è stato ridotto il tempo di trattamento. A tal fine, sono stati eseguiti ulteriori test ad US utilizzando una soluzione di acido citrico, una frequenza di sonicazione di 130 kHz ed un tempo di trattamento di 2.5 minuti.

Al seguito di tali test è stata osservata una leggera diminuzione della percentuale di desorbimento per ciascun metallo considerato. Tuttavia, i rendimenti di desorbimento sono stati soddisfacenti, con percentuali che si sono attestate intorno a valori sempre superiori al 75%.

La seconda parte del lavoro è stata eseguita presso il laboratorio del gruppo di Bioingegneria e Processi Sostenibili (BIOSUV) dell'Università di Vigo (Spagna). Al fine di valutare l'efficacia degli US come pretrattamento, tale tecnologia è stata applicata prima del processo elettrocinetico (EK). A tal fine le efficienze di rimozione mostrate dal processo combinato (US + EK) sono state confrontate con quelle ottenute grazie all'utilizzo del solo processo EK. I risultati relativi al desorbimento di Cd e Zn, hanno mostrato efficienze di trattamento comparabile, tra il solo processo EK ed il processo combinato US + EK, con percentuali prossime al completo desorbimento. Per il Pb, invece, l'utilizzo del pretrattamento ad US ha comportato un significativo aumento della percentuale di desorbimento promuovendo anche un effetto sinergico.

A valle dell'attività sperimentale, i risultati ottenuti hanno dimostrato che la tecnologia ad US potrebbe essere considerata una promettente alternativa per l'abbattimento dei composti organici e dei metalli pesanti dai sedimenti contaminati.

Il processo studiato si è rivelato molto versatile e offre prestazioni interessanti come singolo trattamento o in combinazione con altre tecnologie di bonifica.

Acknowledgements

Here I am at the end of a long journey, which was characterized by a myriad of emotions. This pathway has been shared with many people who have contributed to complete it and they deserve to be thanked.

First of all, I would like to thank my advisor and co-advisor, prof. Vincenzo Belgiorno and prof. Vincenzo Naddeo, for the scientific support they gave to my research and for having believed in me and in my abilities.

During my research period abroad, I had the honor to collaborate with prof. Ángeles Sanromán Braga and prof. Marta Pazos Currás, who were kind to me by making available their scientific knowledge and making me feel at home. In this period the research work was hard, but at the same time very pleasant thanks to the smile of my Spanish colleagues Aida, Veronica and Maria.

A special thanks goes to the SEED colleagues, which were not only coworkers but also a little family. The research activity can be very challenging, nevertheless the work becomes lighter when shared with the right people. All my colleagues are unique but a special place in my heart was reserved for Anna C. and Giusy, who shared the “room of wonders” with me. Among the guys of SEED, a sincere thanks goes to Napodano, who was the lab's Mc Gyver, who turned into possible what first seemed to be impossible.

The most special thanks are dedicate to my family. In this case an entire chapter should be dedicated only to them, but in truth every word would not be able to describe my gratitude for who was my support and my strength, not only during the doctorate period, but in my life. I therefore hope to be able to make them proud of myself and pay them back at least in part of their love.

Finally, a big THANKS to my friend, my psychologist, my “happy island”, my voodoo doll, my “safety valve”, my love Francesco, which more than anyone has undergone my mood changes, thanks for all.

About the author

Angela Fraiese completed her MSc with honors in Environmental Engineering at the University of Salerno discussing a thesis entitled "Advanced Oxidation Processes driven remediation of marine sediments contaminated by PAHs". In 2014, she was admitted to the Ph. D. program in Environmental and Civil Engineering at the Department of Civil Engineering of Salerno University. Since then, her research activity has been mainly focusing on the treatment of contaminated sediment through advanced processes of remediation. During the Ph. D., she was a visiting researcher at Laboratory of Bioengineering and Sustainable Processes (BIOSUV) of University of Vigo (Spain). She is author and co-author of several papers and national and international conference proceeding.

Angela Fraiese ha conseguito con lode la laurea magistrale in Ingegneria per l'ambiente ed il territorio nel 2014 presso l'Università degli Studi di Salerno, discutendo una tesi dal titolo "Processi ad Ossidazione Avanzata per la bonifica di sedimenti marini contaminati da IPA". Nel 2014 è stata ammessa al Corso di Dottorato di Ricerca in Ingegneria Civile per l'Ambiente ed il Territorio presso l'Università degli Studi di Salerno. La sua ricerca è focalizzata sul trattamento dei sedimenti contaminati tramite processi avanzati di bonifica. Durante il dottorato è stata ricercatrice ospite presso il laboratorio di Bioingegneria e Processi Sostenibili (BIOSUV) dell'Università di Vigo (Spagna). È autrice e coautrice di diverse pubblicazioni scientifiche e di atti di convegno nazionali ed internazionali.

1. Introduction

The sediment contamination represents a widespread problem which raises much concern for the possible negative effects on the environment and human health. In the last decades, due to the increasing anthropic activities, a large amount of contaminants have been released into the water bodies (Egardt et al., 2018; El Nemr and El-Sadaawy, 2016; Farmaki et al., 2014; Tournadre, 2014). The sediments, due to their characteristics, represent a preferential site for the adsorption of polluting compounds. In the contaminated sediments a heterogeneous contamination can be usually recognized due to the presence of a variety of both natural and anthropogenic sources (exhaust gases; forest fires, residential heating, mining etc.). In this context, heavy metals and polycyclic aromatic hydrocarbons (PAHs) are frequently found in the sediments and represent main groups of inorganic and organic compounds, respectively (Das et al., 2014; Mahdi Ahmed et al., 2017). These compounds may induce carcinogenic and toxic effects on human health. For this reason, some of them are classified by U.S. Environmental Protection Agency (US EPA) and the International Agency for Research on Cancer (IARC) as “known” or “probable” human carcinogen. Furthermore 16 PAHs are also included in the list of priority pollutants for the US EPA. A further concern about the presence of heavy metals and PAHs in the sediments is related to the possible bioaccumulation in the food chains (Das et al., 2014; Karacık et al., 2009) and their potential resuspension in the aquatic environment (He et al., 2017; Liu et al., 2017).

Along with the attention addressed from the negative impacts on the environment and human health, technical-economical aspects related to the contaminated sediment management is also of key interest. Indeed, it was estimated that each year, in Europe, about 200 million cubic meters of sediments are brought ashore through the dredging activities (Bortone et al., 2007). These activities are necessary to maintain the navigability depth and for environmental remediation purposes. The free disposal in the aquatic system of dredged contaminated sediment is not allowed and hence they should be properly handled. Among the traditional management options there are the landfill and the confined aquatic disposal, which are nowadays still the most used solutions (Bortone et al., 2007). The main drawbacks of these options are the high operation costs and the scarcity of available sites for disposal. In general, beneficial reuse of dredged sediments could be an effective alternative management option compared to the final disposal. Sediments could be used as building material in the civil engineering field or for beach nourishment (Miraoui et al., 2012; Ozer-Erdogan et al., 2016; Said et al., 2015). However, the treatment of this material must be performed before their reuse, in order to avoid possible adverse effects.

Soil remediation technologies are not always suitable for sediment treatment. Indeed, the specific characteristics of the sediments, including the low permeability, the prevalent fine grain fraction and high water content, can affect the treatment efficiency. Therefore, the study of alternative technologies for the treatment of contaminated sediments is increasing the attention of the scientific community, in order to overcome the limitations of the conventional treatment solutions.

Advanced Oxidation Processes (AOPs) are effective, widely used technologies applied for wastewater treatment and water disinfection (Naddeo et al., 2014; Secondes et al., 2014). Because of their flexibility these technologies are adapted also for the remediation of other environmental matrices (Ferrarese et al., 2008; Flotron et al., 2005).

Among AOPs, ultrasound (US) is considered an innovative environmental friendly technology. In regard to the soil and sediment treatment, the US supports the desorption of the contaminant compounds from the particles and the degradation of organic compounds transferred in the liquid phase (Park and Son, 2016; Pee et al., 2015). The optimization of the US process may entail the reduction of the treatment time and prevent the use of chemicals compared to the traditional technologies (Silva and Martins, 2012; Wang et al., 2015). Therefore, based on these advantages, US may provide an alternative technology for the treatment of contaminated sediments.

1.1 Objectives

The overall aim of this Ph.D. research project is the study of the advanced technologies effectiveness for the remediation of contaminated sediments. For this purpose, experimental activity was structured in two main steps:

- the first one focused on the study of US treatment effectiveness in promoting the reduction of both organic and inorganic contamination in a single stage;
- the second part, performed on the basis of the results of the previous phase, focused on the assessment of the US effectiveness as pre-treatment. In detail, US was implemented before the electrokinetic(EK) process.

To this purpose, a preliminary literature review on the sediment remediation treatments and the US processes was undertaken in order to gather background information and define the experimental activity.

The objectives of the first step, performed at the Sanitary Environmental Engineering division (SEED) of Salerno University, were:

- the definition of the removal efficiency of the US treatment, related to both organic and inorganic contaminants;
- the enhancement of the US treatment efficiency in terms of inorganic compound removal;
- the optimization of enhanced US treatment in terms of sonication frequency, treatment time and work solution.

Referring to the second part, which was performed at the laboratory of Bioengineering and Sustainable Processes (BIOSUV) group at the University of Vigo (Spain), the experimental activity pursued the following objectives:

- the evaluation of the EK process efficiency as stand-alone treatment;
- the definition of the removal efficiency for the EK process with US pre-treatment;

- the comparison of the previous processes for the assessment of the US pre-treatment efficiency.

1.2 Outline

The thesis is divided in eight chapters. An overview of the main contaminants of the sediments is reported in the Chapter 2, highlighting the chemical-physical characteristics, the sources and the toxicological properties of the heavy metals and PAHs, selected as target compounds.

The Chapter 3 describes the treatments proposed in the scientific literature for the sediment remediation. These treatments were divided into three main groups, namely biological, chemical-physical and combined treatments.

The principles of ultrasonic processes and the remediation treatments based on the US technology are reviewed in the Chapter 4.

These four chapters are related to the in-depth analysis of scientific literature used for the experimental activity definition. The other chapters describe the experimental activity and discuss the results.

The Chapter 5 describes the investigation plan and the single stages in which it was divided.

The experimental set up and the analytical methods are reported in Chapter 6, in particular, the chapter was organized in four sections, dealing with: i) the characterization of the sediment; ii) the spiking procedure implemented to obtain the desired sediment contamination; iii) the experimental set up and the analytical procedures carried out for US; iv) the devices and methods applied for the EK treatment.

The Chapter 7 shows and discusses the results of the experimental activity related to the two main part of the work, focused on the US treatment as stand-alone treatment and as pre-treatment, respectively.

Conclusive remarks and future perspectives are presented in the Chapter 8.

2. Main sediment contaminants

2.1 Introduction

The contaminated aquatic sediments are defined as "*Soils, sand, organic matter, or minerals that accumulate on the bottom of a water body and contain toxic or hazardous materials that may adversely affect human health or the environment*" (USEPA 1998).

The sediments, due to their characteristics including the wide specific surface and high amount of matter content, promote the adsorption of contaminants (Chen et al., 2013; De Luca et al., 2005; Marini and Frapiccini, 2013). They represent a natural sink for the pollutants, which reach the water bodies through several pathways and then settle in the sediments. Because of the variety of contamination sources, it is possible to find different polluting compounds in the sediments, as organic contaminants, heavy metals and pesticides, which can have detrimental effects on both the environment and the human health.

However, the concerns regarding contaminated sediments are also linked to their management. Indeed, sediments management may influence different sectors (Figure 2.1) and represents a key factor for a sustainable development (Bortone et al., 2007).

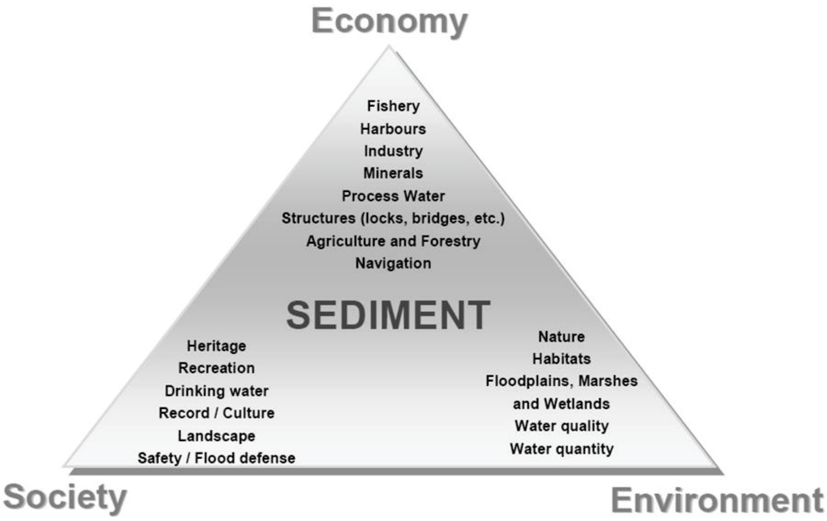


Figure 2.1 The three fields of sustainable sediment management (SedNet 2004)

It was estimated that in Europe, each year, about 200 million cubic meters of sediments are brought ashore through the periodically dredging operations (Figure 2.2). These operations are necessary both to maintain adequate depth for large ships transit and to carry out remediation activities (Bortone et al., 2007; Bortone et al., 2004).

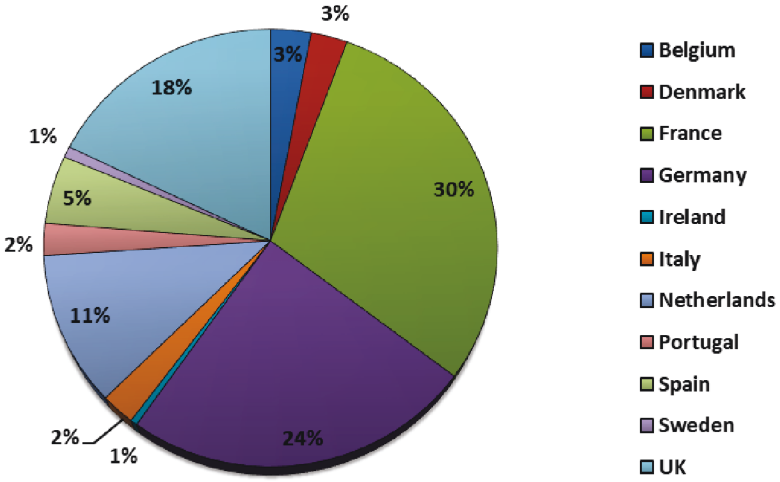


Figure 2.2 Amount of dredged sediments in Europe (adapted from Bridges 2011)

Dredged sediments are partly contaminated and it is necessary a suitable treatment to avoid the landfill or the confined aquatic disposal, which are still the most frequently options of management (Bonomo et al., 2009; Bortone et al., 2007)

The sediments show a heterogeneous contamination, not only in terms of spatial distribution, but also with reference to the type of contaminant, as can be seen from the scientific literature review reported in Table 2.1.

Polycyclic Aromatic Hydrocarbons (PAHs) and heavy metals were selected as organic and inorganic target compounds, respectively. These target compounds were selected since they have been frequently detected in the aquatic sediments. Furthermore, PAHs and heavy metals are well known as toxic and carcinogenic compounds.

In this chapter the main characteristics of the selected target compounds were discussed.

Table 2.1 Main sediment contaminants

		References										
		Simpson et al., 2005	**Varol et al., 2012**	**Fonti et al., 2013**	**Caplat et al., 2005**	**Kilemade et al., 2009**	**Zhu et al., 2013**	**Koh et al., 2006**	**Eijsackers et al., 2009**	**Heininger et al., 2007**	**Huesemann et al., 2009**	**Gorokhov et al., 2010**
Contaminants		**Average concentration [mg/kg]**										
Heavy metals	Antimony	-	-	-	-	-	-	-	-	-	-	-
	Silver	-	-	-	-	-	-	-	-	-	-	-
	Arsenic	-	12	23	-	-	115	-	$1*10^{\wedge-3}$	45	-	-
	Cadmium	-	8	1	-	0.1	86	-	$1*10^{\wedge-3}$	6	-	-
	Chrome	-	158	110	-	-	90	-	$24*10^{\wedge-3}$	181	-	-
	Iron	-	-	44	4.29	-	-	-	-	-	-	-
	Manganese	-	1682	-	415	-	65	-	-	-	-	-
	Mercury	-	-	-	-	-	38	-	$0.6*10^{\wedge-3}$	5	-	-
	Nickel	-	535	46	-	-	-	-	$13*10^{\wedge-3}$	58	-	-
	Lead	-	660	80	166	17	487	-	-	224	-	-
	Copper	-	2860	38	300	16	209	-	$49*10^{\wedge-3}$	196	-	-
	Zinc	-	1062	428	354	94	2702	-	$290*10^{\wedge-3}$	1021	-	-
PAHs	Acenaphthene	-	-	-	-	$2*10^{\wedge-6}$	-	-	-	-	-	-
	Acenaphthylene	-	-	-	-	-	-	-	-	-	-	-
	Anthracene	$25*10^{\wedge-3}$	-	-	-	$12*10^{\wedge-6}$	-	-	1	-	-	-
	Benz[a]anthracene	$64*10^{\wedge-3}$	-	-	-	$41*10^{\wedge-6}$	-	-	2.8	-	-	0.05
	Benzo[a]pyrene	$117*10^{\wedge-3}$	-	-	-	$38*10^{\wedge-6}$	-	-	1.2	-	7	0.84
	Benzo[b]naphtho[2,1-d]thiophene	-	-	-	-	$21*10^{\wedge-6}$	-	-	-	-	-	-
	Benzo[b]fluoranthene	$59*10^{\wedge-3}$	-	-	-	$97*10^{\wedge-6}$	-	-	-	-	-	1.24
	Benz[e]acephenanthrylene	-	-	-	-	-	-	-	-	-	-	-
	Benzo[e]pyrene	-	-	-	-	$62*10^{\wedge-6}$	-	-	-	-	-	0.40
	Benzo[ghi]perylene	$228*10^{\wedge-3}$	-	-	-	$43*10^{\wedge-6}$	-	-	1.6	-	1.3	0.62
	Benzo[k]fluoranthene	$110*10^{\wedge-3}$	-	-	-	$29*10^{\wedge-6}$	-	-	1.3	-	-	-
	Chrysene	$66*10^{\wedge-3}$	-	-	-	$40*10^{\wedge-6}$	-	-	2.4	-	14	0.75
	Dibenz[a,h]anthracene	$20*10^{\wedge-3}$	-	-	-	$8*10^{\wedge-6}$	-	-	-	-	-	-
	Phenanthrene	$98*10^{\wedge-3}$	-	-	-	$59*10^{\wedge-6}$	-	-	-	-	41	0.2
	Fluoranthene	$293*10^{\wedge-3}$	-	-	-	$88*10^{\wedge-6}$	-	-	7.9	-	-	1.04
	Fluorene	-	-	-	-	$9*10^{\wedge-6}$	-	-	2	-	-	-
	Indeno[1,2,3-cd]pyrene	$102*10^{\wedge-3}$	-	-	-	$63*10^{\wedge-6}$	-	-	1.6	-	-	-
	Naphthalene	-	-	-	-	$33*10^{\wedge-6}$	-	-	0.1	-	25	-
	Pyrene	$264*10^{\wedge-3}$	-	-	-	$71*10^{\wedge-6}$	-	-	-	-	-	1.4
	Total PAHs	-	-	-	-	-	-	$228*10^{\wedge-3}$	-	7	183	-

		References										
		Simpson et al., 2005	**Varol et al., 2012**	**Fonti et al., 2013**	**Caplat et al., 2005**	**Kilemade et al., 2009**	**Zhu et al., 2013**	**Koh et al., 2006**	**Eijsackers et al., 2009**	**Heininger et al., 2007**	**Huesemann et al., 2009**	**Gorokhova et al., 2010**
Contaminants		**Average concentration [mg/kg]**										
PCBs	18	-	-	-	-	-	-	-	-	-	-	$6*10^{\wedge-3}$
	28	-	-	-	-	-	-	-	-	-	-	$14*10^{\wedge-3}$
	52	-	-	-	-	-	-	-	-	-	-	$12*10^{\wedge-3}$
	70	-	-	-	-	-	-	-	-	-	-	$3*10^{\wedge-3}$
	90/101	-	-	-	-	-	-	-	-	-	-	$29*10^{\wedge-3}$
	106	-	-	-	-	-	-	-	-	-	-	$7*10^{\wedge-3}$
	110	-	-	-	-	-	-	-	-	-	-	$29*10^{\wedge-3}$
	118	-	-	-	-	-	-	-	-	-	-	$16*10^{\wedge-3}$
	138	-	-	-	-	-	-	-	-	-	-	$47*10^{\wedge-3}$
	149	-	-	-	-	-	-	-	-	-	-	$32*10^{\wedge-3}$
	153	-	-	-	-	-	-	-	-	-	-	$46*10^{\wedge-3}$
	180/193	-	-	-	-	-	-	-	-	-	-	$18*10^{\wedge-3}$
	Total PCBs	-	-	-	-	$3*10^{\wedge-3}$	-	$3*10^{\wedge-3}$	$105*10^{\wedge-3}$	$59*10^{\wedge-3}$	236	-
Chlorinated Pesticides	HCB	-	-	-	-	-	-	-	-	$88*10^{\wedge-3}$	-	-
	HCH	-	-	-	-	-	-	-	-	$130*10^{\wedge-3}$	-	-
	DDT	-	-	-	-	-	-	-	-	-	-	-
	Σ Chlorinated Pesticides	-	-	-	-	$3*10^{\wedge-3}$	-	-	$90*10^{\wedge-3}$	-	-	-

2.2 Polycyclic aromatic hydrocarbons (PAHs)

2.2.1 Chemical and physical properties

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds made up of carbon and hydrogen atoms with a structure composed by two or more fused aromatic rings (CEPA 1994). Based on the aromatic rings number they can be divided into two main groups, the PAHs with low molecular weight (LMWPAHs), which have less than four rings and the PAHs with high molecular weight (HMWPAHs), which are composed of more than four rings. At environment temperature, PAHs are usually coloured and crystalline solid with a low volatility and water solubility. Moreover, their physical characteristics depend heavily on the molecular weight. Indeed, with increasing of the aromatic rings number there is a decrease of the vapour pressure and aqueous solubility (Table 2.2) (Latimer and Zheng, 2003; Meador, 2008). Moreover, these compounds are highly lipophilic and then are able to accumulate in the tissue of plants and animals.

Table 2.2 Chemical-physical characteristics of 16 PAHs priority pollutants

	PAHs	Chemical formula	Molecular weight	N.aromatic rings	Melting point [°C]	Boiling point [°C]	Water solubility at 25° [mg/l]	LogK$_{ow}$ a 25°C	Vapour pressure at 25°C [Pa]	Henry's law constant at 25°C [Pa m^3/mol]
LMW PAHs	**Naphthalene**	$C_{10}H_8$	128.2	2	80	218	3.17*10^^{4}	3.40	1.04*10^^{1}	4.89*10^$^{-2}$
	Acenaphthylene	$C_{12}H_8$	152.2	3	92	-	-	4.07	0.89	114.10^$^{-3}$
	Acenaphthene	$C_{12}H_{10}$	154.2	3	95	279	3.90	3.92	0.29	18.5
	Fluorene	$C_{10}H_{10}$	166.2	3	116	295	1.68	4.18	0.08	9.81
	Anthracene	$C_{14}H_{20}$	178.2	3	216	342	4.36*10^$^{-2}$	4.45	0.80*10^$^{-3}$	5.64
	Phenanthrene	C14H10	178.2	3	100	340	9.77*10^-1	4.57	0.16*10^-1	4.29
HMW PAHs	**Fluoranthene**	$C_{16}H_{10}$	202.3	4	110	384	0.26	5.20	0.12*10^$^{-2}$	1.96
	Pyrene	$C_{16}H_{10}$	202.3	4	151	404	1.35*10^$^{-1}$	5.18	0.60*10^$^{-3}$	1.71
	Benz[a]anthracene	$C_{18}H_{12}$	228.3	4	160	-	0.90*10^$^{-2}$	5.91	2.80*10^$^{-5}$	1.22
	Chrysene	$C_{18}H_{12}$	228.3	4	254	448	0.20*10^$^{-2}$	5.79	5.7*10^$^{-7}$	0.53
	Benzo[a]pyrene	$C_{20}H_{12}$	252.3	5	179	311	0.30*10^$^{-2}$	6.35	8.4*10^$^{-7}$	0.34*10^$^{-1}$
	Benzo[b]fluoranthene	$C_{20}H_{12}$	252.3	5	168	-	0.15*10^$^{-2}$	5.78	-	0.51*10^$^{-1}$
	Benzo[k]fluoranthene	$C_{20}H_{12}$	252.3	5	217	480	0.80*10^$^{-3}$	6.11	-	0.44*10^$^{-1}$
	Benzo[ghi]perylene	$C_{22}H_{12}$	276.3	6	279	-	0.26*10^$^{-3}$	6.90	6*10^$^{-8}$	0.27*10^$^{-1}$
	Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276.3	6	164	-	0.19*10^$^{-3}$	6.84	-	0.29*10^$^{-1}$
	Dibenz[a,h]anthracene	$C_{22}H_{14}$	278.4	6	266	-	0.50*10^$^{-3}$	6.75	3.7*10^$^{-10}$	-

2.2.2 Sources and transport in the environment

The sources of PAHs are both natural and anthropogenic. Natural sources include volcanic eruptions and forest fires, but the anthropogenic are the main sources (Lee, 2010).

In particular, anthropogenic sources can be divided into petrogenic and pyrogenic. The PAHs generated from petrogenic sources are related to the fossil fuel, lubricants and generally, petroleum derivatives. These compounds can be released into the environment mainly through the accidental spills.

The pyrogenic PAHs are derived from the combustion of fossil fuel or biomass, as incomplete combustion and pyrolysis (Abdel-Shafy and Mansour, 2016; De Luca et al., 2005; Li et al., 2015; Stogiannidis and Laane, 2015).

The kind of anthropogenic sources can be identify through the temperature at which PAHs are generated. Indeed, pyrogenic PAHs form at high temperatures from about 350°C and 1200°C, whereas the petrogenic PAHs are related to the substances, as crude oil, which are formed in longer time and at lower temperature of about 100-150°C (Abdel-Shafy and Mansour, 2016). Another way to identify the anthropogenic sources is the number of aromatic rings. Petrogenic sources generate PAHs with two or three aromatic rings, whereas pyrogenic sources produce compounds with four or more aromatic rings (Abdel-Shafy and Mansour, 2016; Chen et al., 2013; De Luca et al., 2005). These one are more diffused in the environment, in particular in the urban areas, because of there are several activities that involve the use of combustion during the industrial process (Figure 2.3) (Araghi et al., 2014; Chen et al., 2013; Kucuksezgin et al., 2013; Li et al., 2015). Moreover, pyrogenic PAHs are heavier and then more persistent in the environment and harder to remove (Giordano et al., 2005).

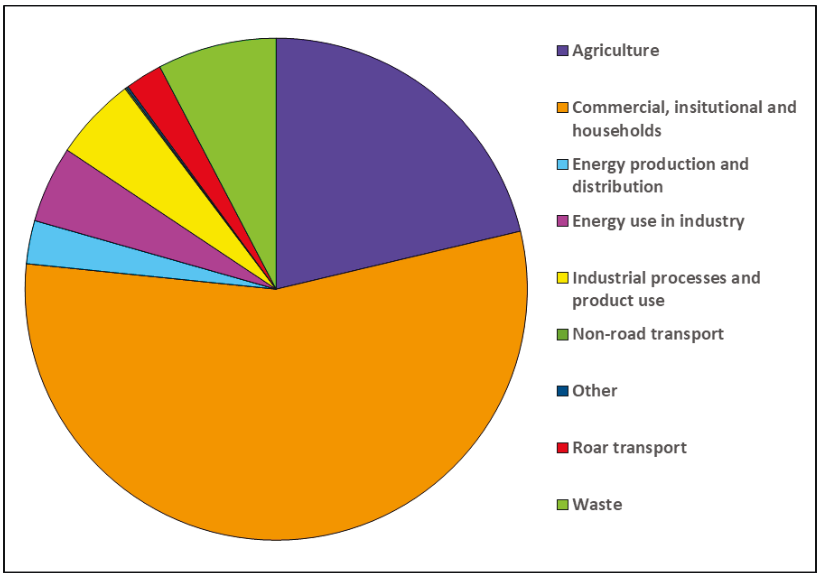


Figure 2.3 PAHs emissions per sector (adapted from www.eea.europa.eu, updated data to 2015)

Therefore, these compounds are generated, more in general, from large point sources or smaller point sources, but after the generation, the water bodies usually represent the common fate. PAHs move in the environment through different means as the urban run-off, direct oil spills, but main means is represented from the atmosphere (Kucuksezgin et al., 2013; Motelay-Massei et al., 2006; Tsapakis et al., 2003). PAHs can spread through the atmosphere as vapour, for some lighter compounds, or adsorbed onto particulate matter. This particulate can reach the water bodies directly depositing on the water surface or with the urban run-off after the deposition on roads or soil (Abdel-Shafy and Mansour, 2016; Latimer and Zheng, 2003). Then, the contaminant compounds spread in the water column and finally settle in the sediments.

2.2.3 Toxicity

PAHs are widespread in the environment and raise particular concerns for their carcinogenic and mutagenic effects for the human (Kim et al., 2013). The detrimental effects of this kind of compounds are known and for this reason some PAHs are classified as "know" or "probable" carcinogenic for the human from the most important international agencies as "*International Agency for Research on Cancer*" (IARC) and the "*US*

Environmental Protection Agency" (US EPA). In particular, 16 PAHs are included in the list of priority pollutant of the US EPA (Figure 2.4).

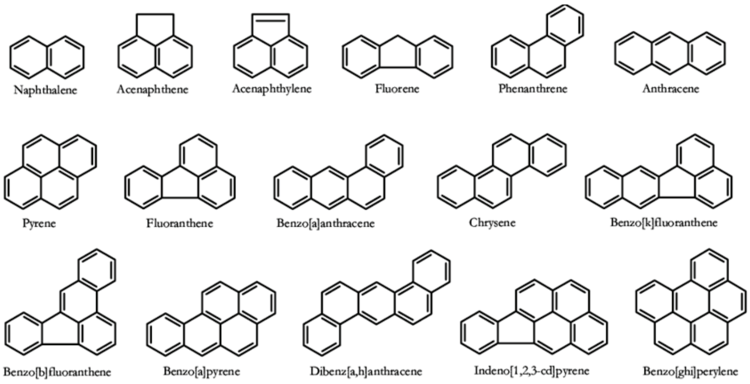


Figure 2.4 Structures of the 16 PAHs included in the list of priority pollutants of US-EPA (modified from Lundstedt, 2003)

PAHs can be adsorbed by different ways, through the dermal contact, inhalation, ingestion and due to their lipophilicity, they can easily dissolved into the fat and enter in the body (Douben, 2003). The effects of the PAHs exposure may entail the DNA damage with formation of tumours, problems for both reproduction and growth for the living organisms (Abdel-Shafy and Mansour, 2016; CEPA 1994). However, the genotoxic and carcinogenic effects are not linked to the direct interaction of the PAHs with the DNA, but to the formation of metabolites, which can interfere with the normal functioning of DNA. In some cases the PAHs can be metabolized by the body and expelled (Abdel-Shafy and Mansour, 2016; Lundstedt, 2003; 1994).

2.3 Heavy metals

2.3.1 Chemical and physical properties

The terms of heavy metals is commonly used to indicate the elements that have a high atomic density five times or more, greater than the water and toxic effects also at low concentration (Tchounwou et al., 2012). The group of heavy metals includes some elements as lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), iron (Fe), zinc (Zn), chromium (Cr), iron (Fe), arsenic (As), silver (Ag), arsenic (As) and mercury (Hg) (Nagajyoti et al., 2010). Heavy metals are generally toxic, persistent in the environment, able to form complexes and they are present in the environment in the form of different oxidation states. However, each element has specific chemical-physical characteristics and this is the reason for which there are no shared definitions based on these characteristics (Das et al., 2014; Mustafa and Komatsu, 2016; Tchounwou et al., 2012).

2.3.2 Sources and transport in the environment

Heavy metals are derived from both natural and anthropic sources. The first one includes the forest fires, the volcanic eruptions and to a lesser extent natural biosynthesis.

Heavy metals are natural constituents of the earth's crust, but their occurrence in the environment is strongly related to the anthropic activities. There are natural and anthropic sources and among the first, in addition to the release from the rocks in which they are contained, there are the volcanic eruption and to a lesser extent natural biosynthesis (Das et al., 2014; Liang et al., 2018). The anthropic sources are usually the main sources and include all the industrial activities, which concern the metal-based operations, mining and also the agriculture activities (Figure 2.5) (Das et al., 2014; Liang et al., 2018; Liu et al., 2014).

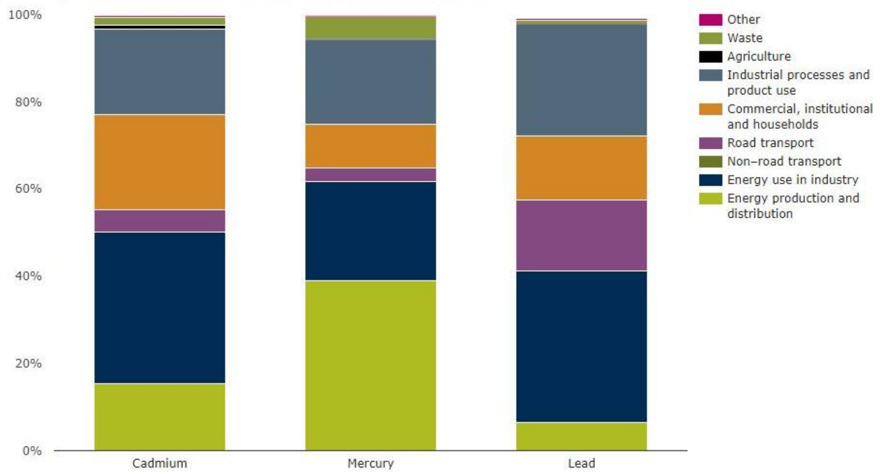


Figure 2.5 Heavy metals emission sectors (update 2015 www.eea.europa.eu)

Heavy metals are present in the environment in different forms and states, which are the consequence of the physical and chemical transformations that undergo (Peng et al., 2009). This characteristic can affect the way to move in the environment. Usually heavy metals are transported in the environment by the atmospheric particulate, the surface runoff and the leaching from the agricultural areas (Das et al., 2014; Egardt et al., 2018; Liang et al., 2018). In particular, the soluble form tend to leach, whereas it is possible that the undissolved forms can move linked to colloidal particles and carried toward the water bodies (Abadin et al., 2007; Faroon et al., 2012). The final fate of this kind of contaminants is represented from the deposition on the water surface and then the adsorption onto the sediments. The adsorption onto the sediments is promoted by the high specific surface area, but changes in chemical and environmental characteristics may again lead to the dispersion and mobilization of contaminants (Egardt et al., 2018). A key parameter is represented from the pH value (Table 2.3), which can affect the solubility of the heavy metals and then, their spread in the environment.

Table 2.3 The limit pH for metal species (adapted from Peng et al., 2009)

	Metal species							
	Zn	**Cd**	**Ni**	**As**	**Cu**	**Pb**	**Al**	**Fe**
pH value	6.0-6.5	6.0	5.0-6.0	5.5-6.0	4.5	4.0	2.5	2.5

2.3.3 Toxicity

The concern about the heavy metals is mainly related to the toxicity effects on the environment and human health. These heavy metals can be divided into essential and non-essential metals (Sfakianakis et al., 2015; Tchounwou et al., 2012). Among the essential metals, there are Ni, Co, Fe, Zn, Cr, which are indispensable for biological functions of the living beings. However, despite their fundamental biological role, these elements can arise toxicity at high concentration (Abadin et al., 2007; Mustafa and Komatsu, 2016; Tchounwou et al., 2012). The non-essential metals, instead, have no a recognized beneficial action, on the contrary, their toxicity is high also at low concentration.

Indeed, due to their dangerous effects on the human health, some heavy metals as Pb, Cd, Cr, Hg, As are recognised as priority metals and classified as “known” or “probable” human carcinogens by the United States

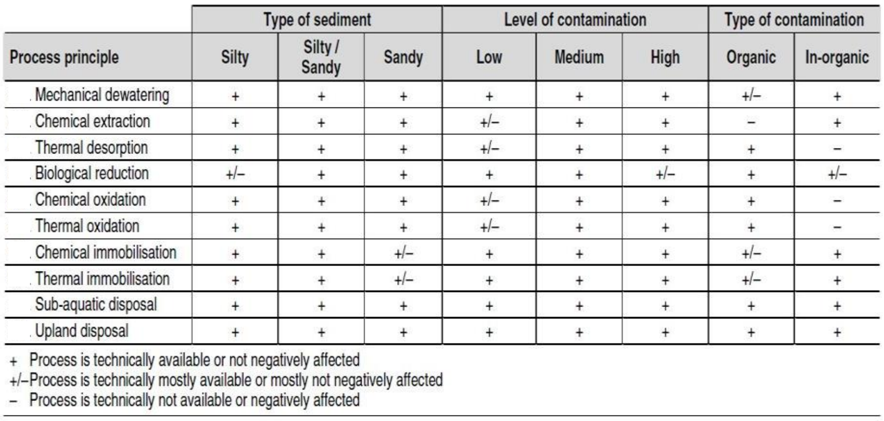
Environmental Protection Agency (U.S. EPA), and the International Agency for Research on Cancer (IARC) (Tchounwou et al., 2012). These compounds can bioaccumulate in the body of animal and enter in the food chain up to the man, for example through the sea food (El Nemr and El-Sadaawy, 2016; Ghrefat et al., 2011; Zhang et al., 2015). Heavy metals can also enter the human body directly through ingestion, inhalation or skin absorption and after to reach the internal organs and the brain through the blood causing several consequences as deformities, cognitive dysfunctions, reproductive system problems (Das et al., 2014; Sfakianakis et al., 2015).

3. Remediation treatments of contaminated sediments

Contaminated sediments and their management has become a relevant concern. Nowadays the most usually management options were landfill and confined aquatic disposal. These options require wide spaces, high costs and are not environmentally sustainable. Therefore, there is a clear need to find alternative solutions for the sediments management, which can also allow a re-use (Bortone et al., 2007). In particular, the international scientific community have been expressing increasing interest for the research of remediation technologies suitable for treating sediments (Bortone et al., 2007; Song et al., 2017).

Generally, the technologies used for the sediments remediation were the same applied for the contaminated soil treatment (Gan et al., 2009). However, the specific characteristics of the sediments, as prevalence of fine fraction and high organic matter content, can affect the treatment (Araghi et al., 2014; Chen et al., 2013; De Luca et al., 2005; Xia and Wang, 2008). The choice of removal treatment must take into account the chemical-physical characteristics of the sediments, as well as type and level of contamination (Table 3.1) (Chen and Chen, 2011; Flotron et al., 2005).

Table 3.1 Technical criteria for the choice of sediment remediation treatment (Bortone et al., 2004)



	Type of sediment			Level of contamination			Type of contamination	
Process principle	Silty	Silty / Sandy	Sandy	Low	Medium	High	Organic	In-organic
Mechanical dewatering	+	+	+	+	+	+	+/–	+
Chemical extraction	+	+	+	+/–	+	+	–	+
Thermal desorption	+	+	+	+/–	+	+	+	–
Biological reduction	+/–	+	+	+	+	+/–	+	+/–
Chemical oxidation	+	+	+	+/–	+	+	+	–
Thermal oxidation	+	+	+	+/–	+	+	+	–
Chemical immobilisation	+	+	+/–	+	+	+	+/–	+
Thermal immobilisation	+	+	+/–	+	+	+	+/–	+
Sub-aquatic disposal	+	+	+	+	+	+	+	+
Upland disposal	+	+	+	+	+	+	+	+

\+ Process is technically available or not negatively affected
+/–Process is technically mostly available or mostly not negatively affected
– Process is technically not available or negatively affected

This chapter provides an overview on the remediation treatments used for the contaminated sediment. The treatments are divided in three main categories biological, chemical-physical and combined treatments.

3.1 Biological treatments

Biological treatments are conventional included among the bioremediation processes. They are treatments, which use biological organisms to degrade or to remove contaminants from the environment. There are different biological treatments and among the most used, there are the biostimulation, bioaugmentation and phytoremediation (Abioye, 2011; Ojuederie and Babalola, 2017; Perelo, 2010).

Biostimulation and bioaugmentation utilize the ability of the microorganisms to degrade or transform pollutant in less toxic compounds (Adams et al., 2015). In particular, when nutrients and oxygen are added to improve the indigenous microbiological community activity one speaks of biostimulation, whereas if microorganisms are added to support microbial communities present, this is bioaugmentation (Adams et al., 2015).

Another well-known biological treatment is phytoremediation, which uses plants to accumulate and degrade a wide range of contaminants. For this treatment, climate conditions are fundamental for plant growth (Gan et al., 2009; Khan et al., 2004).

Biostimulation treatments were successfully used for the contaminated sediments remediation as shown in the work of Chiavola et al. (2010). In this work, the treatment was performed with the use of only autochthonous microorganisms in a sequencing batch reactor. The sediments were spiked with a mixture of PAHs to simulate a real contamination. During the process, there was an increasing PAHs removal, with final removal above 80%, but despite a general high removal, the best performance were obtained for the lighter PAHs. This result highlights that the biological processes are affected to the type of contamination. In this case, Chiavola et al., (2010) attributed the PAHs removal mainly to the microbiological activity.

However, Beolchini et al., (2010) observed that, the microbiological activity is not the only key factor that can contribute to the contaminant removal. Indeed, the enhancement of the available surface area may increase oxygen diffusion and promote the degradation of the HMW hydrocarbons.

Biological treatments are commonly used for the degradation of organic compounds, some applications were also proposed for the heavy metal extraction. In this case, the main effect is the solubilization or the immobilization of the compounds through microorganism or plants (Ojuederie and Babalola, 2017). Also for the inorganic contamination the sediments surface area is an important factor. Indeed, Guven and Akinci (2013) demonstrated that bioleaching of heavy metals is more effective for the fine sediments. This result is related to the larger surface area, which has favored the solubilisation activity performed by bacteria.

Among the biological treatments it was previously mentioned, the phytoremediation. This type of treatment was studied for the sediment remediation (Mânzatu et al., 2015; Peng et al., 2009). The effectiveness of the phytoremediation is related to the characteristics of the contaminants and plants. In general, there are different strategies, which can operate simultaneously for the reduction of the contamination. The main strategies include the phytodegradation that is able to degrade organic contaminants through specific enzymes or the phytoextraction, which is more used in the case of inorganic contaminants (Favas et al., 2014; Ojuederie and Babalola, 2017).

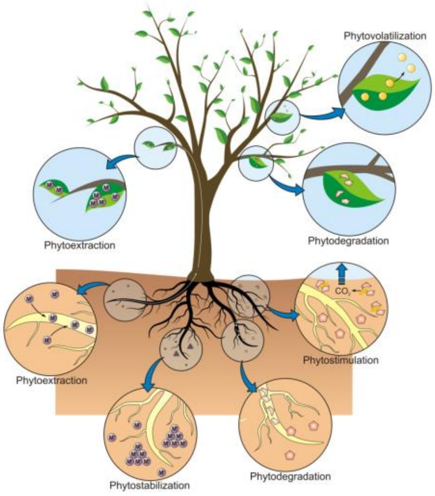


Figure 3.1 Phytoremediation strategies (Favas et al., 2014)

The choice of the plants to use for the phytoremediation is an important factor. In the work of Huesemann et al. (2009) the eelgrass (*Zostera marina*) was used to remove PAHs and PCBs from marine sediments. The results were compared with those of a same experiment for which unplanted sediment were used. For the sediment with eelgrass in 60 weeks, there was a removal of 73% and 60% for PAHs and PCBs, respectively. Less significant results were obtained for the unplanted sediment, which showed a removal of PAHs of 25%, whereas no removal were observed for PCBs.

Referring to the PAHs removal, this result was in contradiction with a similar study. Vervaeke et al. (2003) used willow (*Salix viminalis L.*) to remove both PAHs ad mineral oil from the dredged sediments. After 1.5 year of treatment, the PAHs removal was of 32% in the unplanted sediment and 23% in the planted sediment. Best results were obtained for mineral oil contamination with a removal of 57% and 15% respectively for planted and unplanted sediment. The phytoremediation has not led a significant contribution for the PAHs degradation, which was more favoured from the natural aeration of the unplanted sediment.

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3.2 Chemical-physical treatments

Chemical-physical treatments entail the separation of the contaminants from solid matrix, through chemical processes, which convert pollutants into substances easier to eliminate and physical processes, which allow the contaminants transfer from the sediments to the liquid phase (Gan et al., 2009; Khan et al., 2004). These treatments are among the most utilized remediation treatments, which include several applications also for the contaminated sediments, as sediment washing (SW), electrokinetic (EK) processes and Advanced Oxidation Processes (AOPs) (Akcil et al., 2015; Khalid et al., 2017).

The first treatment concerns the separation of contaminants from the sediments surface through washing solutions. Water-based solutions are used to solubilize the contaminants allowing the transfer from the solid to the liquid phase (Akcil et al., 2015; Dermont et al., 2008; Park and Son, 2016). In this treatment, there are two main actions, the mechanical action of rubbing the particles and the chemical action of the solutions to dissolve the contaminants (Bortone et al., 2007).

This treatment is easy to apply and was preceded from a particle size separation, to remove the coarse fraction which is usually the less contaminated (Mulligan et al., 2001). A disadvantage of this treatment is the high amount of solution necessary, also two or three volumes of solution per volume of sediment (Bortone et al., 2007). In this regard, recovery of washing solutions represent a key factor. Deng et al. (2017) has investigated the reclamation of ethylenediaminetetraacetic acid (EDTA) from river sediments. EDTA was used to remove Pb, Cd, Cu and Zn from the sediments and its reclamation was obtained by sodium polyamidoamine-multi dithiocarbamate (PAMAM-DTC). This agent was stirred with EDTA solution for 30 min allowing the precipitation of metal ions (Figure 3.2). The best results were obtained for Pb, Cd and Cu with residual concentrations under detective limit. This procedure allowed the reuse of the solution for another three cycles, with results comparable to those achieved using fresh EDTA.

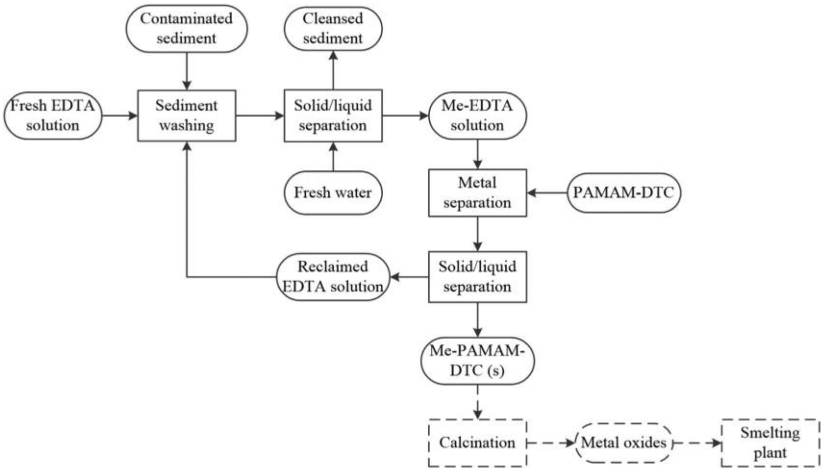

Figure 3.2 Flowchart of sediment washing by EDTA, with EDTA reclamation (Deng et al., 2017)

EK process involves the application of low intensity electric current field, directly into the sediments through the inserting of electrodes. During the EK the electrolysis of the water occurs with the generation of an acid solution (H^+) at the anode side and an alkaline solution (OH^-) to the cathode (Reddy et al., 1999; Ricart et al., 1999) The effectiveness of this process is based on different removal mechanisms and the most significant are the electromigration and electro-osmosis. The electromigration promotes the movement of the charged contaminants toward the electrode with opposite charge, whereas the uncharged contaminants are transporting through the osmotic flow, which usually is from the anode to the cathode (Gan et al., 2009; Pazos et al., 2010; Rozas and Castellote, 2012).

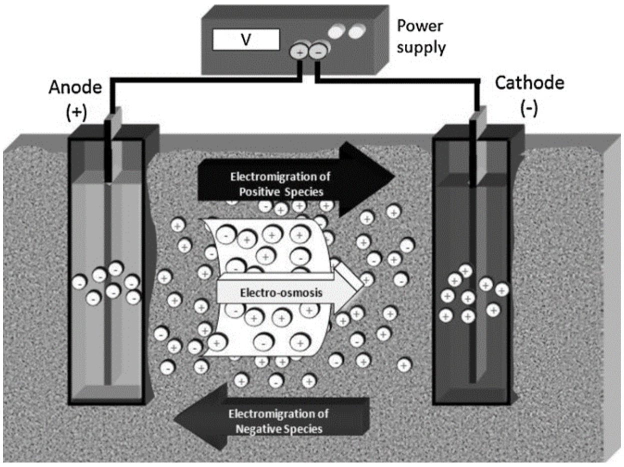

Figure 3.3 Schematic representation of electrokinetic process (Pazos et al., 2010)

The acid front, generated to the anode side, tends to move toward the cathode and during the movement can solubilize the metal species allowing their transport, whereas near the cathode there is the precipitation of metals due to the alkaline front (Falciglia et al., 2017). EK process is one of the most suitable remediation technology for the treatment of the matrices with low permeability as sediments (Ammami et al., 2015; De Gioannis et al., 2008; Song et al., 2016). This process was mainly used for the heavy metal removal (Iannelli et al., 2015; Kornilovich et al., 2005; Rozas and Castellote, 2012), but several studied have also demonstrated its effectiveness for the remediation of matrices with organic contamination (Alcántara et al., 2012; Colacicco et al., 2010; Guedes et al., 2014).

In the case of inorganic contamination, in order to avoid the precipitation of the metal species, chelating agents were used during the treatment. Among the several chelating agents, the most used are ethylenediamine tetraacetic acid (EDTA) and citric acid (Dermont et al., 2008; Leštan et al., 2008; Rozas and Castellote, 2012; Song et al., 2016). In particular, EDTA is able to form stable complexes with the metal species favoring the removal. The main disadvantage of this agent is represented from the high cost and narrow pH range in which EDTA is soluble and, therefore, able to form complexes (Nogueira et al., 2007; Peters, 1999). The citric acid is an ecofriendly agent and it is used not only in order to form complexes, but also to maintain the pH low promoting the metal species solubilization (Cameselle and Pena, 2016; Nogueira et al., 2007).

Organic compounds, instead, are usually less or absolutely not water soluble and thus, more difficult to remove from the matrix. In order to promote their solubilization surfactants are used, which are able to form micelle for the organic compound removal (Ammami et al., 2015; Colacicco et al., 2010; Falciglia et al., 2017; Pazos et al., 2010).

Different processing fluids are used in the scientific works to assess the effects on the heavy metal desorption yields. Kim et al. (2011) investigated the suitability of the EDTA, citric acid, nitric acid (HNO_3), and hydrochloric acid (HCl) solutions to remove Ni, Cu, Zn and Pb from the dredged marine sediments. At the end of the processes the best performances were obtained from the HCl and citric acid with a reduction of 71.5% Ni, 68.6% Cu, 62.4% Zn and 65.3% Pb for HCl. Whereas, citric acid obtained removal percentage of 563%, 71.3%, 60.3% and 54% for Ni, Cu, Zn and Pb, respectively. From these results, is possible to see how in the same experimental conditions, the change of processing fluid can have different effect in term of desorption yield. Indeed, the EK efficiency is conditioned on both the type of matrix and nature of contaminant. This result is in agreement with the work of Rozas and Castellote (2012), which has used various solutions obtaining different removal percentages for each compound. In the work of Iannelli et al. (2015) the strong acids HCl and HNO_3 have obtained the best results to reduce the heavy metal contamination from the dredged sediments. This result is mainly related to the lower pH values achieving with the use of this type of acids. However, the chemical-physical characteristics of sample, at the end of the process, are an important element to take into account for the choice of the suitable processing fluid. Indeed, the strong acids can entail the destruction of the sediment structure and, therefore, compromise a possible reuse (Dermont et al., 2008).

Usually in the real sediments, there is a co-contamination of organic and inorganic compounds. In this case, the use of chelating agents is not enough and it is necessary to add surfactants to obtain a reduction also of organic compounds (Alcántara et al., 2012; Ammami et al., 2015; Falciglia et al., 2017). However, the use of surfactants not always produce significant results in terms of organic contaminant removal, as demonstrated in some works carried out with a non-ionic surfactant, TWEEN 80 (Colacicco et al., 2010; Hahladakis et al., 2014). Nevertheless, other surfactants can be more effective, as demonstrated in the work of Hahladakis et al. (2013), in which the effectiveness of two new non-ionic surfactants, namely Nonidet P40 and Poloxamer 40, have been compared with that of the TWEEN80, in order to remove PAHs from real sediments during the EK treatment. The comparison showed the low removal efficacy of TWEEN80, while Nonidet P40 and Poloxamer 40 obtained removal yields of 48% and 43%, respectively. The simultaneous use of chelating agents and surfactants can allow good results for both organic and inorganic contaminants. Ammami et al. (2015) has performed the EK treatment on dredged sediments with a co-contamination of heavy metals and PAHs. In this work, the combained use of citric acid and a non-ionic surfactant (TWEEN20), has achieved the best results. In particular, the increase of citric acid amount was able to enhance the inorganic compound removal due to the higher solubilization of heavy metals. At the same time, the chelating agents allow the increase of the osmotic flow, which can transport the PAHs that are incorporated into non-ionic surfactant. Thus, the EK process is also able to treat sediments with a contamination of different nature, however is necessary to take into account that this process is significant affected to the presence of organic compounds. Indeed, when in the sediment there are organic contaminants, in the system occur a decrease of the electric field, which may condition the treatment efficiency. This effect was evident in the work of Falciglia et al. (2017), where in the same experimental conditions, the presence of PAHs led to a decrease of the heavy metals removal of about 5%.

AOPs base their effectiveness on the hydroxyl radical ($OH^{\bullet}$) production. The $OH^{\bullet}$ is one of the most powerful oxidizing agents, which can involve the oxidation of the organic compounds until the complete mineralization in water, carbon dioxide, inorganic ions (Glaze et al., 1987; Sirés et al., 2014). These processes are widespread mainly for the treatment of wastewater (Andreozzi et al., 1999; Li et al., 2017). However, due to their versatility given by the possibility of generating radicals through different ways, they have also found application in the treatment of contaminated solid matrices (Chen et al., 2016). Among the several techniques used in AOPs, there are the Fenton's reagent processes (Ferrarese et al., 2008; Gan et al., 2009; Jonsson, 2006; Rivas, 2006). Fenton's reagent process entails the formation of $OH^{\bullet}$ through the decomposition of an oxidant, which usually is hydrogen peroxide (H_2O_2), in the presence of ferrous sulphate. (Babuponnusami and Muthukumar, 2014; Jonsson et al., 2007; Nafie, 2010; Yap et al., 2011). The reaction is described in the following equation (Ferrarese et al., 2008; Jonsson et al., 2007):

$$\mathrm{H_2O_2 + Fe^{2+} \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+}}$$

The Fenton's reagent process has proved effective in the oxidation of organic contaminants from solid matrices (Rivas, 2006), however its effectiveness is strongly dependent on the type of matrix, nature and level of contamination as demonstrated by Flotron et al. (2005). In this work, Fenton's reagent process was applied to reduce the native and spiked PAHs from soil, sludge and marine sediments. The best degradation yields were obtained for the spiked matrices, with percentages between 38% and 100%, whereas the matrices without spiked PAHs have reached removal percentages from 0% to 85%. The difference among the results can be attributed to the higher adsorption of native contaminants into matrices, which led to greater removal difficulties. Fenton's reagent process proved to be particularly suitable for sediment treatment. Indeed, for this matrix, the process has achieved removal ranges of 10%-85% and 98%-100% for native and spiked PAHs, respectively. The results obtained for the sediment remediation were in agreement with Ferrarese et al. (2008), for which a PAHs removal percentage of 96% was achieved after the treatment.

In both works, in order to obtain good removal efficiency, high oxidant dosages were used. Indeed, one of the main parameters that affects Fenton's reagent process is the organic matter content. This substance is considered an oxidant scavenger and tends to react with the hydroxyl radicals, which are consumed (Jonsson et al., 2007) and thus, not available for the degradation process. Thus, in order to degrade the PAHs a higher amount of these oxidants is necessary.

Among the AOPs an innovative treatment is represented from the ultrasound (US) treatment. US technology was more widely used for the wastewater treatment (Mahamuni and Adewuyi, 2010; Manariotis et al., 2011; Naddeo et al., 2013; Rubio-Clemente et al., 2014), but it has also attracted increasing attention for the treatment of contaminated soils and sediments (Adewuyi, 2001; Collings et al., 2006; Duong et al., 2010). US process is considered as a treatment environmental friendly, clean and fast (Silva and Martins, 2012). Its effectiveness is mainly attributed to the cavitation phenomenon, which can generate chemical and mechanical effects. These effects can lead to the fragmentation of the soil/sediment structure, promoting the desorption of the contaminant compounds and the degradation of the organic compounds (Mason, 1997). The oxidizing action is related to the $OH^{\bullet}$ generation through the water decomposition (Mahamuni and Adewuyi, 2010).

The effectiveness of US in both soil and sediment remediation was not thorough enough and the publications relating to their application are still limited. A more detailed overview on the scientific literature related to the US applications, will be discussed in the next chapter.

3.3 Combined remediation treatments

There are different technologies suitable for the contaminated sediment treatment. Despite their effectiveness they can have several disadvantages such as the high selectivity towards contaminants, long treatment times or require excessive consumption of reagents. Thus, the treatment combination could be useful to overcome the limits of some treatments, obtaining advantages from each one.

The co-contamination of both organic and inorganic compounds may represent a problem for the electrokinetic processes. Indeed, the organic compounds can affect the electric current circulating during the treatment and lead to the removal efficiency reduction. This phenomenon was observed to Falciglia et al. (2017), which obtained a decrease of about 5% in Hg removal in presence of PAHs contamination. In order to avoid interference on the treatment due to the presence of organic compounds, surfactants are usually used (Alcántara et al., 2012). Nevertheless, the use of these chemicals has not always led to an improvement in the process efficiency, as shown in the work of (Colacicco et al., 2010). In this work, a low PAHs removal was obtained even after the addition of surfactants.

Pazos et al. (2013), coupled an AOPs with the electrokinetic process, to reduce both organic and inorganic contamination from the marine sediments at the same time. Fenton's reagent process was used as AOPs to degrade petroleum hydrocarbon (THP) and EDTA to solubilize heavy metals. To compare the results an electrokinetic (EK) process alone was also carried out. The EK process showed best results for the heavy metals removal, due to the action of the EDTA on this type of contaminants, on the other hand a less THP removal (31%) was detected. In the combined process, there was a considerable increase of the THP removal, from 31% to 90%. This reduction of organic compounds has allowed greater mobilization of heavy metals with an increase in removal efficiency. For heavy metals the removal obtained with EK and the combined process were 44.1% and 57.3% of Zn, 42.9% and 59.8% of Pb, 39.7% and 59.4% of Cu, 46.1% and 54.5% Hg, respectively. In this case, the combination of different treatments allows to take advantages from the use of each process for a general improvement of treatment efficiency.

In the case of matrices with a high contamination, the use of bioremediation might be not effective for their treatment, because of the toxicity induced on the microorganisms. Thus, a combination with others technologies can be useful (Huang et al., 2017).

Hu et al. (2018) studied the combination of Fenton process with bioremediation, to remove bisphenol A (BPA) from river sediments. The bioremediation was performed with the use of white-rot fungi, *Phanerochaete chrysosporium* (*P. chrysosporium*), which is able to secrete organic acids. Fenton's reagent process alone was less effective compared to the use of *P. chrysosporium*, indeed they were achieved a removal percentage of 14.48%, and 21.59%, respectively. The best result was obtained in the combined treatment with BPA reduction of 58.23%. The combination of Fenton process and the use of *P. chrysosporium* involved a synergic effect. During the combined process there was an improvement in the *P. chrysosporium* development, due to the iron of the Fenton reagent and at the same time, the organic acids generated by fungi promote the Fenton reaction.

In the works discussed above the treatment combination was used to obtain different results. In the work of Pazos et al. (2013), two treatments were combined to have an improvement in the heavy metals through the reduction of PAHs contamination and then overall improvement. Whereas, Hu et al. (2018) used a combined treatment to obtain a synergic effect to remove one kind of contamination.

Another way to take advantage from more treatments is to use them in sequence, as in the work of Yu et al. (2009). In this case, an in-situ chemical stabilization and an ex-situ composting were used to reduce the toxicity of the sediments. The first one treatment was carried out using phosphate allowing a stabilization of 65%, 82.2% and 90% for Zn, Cu and Pb, respectively. Subsequently, with the composting carried out by adding amendments, there was a further stabilization due to the reduction of the bio-available. Indeed, there was an increase of the organic and residual form, which are less mobile compared to the exchangeable form, a carbonate form, and an Fe-Mn oxide form. In the work of Yu et al. (2009), therefore, the use of treatment in sequence allowed an improvement in sediment quality.

4. Ultrasonic processes

4.1 Introduction

US technologies are commonly included among the AOPs. Their effectiveness was widely investigated for the wastewater treatment (Mahamuni and Adewuyi, 2010). In detail, the main applications are related to the degradation of organic compounds in aqueous solutions and more recently also to the removal of emerging contaminants (Cesaro and Belgiorno, 2013; Manariotis et al., 2011; Naddeo et al., 2012, 2015; Park et al., 2000; Prado et al., 2017; Psillakis et al., 2004; Secondes et al., 2014). Moreover, this technology showed growing interest as pre-treatment to enhance anaerobic digestion (Cesaro et al., 2014; Kondusamy and Kalamdhad, 2014; Quiroga et al., 2014) and in the field of analytical chemistry (Banjoo and Nelson, 2005; Bendicho et al., 2012).

US applications have also grown exponentially in the environmental engineering field, for the treatment of different contaminated matrices (Adewuyi, 2001; Mason, 2007) as soil and sediments. Nevertheless, in scientific literature the publications on this issue are still few.

In the present chapter the principle of US processes, the effect of the US treatment parameters are illustrated and an overview of the US process applications was discussed, with particular reference to the soil and sediment remediation.

4.2 Principle of ultrasonic processes

Ultrasounds are sound waves above audible threshold of the human being (20 kHz). The usually range of ultrasound frequency is between 20 kHz and 10 MHz, in particular the conventional power ultrasound range for the sonochemistry applications is between 20 kHz and 2 MHz, whereas higher frequencies are more used in the medical field (Figure 4.1) (Mason, 1997).

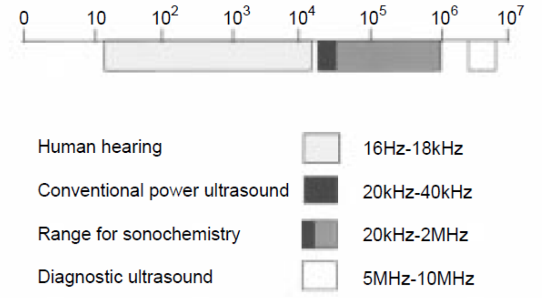

Figure 4.1 Sound frequency ranges (Mason, 1997)

Ultrasound waves, as sound waves in general, are spreads in the environment through alternating compression and rarefaction cycles (Figure 4.2).

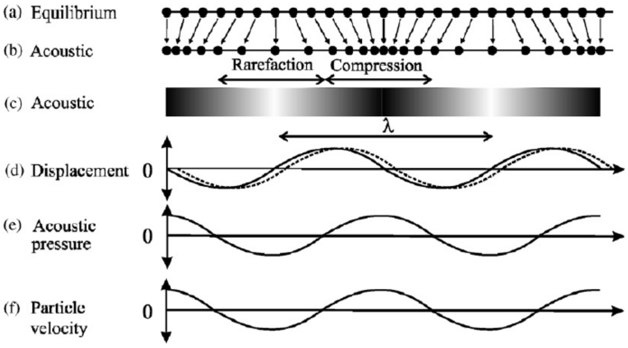

Figure 4.2 Schematic of a one-dimensional single-frequency compressional longitudinal acoustic wave propagating linearly (Leighton, 2006)

During the crossing of the medium, the average distance between the molecules varies as they oscillate about their mean position. In the liquid medium, when there is the negative pressure large enough, the distance between the molecules can be greater than the critical molecular distance to hold the liquid intact, then there is a separation in the liquid molecules and consequently the formation of voids namely the cavitation bubbles (Capelo-Martínez, 2009; Leighton, 2006; Suslick, 1989).

The ultrasound processes based their effectiveness on the cavitation phenomenon, which concern the vapour bubble formation, growth and violent collapse. Cavitation can generate chemical and physical effects, which are the consequence of two kind of cavitation “stable” and “transient”. In the stable cavitation, the bubbles oscillate for several acoustic cycles about an equilibrium size. Instead, in the transient cavitation the bubbles oscillate only for few acoustic cycles until a sudden collapse (Capelo-Martínez, 2009; Mason, 1997; Thompson and Doraiswamy, 1999). As consequence of this collapse, there is a significant release of energy, which can be explained through the hot-spot theory. This theory assert that with the collapse of vapour bubbles there is local extreme variations of the pressure and temperature, up to 2000 atm and 5000 °C, respectively (Adewuyi, 2001; Mason, 1997; Suslick, 1989) (Figure 4.3).

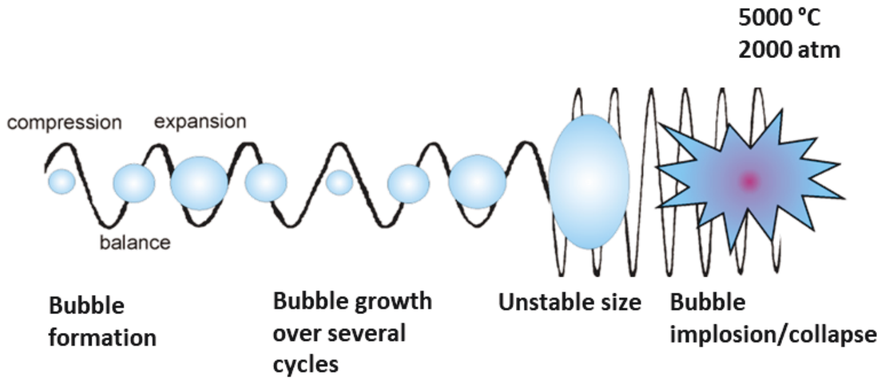

Figure 4.3 Cavitation phenomenon (Turánek et al., 2015)

The chemical effects of the cavitation are to the formation of hydroxyl radicals ($OH^{\bullet}$), which are one of the most powerful oxidizing species and are able to make the degradation of the organic compounds (Sirés et al., 2014). The mechanical effects lead to the fragmentation of the solid particles (Figure 4.4) promoting desorption of contaminants compound or in general the cleaning of solid surfaces (Pokhrel et al., 2016; Son et al., 2012).

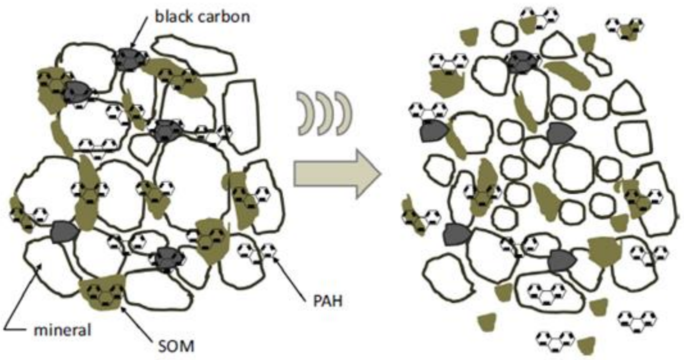

Figure 4.4 Mechanical effect of ultrasound waves (Pee et al., 2015)

4.3 Parameters affecting ultrasonic treatment

US treatment is based on the cavitation phenomenon, which is influenced by several process parameters. In the studies dealing with US technologies frequency, power and sonication time are the parameters mainly considered.

In order to investigate their effect on the remediation efficiency in the following paragraphs an overview of these parameters is provided.

4.3.1 Ultrasonic frequency

In the sonochemistry, the common range of frequency is between 20 kHz and 40 kHz, whereas higher frequency may negatively affected the cavitation phenomenon.

In detail, at high frequencies is more difficult to generate the cavitation, because the cycle of rarefaction and compression shortens and then its duration could be insufficient to generate negative pressure for the cavitation occurs (Mason, 1997; Thompson and Doraiswamy, 1999).

The variation of sonication frequency, therefore, influences the bubble size, which decreases with the increasing of frequency (Figure 4.5) (Brotchie et al., 2009).

Smaller bubbles are associated with a more degradation effective due to the greatest number of cavitation events and, as a consequence, the higher generation of free radicals.

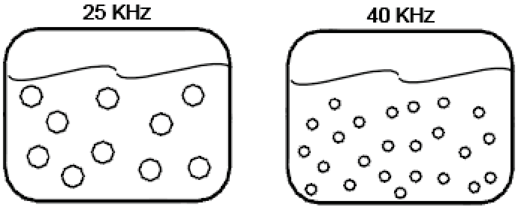

Figure 4.5 Scheme of bubble dimension varying frequency value (Silva and Martins, 2012)

Conversely, large bubbles, which are generated at low frequencies, are able to produce more violent collapse and then, stronger mechanical effects (Son et al., 2011; Thompson and Doraiswamy, 1999). The mechanical effect was observed from Son et al., (2011), which in order to find the optimal sonication frequency for the combined ultrasonic-mechanical soil washing, tested the effect of the cavitation on an aluminium foil (Figure 4.6).

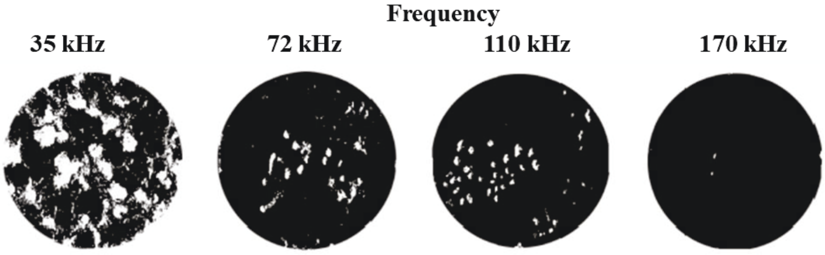

Figure 4.6 Damaged foil images caused by sonication at different frequencies and at constant ultrasonic power level (adapted from Son et al., 2011)

During the tests was noted an increase in damage for the aluminium foil at lower frequency (white spots). Such damage represent indirectly the mechanical effect of ultrasound which is more significant at lower frequencies (Mason, 1997). This effect can be a positive factor for the soil and sediment remediation, increasing the surface available for the treatment and promoting the contaminant desorption.

Nevertheless, it must be taken into account that an excessive fragmentation could lead a sharpe decrease of the particle size and therefore a substantial change in the original structure.

The high frequency, indeed, entails an improvement of organic compound degradation in liquid phase, which represent a strength for the reduction of organic compounds in the water solutions (Psillakis et al., 2004), but also soil and sediment remediation for which the contaminants desorbed from the slid surface may be degraded in the liquid medium (Collings et al., 2006).

4.3.2 Ultrasonic power

Generally, as the power increases, there is an increase of both the cavitation bubble size (Figure 4.7) and degradation yield (Figure 4.8) (Brotchie et al., 2009; Manariotis et al., 2011).

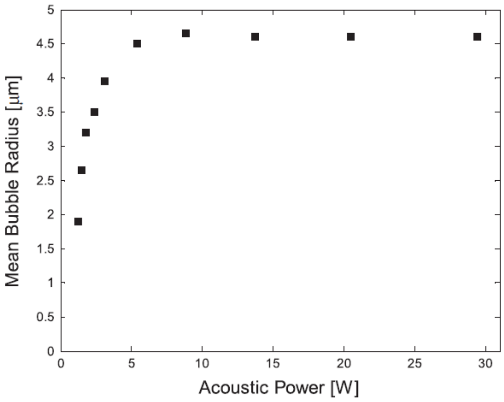

Figure 4.7 Bubble radius as a function of sonication power (Brotchie et al., 2009)

Indeed, with the increase of power there is a higher number of cavitation bubbles and then greater sonochemical effects (Mason and Peters 2002).

This evidence was investigated in the work of Manariotis et al. (2011), which, in order to degrade PAHs from the pure aqueous solution, performed different tests at various frequencies and power levels.

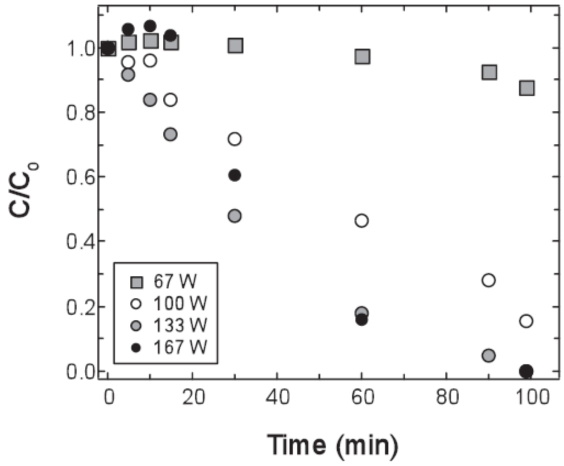

Figure 4.8 Phenanthrene degradation as a function of time at different input power levels and constant frequency 582 kHz (Manariotis et al., 2011)

However, power and frequency of sonication are strongly related and the effect of the two parameters should be balanced to maintain an adequate level of cavitation (Pokhrel et al., 2016). For this purpose, as the frequency increases, the power should also increase, nevertheless, the effect on the bubble size is not always linear by varying these parameters (Manariotis et al., 2011). This observation is in agreement with the work of Merouani et al. (2013), which in a theoretical study observed three ranges of frequencies, namely 200-300 kHz, 500-1000 kHz and over 1000 kHz for which a similar increase of power and frequency can entails an effect on the bubble growth, linear, quasi-linear or lead to a reduction, respectively.

These outcomes demonstrate how for the remediation treatments the extreme conditions of frequency and power of sonication are not necessarily those that guarantee the best removal efficiency.

4.3.3 Sonication time

Sonication time is one of the most studied parameters in the remediation treatments. The effect of the time can have difference influences on the soil and sediment remediation efficiency. Generally, with the sonication extension was observed an improvement of the organic compound degradation rate, a reason may be related to the longer contact time between contaminants and hydroxyl radical (Collings et al., 2006). Another reason is represented from the increase in the bioaccessible sites as demonstrated from Pee et al. (2015).

This phenomenon allows a higher mass transfer of the contaminant in the liquid phase promoting their successively degradation in this phase.

However, long treatment time may also negatively affect the remediation efficiency. Indeed, in the case of diesel contamination Feng and Aldrich (2000) observed that with the extension of sonication time, after an initial increase of removal, there was an efficiency decrease. This evidence was correlated at a difference in oil droplets concentration, between the solid particles and the aqueous solution. This difference allows the re-adsorption of the contaminants onto the soil particle surface and then a reduction of the removal efficiency.

Another consequence tied to the treatment time is the fragmentation of the particles (Pokhrel et al., 2016; Son et al., 2012). Indeed, the exposure of the particles to the continuous cavitation mechanical effect, can entails the reduction of their size as is possible to see in the Figure 4.9.

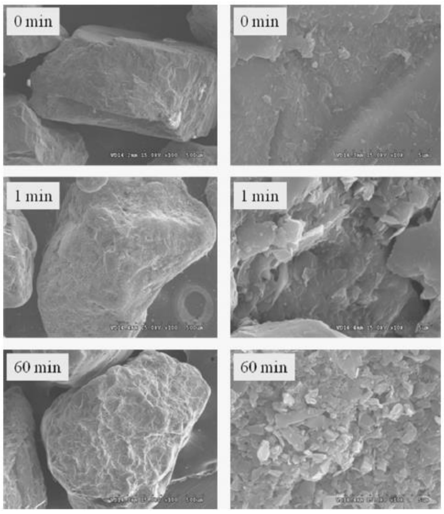

Figure 4.9 Images of the soil particles surface after ultrasound irradiation at different times and magnification (100 x magnification at left-side and 10,000 x magnification at right-side) (Son et al., 2012)

These observations highlight how for the soil and sediment remediation excessive treatment times, could be not justified.

4.4 Ultrasound remediation for contaminated sediments

The constant search of environmental friendly, clean and fast treatments, has led to apply ultrasonic technology also for soil and sediments remediation. In order to treat this kind of matrices, it could be necessary that occurs a desorption of the contaminant to the aqueous phase for a further treatment in this phase (Pee et al., 2015). This process is possible with the use of US, which are able to generate physical and chemical effects (Mason, 1997). The use of US, however, has not been sufficiently investigated for soil and sediment remediation.

Regarding soil remediation, promising results were obtained for the degradation of organic compounds. Duong et al. (2010) applied US waves to remove phenanthrene (PHE) and hexachlorobenzene (HCB) from kaolin slurry sample. After 15 hours of treatment, degradation percentages of 45% and about 100% were obtained for PHE and HCB, respectively. These results are related to the US effect to enhance the contaminant desorption and in particular, the lack of organic matter could be the reason of high removal percentages. In fact, the presence of organic matter can affect the contaminant availability for degradation (Pee et al., 2015). Whereas, the difference of removal between the contaminants may be attributed to the chemical structure (Duong et al., 2010).

US treatment could be considered as an alternative soil washing methods (Mason, 2007). However, their effectiveness was more evaluated in combination or as pre-treatment to enhance the traditional soil washing for heavy metals removal. In the work of Park and Son (2016) an ultrasonic/mechanical soil washing process was performed (Figure 4.10).

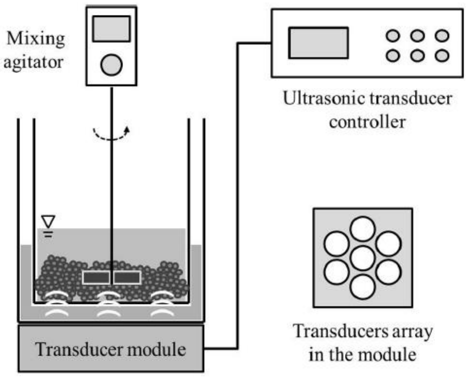

Figure 4.10 Schematic of ultrasonic/mechanical soil washing process (Park and Son, 2016)

During the process, different combinations were implemented in terms of soil/liquid ratio (1:2 and 1:3) and acid solution concentration (0.5-1M HCl). The use of US waves have allows an increase of desorption up to 29% compared to the mechanical soil washing alone, obtaining a maximum removal of 76.2% in 30 minutes. This result demonstrated the significant contribute of the US on the treatment, moreover, in the experiments with less favourable conditions the US contribute was more evident. Indeed, at the same acid solution concentration, but with the less soil /liquid ratio, the use of US led to a higher removal increase of 38.3%, whereas, with 1:3 soil/liquid ratio and the less acid solution there was an improvement up to 52%. The employ of US technology not only allows reducing the washing solutions and the concentrations of the solvents, but also the treatment times as shown by Wang et al. (2015). In this work, US (10 min) was applied before or after a conventional mechanical soil washing (4 h), with different washing solutions. The combination of US and soil washing treatment permitted to obtain a general enhancement of the process up to about 34% (Figure 4.11). Despite these good results, it can be noted how with 10 min of US was possible to achieved comparable results with those obtained by 4 h of mechanical soil washing, with a time reduction equal to 96%. This result highlights how with the use of US is possible to obtain a reduction of the treatment times, in comparison to conventional treatments.

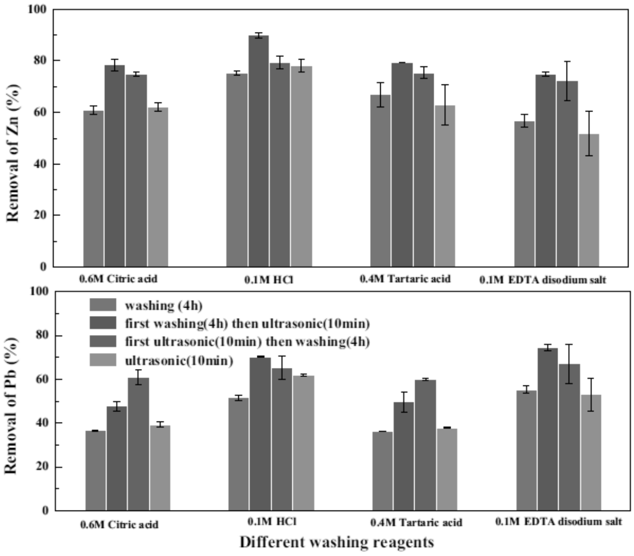

Figure 4.11 Removal efficiency of the combined ultrasonic-mechanical soil washing treatment (Wang et al., 2015)

As mentioned above, few studies have also investigated the effectiveness of US for contaminated sediment remediation (Agarwal and Liu, 2015; Peng et al., 2009), pointing out that the best results were obtained for the organic contaminants (Feng and Aldrich, 2000; Mason et al., 2004) and that by varying the US operational parameters is possible to enhance the process yields. In the work of Collings et al. (2006) riverine sediments with PAHs contamination were treated under three different US power. It was evident the enhancement of the treatment for increasing power, obtaining, after 3 min treatment, percentage of about 35%, 70% and 80% at 150 W, 1-1.5 kW and 4 kW, respectively. This result could be explained with the increase of the reaction rate at higher power (Park et al., 2000; Psillakis et al., 2004; Thompson and Doraiswamy, 1999).

Good results were also obtained for the desorption of diesel from the sand (Feng and Aldrich, 2000; Son et al., 2011). For this purpose Son et al. (2011), before to implement a combined ultrasonic-mechanical soil washing studied the mechanical effect of the frequency of sonication. In particular, to choice the best frequency for the treatment, a preliminary experiment was carried out with the use of an aluminium foil sonicated at four frequencies, namely 35kHz, 72 kHz, 110 kHz and 170 kHz. After the tests, the lower frequency was selected as the more effective, as it produced the stronger mechanical effects, highlighted by the damage to the aluminium foil. The use of this frequency was able to enhance the desorption of diesel, and the combination of ultrasound and washing treatment entails a reduction of 75% in the treatment time. Indeed, it was possible to obtain comparable results (75% diesel removal) with those observed after four conventional washing operation.

In the case of organic contamination the US effectiveness can be associated to both the mechanical action, which promotes the contaminant desorption, and the chemical effect for subsequent degradation. For heavy metals, however, their non-biodegradability is one of the major problems for treatment. Nevertheless, US was implemented with other technologies to overcome this problem, facilitating the desorption from the sediments, to allow a possible further treatment in other phase or their stabilization.

In the work of Meegoda and Perera, (2001), US waves and vacuum pressure were coupled to remove Cr from dredged sediments, previously separated in coarse and fine (silt and clay) fractions. High removal efficiencies were obtained for both the coarse fraction and the silt, with percentages of 92% and 83%, respectively. However, in order to achieve these results the treatment times were very different: 15 min and 90 min of treatment were necessary for the coarse and silt fraction, respectively. Any significant effect was observed for the clay fraction, in which the Cr resulted stable and heavily adsorbed. In this work was evident how the US is able to promote the desorption of the heavy metals from sediment with different grain size distribution, although the very fine fraction could be a problem for the treatment.

The mechanical effect of US technology was also used in combination with bioremediation treatments. US process was implemented in combination of a transgenic green alga (*C. reinhardtii)* in the study of He et al. (2011).This type of alga is able to bind the heavy metals, which are dissolved into the liquid phase. The advantage related to the use of US is due to the release of heavy metals (Hg) in the liquid phase: in this way they are available for the alga adsorption. In the work of He et al. (2011) the beneficial contribution of US was more evident in the solution with pH 8. This result can be explained with the formation of strong complexes with the natural organic matter (NOM) and the heavy metal (NOM-Hg), which may reduce the availability of Hg for the algae. At pH 8 and with the support of US, NOM dissolves.

A simultaneous presence of organic and inorganic contaminants is common in the real sediments. The different chemical characteristics of the polluted compounds can affect the treatment efficiency and in order to surmount this drawback, treatments with difference abilities may be used in combination.

In this regard, electrokinetic process and US (Figure 4.12) were combined in the work of Chung et al. (2006), for the removal of both lead and ethylene glycol from contaminated sand. The EK process was, indeed, intended to reduce heavy metal contamination; the US was considered due to its effectiveness towards organic compounds.

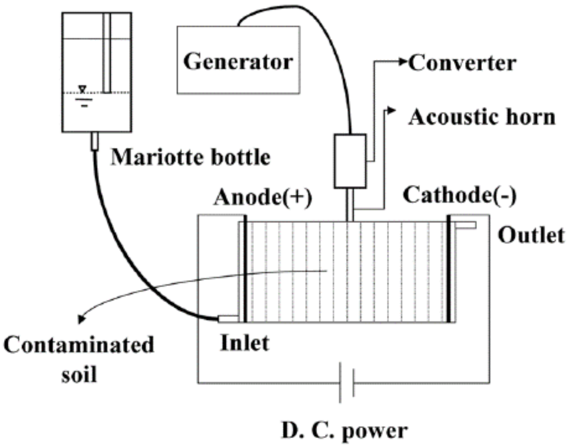

Figure 4.12 Electrokinetic and ultrasonic combined system schematic set up (Chung et al., 2006)

The electrokinetic process alone was able to reduce both inorganic and organic contamination of 75% and 69%, respectively. The combination with US led an improvement of the treatment more pronounced for the ethylene glycol with an increase of 21%, whereas for the lead there was a final removal of 80%. The influence of the US on the contaminant removal could be associated to the increase in the porosity and permeability of the solid medium, which improved, in turn, the flow of the processing fluid and then the contaminant movement through the sediments (Chung and Kamon, 2005).

Literature studies have shown the potential of US technology as a remediation strategy for contaminated sediment. However, scientific studies in this regard are still limited and usually devoted to either assess the desorption yields of inorganic compounds from soil or the degradation or the organic ones, especially in liquid matrices.

The contamination of sediments is usually highly heterogeneous and both organic and inorganic pollutants are simultaneously present. In this regard, the present research focused on the study of US treatment effectiveness for the remediation of sediments polluted by both heavy metals and PAHs.

5. Experimental activity

Over the years, different polluting compounds have been discharge in the aquatic environment because of a not proper management or accidental release. These compounds have different sources and reach the water bodies through various pathways, but the end point is often represented by the sediments (Bouloubassi et al., 2012; Dou et al., 2013; Tornero and Hanke, 2016).

In particular, due to their high persistence in the environment, the heavy metals and the PAHs are among the most detected contaminants in the sediments (Kucuksezgin et al., 2013; Liu et al., 2015; Mahdi Ahmed et al., 2017; Traven et al., 2015). The main concern is relates to the toxic and carcinogenic effects that these compounds can have for the environment and the human health (Abdel-Shafy and Mansour, 2016; El Nemr and El-Sadaawy, 2016). The sediments represent, therefore, a potential reservoir for the contaminants, but varying the external conditions they can also became a source of contaminants (Sundelin and Eriksson, 2001).

Given their strategic importance for the aquatic environment, the contamination of sediments is a global concern and the contaminated sediment management represent a key factor.

The traditional management strategies of dredged sediments includes the replacement in the water bodies or the landfill disposal depending on the contamination degree. In order to limit the amount of contaminated sediments in the landfills and the dangers associated with them, it is necessary to reduce the contamination. For this purpose, a specific treatment must be selected, taking into account the simultaneous presence of different compounds.

In the scientific literature, the advanced oxidation processes (AOPs) are arousing increasing interest also for the treatment of contaminated solid matrices (Bocos et al., 2015; Cheng et al., 2016; Ferrarese et al., 2008; Rivas, 2006). Indeed, these processes were widely used for the treatment of the aqueous solutions and their effectiveness is demonstrated by several scientific works (Cesaro and Belgiorno, 2016; Esplugas et al., 2002). Among the AOPs there are the processes which use US technologies for the treatment.

US is widely employed in different fields of science and technology (Gallego-Juarez, 2010; Silva and Martins, 2012) and in particular, in the environmental engineering field, this technology was used for the treatment of different matrices, as wastewater, organic waste and sludge (Cesaro et al., 2014; Li et al., 2017; Naddeo et al., 2015; Secondes et al., 2014).

The US treatment has always attracted international scientific attention for the speed of treatment and for the possibility to avoid or reduce the chemical solvent use, compared with the conventional treatments (Park and Son, 2016; Son et al., 2011, 2012; Thangavadivel et al., 2011).

The effectiveness US treatment is based on the cavitation phenomenon, which involves chemical and physical effects (Adewuyi, 2001; Mason, 1997; Suslick, 1989). The chemical effects lead to the generation of hydroxyl radical ($OH^{\bullet}$), which are potent chemical oxidants, allowing the mineralization of organic pollutants or their degradation to less harmful compounds (David, 2009; Manariotis et al., 2011; Psillakis et al., 2004).

Whereas, through the physical effects, the fragmentation of solid particles occurs, promoting the contaminants desorption (Mason et al., 2004; Pee et al., 2015; Son et al., 2011). Therefore, because of these features the ultrasonic treatment represent a promising treatment for the sediment remediation.

In this work, the research was oriented towards the study of the US effectiveness both as a treatment and as a pre-treatment of contaminated sediment.

5.1 Experimental plan

The main aim of this research activity was to study the effectiveness of the advanced technologies, to reduce organic and inorganic contaminants from sediments. This objective was pursued through the application of the US technology, which was evaluated for both as stand-alone treatment and as pre-treatment.

In particular, US effectiveness was investigated as pre-treatment to a remediation technology, which is represented by the EK process. This technology is generally known to be effective in the removal of heavy metal from soil and sediments.

Thus, the experimental activity was divided into two main steps:

- The first step focused on the assessment of the ultrasonic treatment effectiveness for the remediation of contaminated sediments. This treatment was selected for the ultrasound ability to promote the mineralization of organic contaminants in the liquid phase and the desorption of the inorganic contaminants from the solid matrix. Subsequently, in order to define the optimal treatment conditions, both process enhancement and optimization were performed;
- In the second phase, the potential application of US technology as pre-treatment was investigated. To this end, the EK process was combined with the ultrasonic treatment (US+EK) and the performances evaluated with particular reference to the desorption of heavy metals.

In detail, the experimental activity concerns the stand-alone ultrasonic treatment, was carried out at the laboratory of the Sanitary Environmental Engineering Division (SEED) of Salerno University.

Whereas, the second step was performed at the laboratory of the Bioengineering and Sustainable Processes (BIOSUV) group at the University of Vigo (Spain).

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6. Materials and methods

In the following paragraphs, a description of the experimental set up and the analytical methods followed to carry out the research is outlined. For this purpose, the chapter was divided in four main sections dealing with:

i) the methods adopted to characterize the material used for the experimental activity. in terms of grain size distribution, mineral analysis, buffering capacity, point of zero charge, pH and electrical conductivity;
ii) the spiking procedure the spiking procedure implemented to obtain the desired sediment contamination;
iii) the experimental set up and the analytical procedures carried out for US;
iv) the devices and methods applied for the EK treatment.

6.1 Chemical-physical characterization of sediments

6.1.1 Sediment sample

The mineralogical composition and the grain size of the real sediments are much variable due to the type of the source rocks and the physical-chemical processes, which generated them. In order to obtain a representative sediment model, a proportional composition of silica and fine quartz sand was considered. The mixed sample contained 20% w/w of silica sand (Sataf srl) and 80 % w/w fine quartz sand (BluLine), with a maximum grain size of 1.7 mm.

The use of clean sand allow to avoiding the possible interference during the treatment and in the analytical phase.

6.1.2 Grain size distribution

The sample used for the experiments was constituted mainly by fine sand, as is possible to see from the following figure (Figure 6.1).

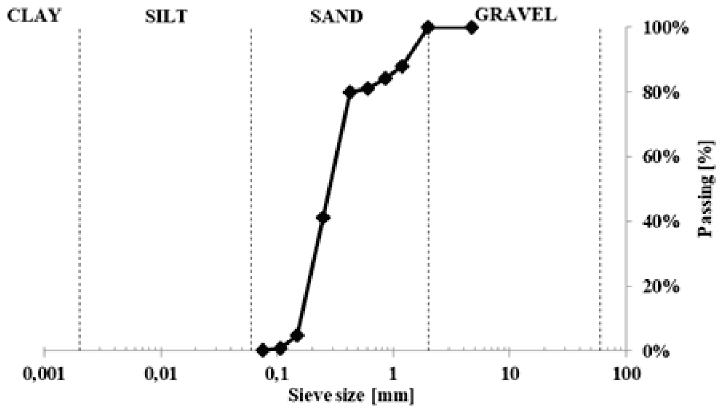


Figure 6.1 Grain size distribution

Grain size distribution was determined in accordance with ASTM D422-63 standard method. Grain size analysis was carried out at the Geotechnical Engineering Laboratory of the University of Salerno. A set of sieves with different ascending order of sieve numbers, from 4 at top to 200 at bottom, was used to separate each fraction of sediment (Figure 6.2). The sediment (500 gr) was poured into the top sieve and after the sieve stack was placed in the mechanical shaker for 30 min.

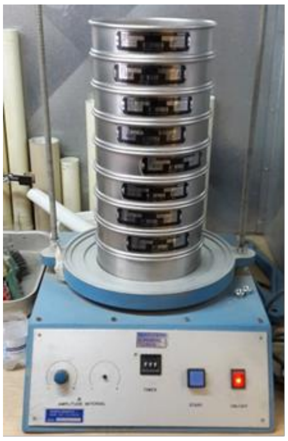


Figure 6.2 Mechanical shaker

At the end of this operation, the sediment retained in each sieve was weight (P), as well as the sediment at the bottom, and after were calculated:

- Partial retained

$$T_i\,(\%) = 100 * \frac{P_i}{\sum_{i=1}^{N} P_i}$$

- Cumulative retained

$$TC_i\,(\%) = 100 * \frac{\sum_{j=1}^{i} P_j}{\sum_{i=1}^{N} P_i}$$

- Cumulative passing

$$PC_i\,(\%) = 100 - TC_i(\%)$$

The weighs obtained were reported in the Table 6.1.

Table 6.1 The grain size analysis

Sieve Number	Mesh size [mm]	Sediment retained [gr]	Cumulative retained [gr]	Passing [%]
4	4.75	0	0	100
10	2	0	0	100
16	1.18	60.73	60.73	87.85
20	0.85	18.39	79.12	84.12
30	0.60	16.01	95.13	80.97
40	0.425	5.38	100.51	79.90
60	0.25	192.87	293.38	41.32

Sieve Number	Mesh size [mm]	Sediment retained [gr]	Cumulative retained [gr]	Passing [%]
100	0.15	182.5	475.88	4.82
140	0.106	19.36	495.24	0.95
200	0.075	3.11	498.35	0.33

6.1.3 Mineralogical analysis

The identification of the chemical composition of sediment was performed using X-ray powder diffractometer (XRD, Bruker D8 advance). The work set up was the following:

- Cu Kα radiation;
- 35 keV accelerating voltage;
- 40 mA current;
- 10-80° scanning range;
- 0.5 s/step (0.0296°/step) scan speed.

The mineralogy determined by XRD analysis, showed a predominant composition of quartz (Figure 6.3).

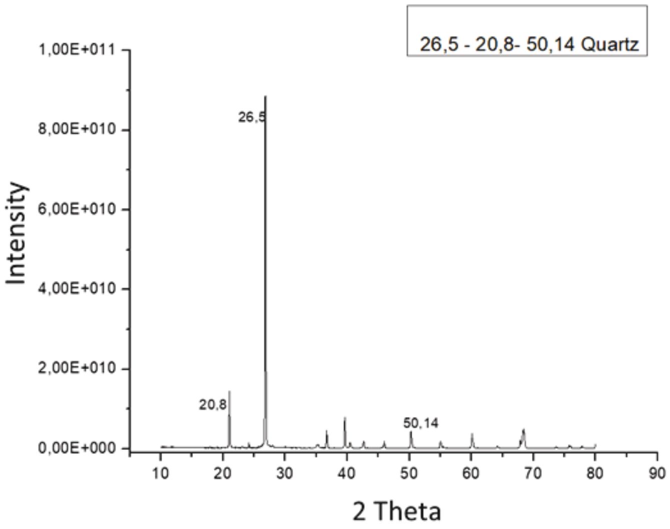


Figure 6.3 XRD pattern of sediments

6.1.4 Acid buffering capacity, point of zero charge, pH, electrical conductivity

The sediment was characterized in terms of acid buffering capacity, point of zero charge, pH and electrical conductivity.

Buffering capacity

Buffering capacity is the ability of a substance to maintain the pH value rather constant, when an acid or a base are added to it.

The acid buffering capacity was measured according to the titration procedure reported by Reddy et al. (1999). In a glass beaker 2 gr of sediment and 30 ml of distilled water were stirred for 30 min with a magnetic stirrer. At the end of this 30 min the pH was measured by pH meter (Fisher Scientific-accumet XL600). The second step was to add 1 ml of 1 M hydrochloric acid (HCl) each 30 min and measure the pH thereafter. The titration curve was plotted in terms of pH value versus ml of HCl added. In Figure 6.4 is possible to see a low buffering capacity behaviour, highlighted from a quick change of the pH value after the addition of HCl.

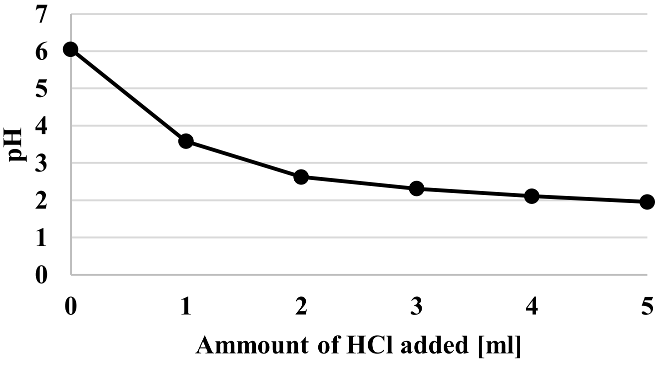


Figure 6.4 Titration curve acid buffering capacity

The low buffering capacity is in agreement with the lack of calcium carbonate, as showed from the XRD analysis, which entails the low capacity to neutralise H^+ (Kim et al., 2006; Missaoui et al., 2016; Yoo et al., 2013).

Point of zero charge

The point of zero charge (PZC) is the pH value for which the charge on a surface of the sediment is zero (Appel et al., 2003; Mahmood et al., 2011).

The PZC of the sediment sample was determined in according with the method "*Powder Addition*", as described by Cristiano et al. (2011). In the graph below (Figure 6.5), the variation of the pH versus the initial pH value (pHi) was plotted.

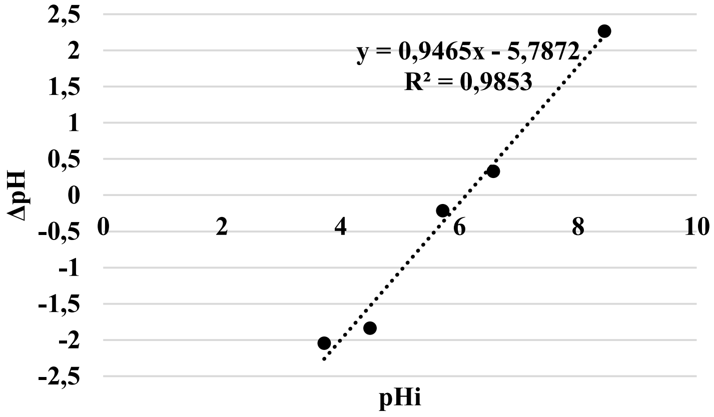


Figure 6.5 The variation of pH (ΔpH) versus the initial pH (pHi)

In order to determine the PZC value, a solution of sodium nitrate ($NaNO_3$) (250 ml) (Fisher Scientific, UK), with an initial pH of 6, was prepared. After adding some drops of sodium hydroxide (NaOH 1 M) (Fisher Scientific, UK) or nitric acid (HNO_3 1 M) (Fisher Scientific, UK), the pH was adjusted to pH 4.5, 6, 6.5, 8 and 10 to obtain five different solution (50 ml). Subsequently, 1gr of sediment was placed into a flask of 250 ml (Figure 6.6a) containing one of the previous solutions, this procedure was repeated for all the solutions. The flasks were put into the shaker (Thermo Fisher Scientific) at 25°C, to 150 rpm for 24 h (Figure 6.6b).

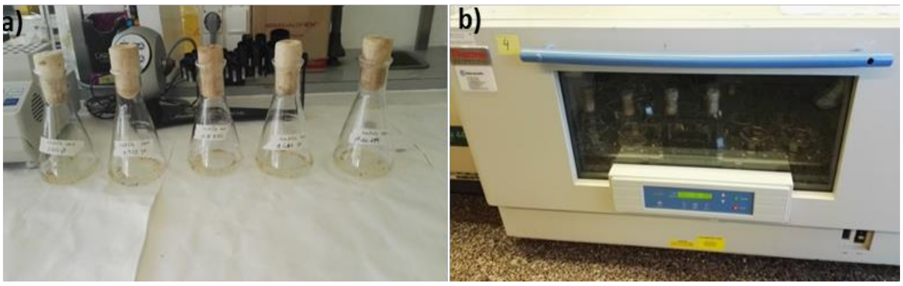


Figure 6.6 Flasks(a) and shaker (Thermo Fisher Scientific) (b)

After 24 h the samples were centrifuged for 10 min to 8500 rpm (Rotina 380r-Hettich Zentrifugen) and the pH was measured (Figure 6.7).

Figure 6.7 Centrifuge (Rotina 380r-Hettich Zentrifugen)

Through the straight-line equation, it was possible to obtain the PZC of the sediment, which is 6.2.

pH

One gram of dry sample was mixed with 20 mL of deionized water and after the pH was measured with a benchtop pH meter (HANNA Instruments HI5522) in accordance with the procedure of Bocos et al. (2015)

Electrical conductivity

Electrical conductivity was determined in a suspension of 2 g of sediment and 10 ml of deionized water. The sample was placed on a magnetic stirrer for 30 min and after the filtration, the conductivity was measured in the liquid fraction by benchtop conductivity meter (HANNA Instruments HI5522) (Bocos et al., 2015).

6.2 Contamination procedure

6.2.1 Organic contamination procedure

The organic compounds selected for the spiking procedure, belong to the group of Polycyclic Aromatic Hydrocarbons (PAH). In particular, the organic target compounds were chosen among the sixteen PAH, which are included in the list of priority pollutants of the Unite States Environmental Protection Agency (US EPA), namely benz(α)anthracene (B(α)A) and benzo(α)pyrene (B(α)P) (Figure 6.8). All contaminants used were purchased from Sigma Aldrich.

Figure 6.8 Organic compounds used for the spiking procedure (Sigma-aldrich)

The spiking procedure was carried out in according to Russo et al. (2012).

In order to take into account the Italian limit legislation and for analytical requirements, the initial concentration was established at least the double values of the limit concentration allowed by the D.Lgs.152/06. In detail this value correspond to the maximum concentration for soil in industrial e commercial sites.

With the purpose of obtaining desired concentration of about 20 mg/kg_{ss} for each contaminant, a solution was prepared by dissolving 2 mg of B(α)A and B(α)P, in 10 ml of dichloromethane (VWR CHEMICALS). This solution was mixed by stainless steel spoon with 100 gr of dried sediments, to homogenize the sample. After, to allow the volatilization of the solvent, the sample was placed under the fume hood, at laboratory temperature and in darkness for three days.

6.2.2 Inorganic contamination procedure

The heavy metals selected, as inorganic compounds model for the spiking procedure, were cadmium (Cd), lead (Pb) and zinc (Zn) (Figure 6.9). All contaminants used were purchased from Sigma Aldrich.

Figure 6.9 Inorganic compounds used for the spiking procedure (Sigma-aldrich)

The heavy metal contamination was carried out by dissolving the metal nitrates in the deionized water (Milli-Q system from Millipore) in accordance with Rozas and Castellote (2012). Specifically, during the contamination were used, cadmium nitrate tetrahydrate (CdN_2O_6+$4H_2O$), lead (II) nitrate (N_2O_6Pb) and zinc nitrate hexahydrate (ZnN_2O_6+$6H_2O$). In order to have a final contamination of 30 mg/kg_{ss}, 2000 mg/kg_{ss} and 3000 mg/kg_{ss} respectively for Cd, Pb and Zn, established as described in the previous paragraph, a stock solution was prepared by dissolving 8.22 mg of CdN_2O_6+$4H_2O$, 320 mg of N_2O_6Pb and 1365 mg of ZnN_2O_6+$6H_2O$ in 50 ml of deionized water (Milli-Q system from Millipore). This solution was poured onto 100 gr of sediments and the mix of sediment and contaminants was left in contact for one hour. After an hour, the sample was placed in an oven (Inter Continental Equipment) at 105 °C for 24 h to allow the drying.

6.3 Ultrasonic treatment

6.3.1 Ultrasonic treatment set-up

The batch tests were performed at the Laboratory of Sanitary and Environmental Engineering Division (SEED) of the University of Salerno, at laboratory scale.

Ultrasound treatment was carried out using an ultrasonic bath (Elma TI-H 10) with a maximum tank capacity of 8.6 litres, an ultrasonic power effective of 200 W and a frequency variable from 35 to 130 kHz (Figure 6.10).

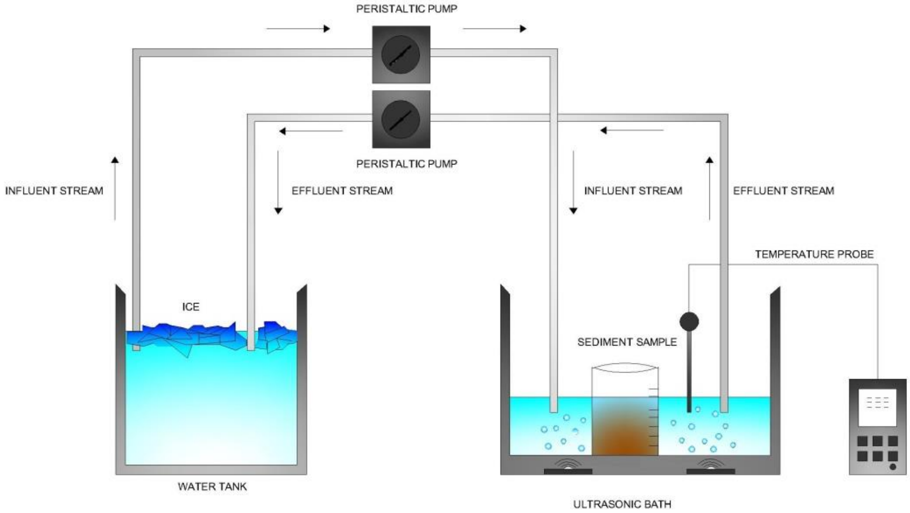


Figure 6.10 Ultrasonic treatment flowsheet

During the treatment, the samples were subjected to sonication at different treatment times of 5, 10, 15, 30, 60 minutes and at frequencies of 35 kHz and 130 kHz. These parameters were generally used, but during the experiments, the combination was varied.

In order to allow the spread of ultrasonic waves and to occur the phenomenon of cavitation (Mason, 1997), a sand slurry sample was prepared with 20 gr of contaminated sediment and 40 ml of deionized water (w/w 1:2)

(Shrestha et al., 2009). The sample was put into a beaker of 250 ml and placed into ultrasonic bath at an ultrasonic density of 110 W/L. A cold-water recirculation was realized using two peristaltic pumps (Watson Marlow SciQ 323), to avoid overheating of the sample. During the treatment, the temperature was maintained below the 30 °C.

Moreover, during the enhanced treatment others work solutions were used. In detail, the enhancement was carried out through two solutions, a 0.1 M solution of citric acid and a 0.1 M solution of ethylenediaminetetraacetate (EDTA).

These chemicals are chelating agents and they were selected mainly to take advantage of their ability to solubilize or to form complexes with heavy metals (Leštan et al., 2008; Dermont et al., 2008). The concentration of 0.1 M was established in accordance with scientific work, which demonstrated its effectiveness for the heavy metal desorption (Cameselle and Pena, 2016; Pazos et al., 2008).

6.3.2 Analytical set up

PAH extraction and determination

Before the determination of the contaminant concentration in the sediments, the extraction was implemented in accordance with the method US EPA 3550b. The sediments (5 gr), previously dried in an oven at 105 °C for 24 h, were put into a beaker with 20 ml of cycloexhane (CarloErba) and duly covered with aluminium foil, to avoid the evaporation. The sample was placed in an ultrasonic bath (Transonic TS 540) for 20 min (Figure 6.11).

Figure 6.11 Ultrasonic bath (Transonic TS 540)

After the sonication the sample was mixed with anhydrous sodium sulphate (Carlo Erba) and left for 30 min, to remove the possible moisture content. The mixture of sediments, solvent and anhydrous sodium sulphate was filtered by a cellulosic filter of 2.5 μm (Whatman 42) with a vacuum pump (Vacuubrand MZ 2C/1.7). The liquid extract was poured into a round bottom flask and placed in a Rotavapor (Heidolph VV 2000) set to 60 °C 90 rpm, to allow the evaporation of the solvent. The residual dry matter was re-dissolved with 10 ml of dichloromethane (Carlo Erba) for the determination. A gas chromatograph coupled with a mass selective detector (GC-MS Thermofinningan DSQ Trace) was used for the determination in accordance with the method US EPA 8270c (Figure 6.12).

Figure 6.12 GC-MS (Thermofinningan DSQ Trace)

The sample was directly injected in the GC-MS through a 10 μl glass syringe. The GC-MS used to quantify the PAH extract is made up of a 0.25 mm (id) 30 m methyl siloxane capillary column and 0.25 mm thick (Restec). The temperature program was set as described below: the temperature was held at 65 °C for 0.5 min, after increased at the rate of 15 °C min^{-1} up to 240 °C and left for 0.5 min. Finally, the temperature increased at the rate of 4 °C min^{-1} up to 280 °C and maintained for 15 min. As carrier gas was used helium, with a constant flow of 0.5 mL min^{-1}.

Heavy metals extraction and determination

The heavy metals concentration was obtained through a first step of extraction and subsequent determination. A microwave assisted acid digestion was performed in accordance with the method US EPA 3051a, to extract the contaminants. In a Teflon vessel, 1 gr of sediment was put inside with 10 ml of nitric acid (HNO_3) concentrated to 65% (VWR Prolabo) and placed into the microwave system (Mars Xpress CEM) for 30 min (Figure 6.13).

Figure 6.13 Microwave (Mars Xpress CEM)

At the end of the digestion the sample was filtered with a cellulosic filter of 2.5 µm (Whatman 42), the liquid phase was diluted to 100 ml. The determination was carried out by an inductively coupled plasma optical emission spectrometry (ICP-OES Thermo electron corporation-Icap6000 series) in accordance with the method US EPA 6020a (Figure 6.14).

Figure 6.14 ICP-OES (Thermo electron corporation-Icap6000 series)

pH

The pH values were measured according to the procedure described in the section 6.1.4, using the benchtop meter Fisher Scientific-accumet XL600.

Turbidity

The turbidity of the water after treatment was measured by bench turbidimeter (HACH 2100N Turbidimeter).

6.4 Electrokinetic process with ultrasonic pre-treatment

6.4.1 Ultrasonic pre-treatment set-up

The US pre-treatment was carried out at the lower frequency for 10 min by an ultrasonic bath (Module generators Weber Ultrasonics Sonic Digital MG 1000 TDMF 40-80-120) (Figure 6.15).

Figure 6.15 Module generators ultrasonic bath (Weber Ultrasonics Sonic Digital MG 1000 TDMF 40-80-120)

The others process parameters were the same as those described in the section 6.3.1.

At the end of the treatment, the sample was filtered to separate the liquid from the solid and the sediment was used to fill the EK cell.

6.4.2 Electrokinetic treatment set-up

Electrokinetic process was accomplished by a glass electrokinetic cell (Pazos et al., 2013) (Figure 6.16).

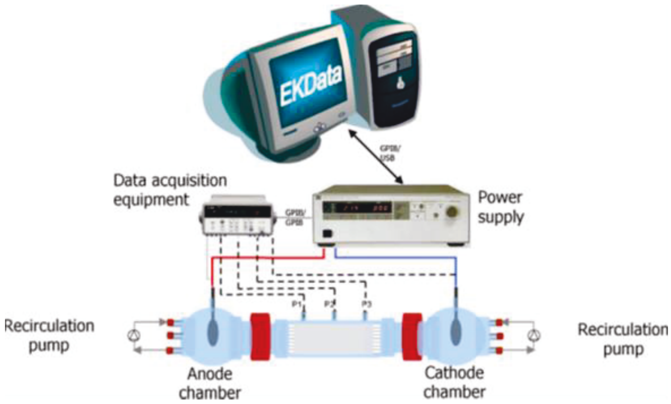


Figure 6.16 Electrokinetic cell and EK-data acquisition system (Pazos et al., 2013)

The system for the treatment is composed by three main parts, a central tube (100 mm length and 32 mm of internal diameter), in which the sediment was placed (about 200 gr dry weight) and two electrode chambers with process fluid (300 ml). The chambers are in both extremes of the central tube and all system is of glass (Figure 6.17).

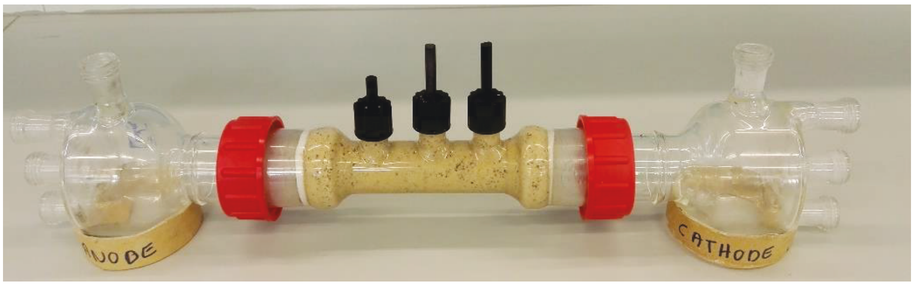


Figure 6.17 Electrokinetic cell

Between the central tube and the electrode chambers, there are filters paper and porous stones to avoid the direct contact of process fluid with the sample to treat. In order to apply the electric field, with a constant potential difference of 30 V (Falciglia et al., 2015; Pazos et al., 2013; Rozas and Castellote, 2012), graphite electrodes (Carbone Lorraine) were placed in both the electrode chambers and the current was provided through a power supply (Agilent 6634b) (Figure 6.18).

Figure 6.18 System power supply (Agilent 6634b)

Moreover, to monitoring the electric field during the process, others three electrodes were positioned to appropriate distances in the central tube. An acquisition software called EK-Data made the acquisition of all the electrical data automatically (Figure 6.19).

Figure 6.19 Data acquisition equipment

Furthermore, the values of voltage drop, current, intensity and pH in the electrode chambers, were taken periodically to monitoring the functionality (Pazos et al., 2013). The treatment was carried out for twenty days and as process fluid a solution of 0.1M sodium sulphate (Na_2SO_4) (Sigma Aldrich) and 0.1 M citric acid ($C_6H_8O_7$) (Sigma Aldrich) was prepared to fill the electrode chambers. Sodium sulphate was used as electrolyte, to promote the conductivity (Alcántara et al., 2008; Bocos et al., 2015). Citric acid was added to obtain a low pH to improve the solubilisation of heavy metals (Ammami et al., 2015; Cameselle and Pena, 2016; Pazos et al., 2009, 2012). In order to maintain the acid environment in the cathode chamber a pH controller (EMEC) was inserted with a solution of 0.1 M

Na_2SO_4 and 1 M $C_6H_8O_7$, to avoid that the level increased above the pH 4 (Gidarakos and Giannis, 2006; Pazos et al., 2009). In addition, the electrode chambers were connected to pumps, to control the level of the solution and to maintain the homogeneous solution (Figure 6.20). The process fluid was renovated periodically.

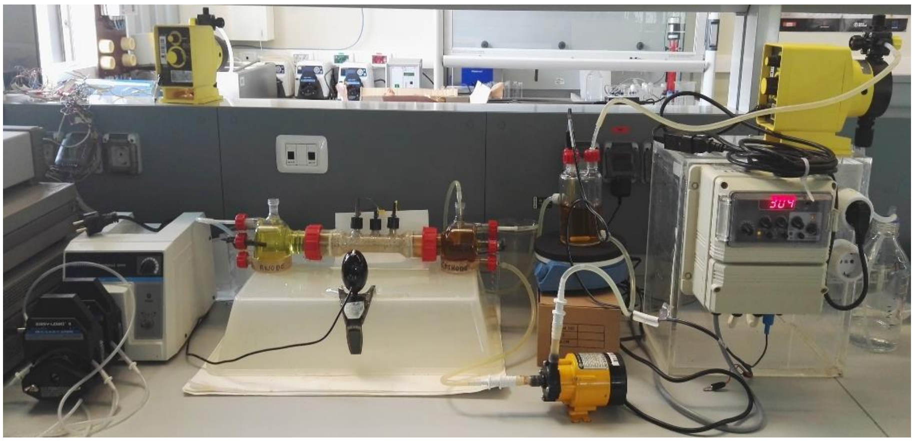


Figure 6.20 Real system for electrokinetic treatment

6.4.3 Analytical set up

PAH extraction and determination

Extraction and determination of PAH were carried out as described in the section 0. Fisherbrand (model FB11203) (Figure 6.21) was used as ultrasonic bath.

Figure 6.21 Ultrasonic bath (Fisherbrand model FB11203)

Heavy metals extraction and determination

Heavy metals were extracted from the sediment in accordance with the Danish standard 259 procedure, as described in the work of Ottosen et al. (2013). A sample of 1 gr of sediment and 20 ml of HNO_3/deionized water solution (1:1) was put into the autoclave (P-Selecta, Presoclave II) at 200 kPa and 120 °C for 30 min (Figure 6.22).

Figure 6.22 Autoclave (P-Selecta, Presoclave II)

After the sample was filtered to separate the two phases through the vacuum pump and 0.45 μm cellulose nitrate filter (Sartorius Stedim Biotech). The liquid filtered was diluted at 100 ml and the heavy metals concentration was determined by Inductively Coupled Plasma Optical Emission Spectrometry (Perkin Elmer Optima 4300 DV) in accordance with the method US EPA 6020a.

In particular, after EK treatment, the sample was divide into three section, called Sec.1, Sec.2 and Sec.3 from the anode chamber to the cathode chamber, and the heavy metals extraction was carried out for each section.

Electrical conductivity

Electrical conductivity was measured according to the procedure described in the section 6.1.4, using the benchtop meter Fisher Scientific-accumet XL600.

pH

The pH values were measured according to the procedure described in the section 6.1.4, using the benchtop meter Fisher Scientific-accumet XL600.

Moisture content

Moisture content was measured after the treatment in each section of the sample. The moisture content was calculated as the difference between the weight of the sediment before and after the drying in oven at 105 °C for 24 h.

7. Results and discussions

In the present chapter, the results of the research activity are presented and discussed into two main sections:

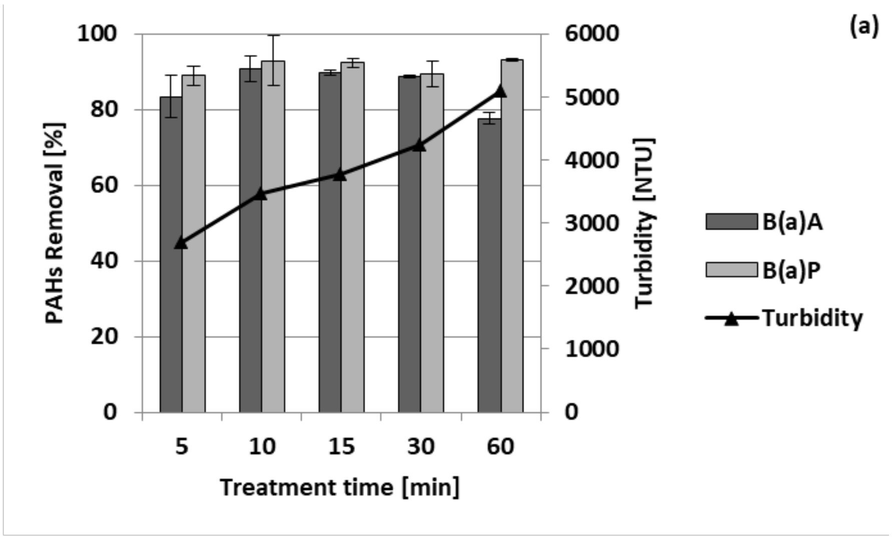
- the first one focused on the study of US treatment effectiveness to reduce of both organic and inorganic contamination in a single stage. Subsequently, in order to define the optimal treatment conditions, both process enhancement and optimization were performed;
- the second part, performed on the basis of the results of the previous phase, was devoted to the assessment of the US effectiveness as pre-treatment. In detail, US was implemented before the EK processes.

7.1 Ultrasonic treatment effectiveness

The application of ultrasonic waves entails the occurrence of the cavitation phenomenon. The cavitation involves mechanical and chemical effects, which are able to enhance the desorption and the mineralization of inorganic and organic compounds, respectively (Adewuyi, 2001; Lu and Weavers, 2002; Pee et al., 2015). During the experiments, the treatment time and frequency of sonication were varied to evaluate the effects of the process parameters on the organic and inorganic contaminants removal yields.

Results demonstrated that the US treatment was able to achieve an overall reduction of the contaminant concentration.

Regarding the organic contamination, a point worth of attention is the good performance, in terms of contaminant removal, obtained despite the sonication frequency as well as the treatment time. Indeed, after just 5 minutes of treatment, an organic compound average removal of 88% occurred. (Figure 7.1).



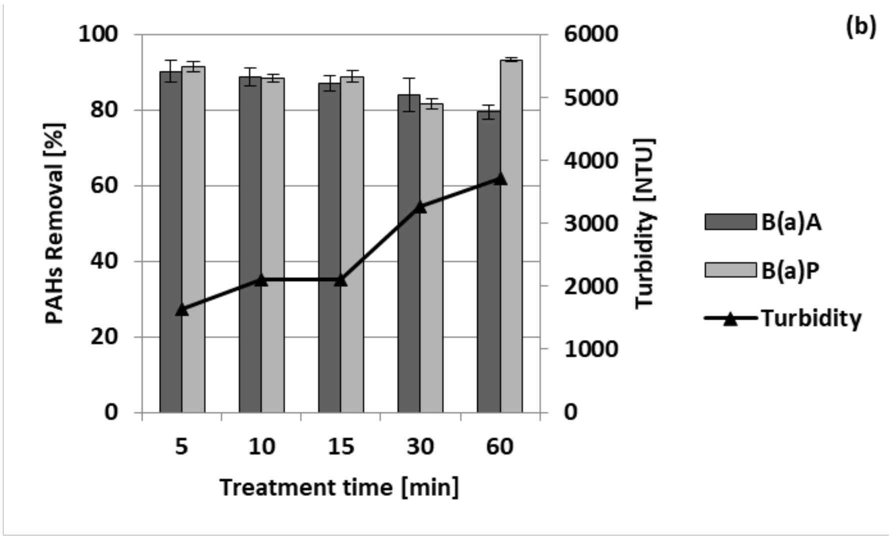


Figure 7.1 Removal percentage of PAHs after treatment at 35 kHz (a) and 130 kHz (b), with turbidity profile

These high removal yields, could be explained with the influence of the level of organic contamination, which is relatively high compared to that generally found onto the contaminated sediments in field ($41x10^{\wedge-6}$–7 mg/kg_{ss}) (Eijsackers et al., 2009; Gorokhova et al., 2010; Huesemann et al., 2009; Kilemade et al., 2009).

Indeed, in presence of a high level of contamination the polluting compounds are present as different layers onto the solid particles. In this case could be possible to have an easier removal of contaminants due to the weaker forces with which these compounds are bounded to the sediments (Feng and Aldrich, 2000; Jonsson, 2006; Song et al., 2012).

Another factor to take into consideration is the aging of contamination. This phenomenon entails a progressive increase in the persistence of contaminants and consequent decrease in their availability (Ling et al., 2010; Nam and Kim, 2002). Consequently, since the artificial contamination is unaged, the contaminant compounds are weakly sorbed onto the sediment particles and, thus, easily removable.

Moreover, the high performances achieved may be further influenced by the lack of organic matter in the sediment (Gaultier et al., 2008; Gerard Cornelissen et al., 2005; Pee et al., 2015). The organic compounds, indeed, tend to bind in the organic matter with strong bonds resulting more difficult to remove (Gaultier et al., 2008).

The slight influence of the treatment time on the removal efficiency is in agreement with the works of (Shrestha et al., 2009) and (Song et al., 2012), which have found a not significant improvement of the removal yield with increasing sonication time.

In addition, it must be taken into account that, the application of ultrasonic waves involves the fragmentation of the solid particles (Pokhrel et al., 2016; Son et al., 2012). In Figure 7.1, it is possible to evaluate the mechanical effect of the US on the particles fragmentation represented in terms of turbidity. It was evident how at the longer treatment times corresponded the highest turbidity values and, thus, the greatest fragmentation of solid particles. It could be also observed a higher turbidity for the samples treated at the lower frequency (35 kHz), compared to those treated at 130 kHz. This is a consequence of the cavitation phenomenon, which involves a more significant mechanical effect at the lower frequencies, as also demonstrated by Son et al., (2011). For this reason, despite the fact that it promotes the contaminants desorption, mechanical effects could be also considered responsible for the modification of the grain size distribution. Since that long sonication times are not recommended for the treatment of solid matrices, especially for a possible reuse (Feng and Aldrich, 2000).

Promising results were also obtained for heavy metals desorption. Desorption yields were almost constants during the treatment and a not significant influence of the frequency and treatment time was observed (Figure 7.2).

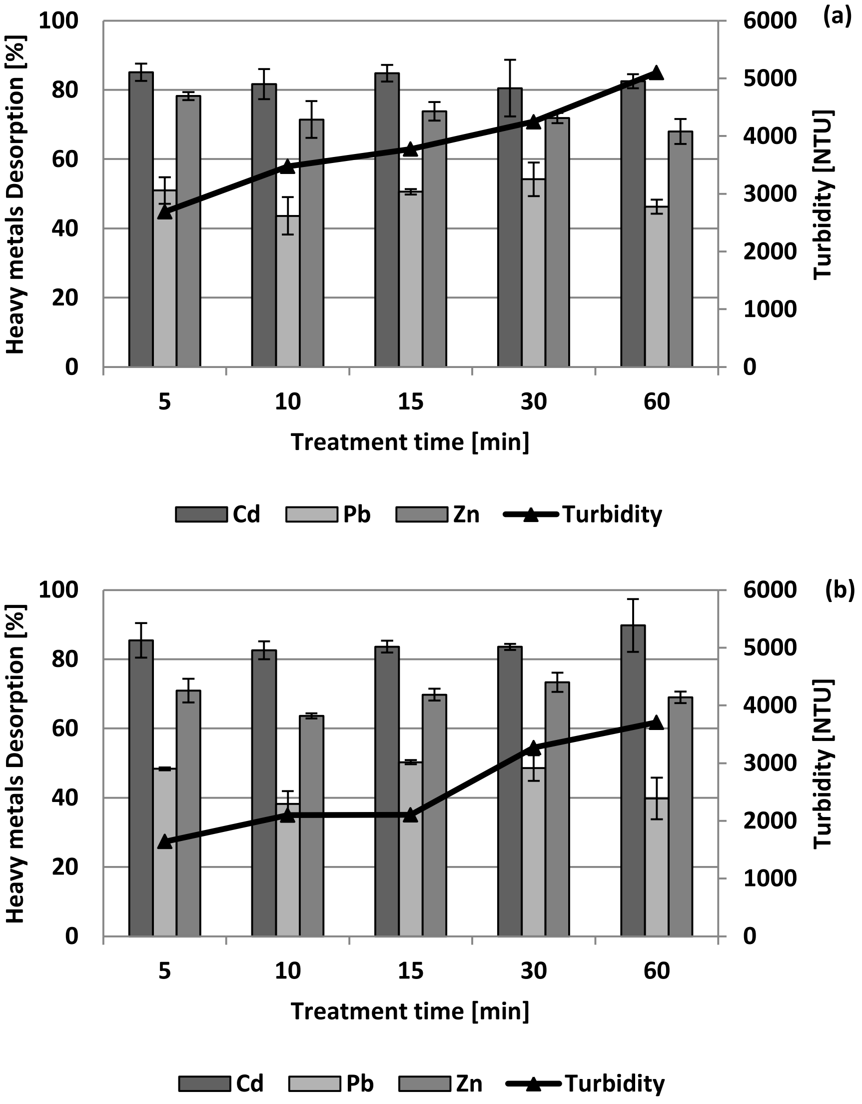


Figure 7.2 Desorption percentage of heavy metals after treatment at 35 kHz (a) and 130 kHz (b), with turbidity profile

Nevertheless, different results were obtained for the single inorganic contaminants.The best performance were reached for Cd and Zn with removal percentages, on average, of 84% and 70%, respectively. Whereas, the Pb concentration was more difficult to reduce. This behaviour could be related to the strong influence that the pH has on the mobility of heavy metals (Peng et al., 2009).

It is worth pointing out that the experiments were carried out in water, at a pH around 6, which is the preferred condition for both Cd and Zn solubilisation. Conversely, for the Pb solubilisation is necessary an acid environment (Pedersen et al., 2017). US waves do not allow the development of H^+ or OH^- ions (Shrestha et al., 2009) and , thus, the change of the pH. Indeed, during the treatment the pH value was remained more or less stable in the range of 5.8-6.1, how was observed through the pH value determination carried out at the end of the experiments (Figure 7.3).

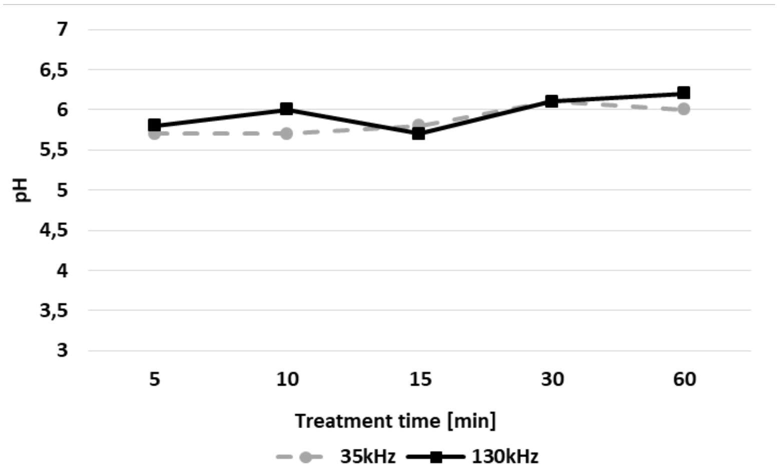


Figure 7.3 pH of the sediment after US

Therefore, this evidence could mean that the desorption percentage reached for the Pb, was only due to the mechanical effect of the cavitation phenomenon. Indeed, US as their capacity to lead the soil particles fragmentation promoting the contaminant desorption, was used in literature to enhance the soil washing (Rivero-Huguet and Marshall, 2011; Wang et al., 2015). Nevertheless, it is worth noting that, despite there was an increase in particle breakage over the time, highlighted by the trend of the turbidity, an increase in desorption yield was not noted. Thus, it is possible to considered that, the greater part of contaminants were desorbed in few minutes of treatment. Consequently a long sonication time seems not to be justified.

7.2 Enhanced ultrasonic treatment

Enhanced US treatment was also investigated, taking into account the results presented in section 7.1.

The process enhancement was carried out in order to improve the heavy metals desorption. For this purpose, both citric acid and ethylenediaminetetraacetic acid (EDTA) were used.

These chemicals are among the most frequently used to promote the heavy metal desorption from soil and sediments (Ammami et al., 2014; Cameselle and Pena, 2016; Leštan et al., 2008).

Citric acid is a weak acid and several scientific works have demonstrated its efficiency for the treatment of heavy metals-contaminated sediments (Ammami et al., 2015; Hahladakis et al., 2014). Its effects rely on the ability to maintain a low pH, which promotes the metal solubilisation (Alcántara et al., 2012; Cameselle and Pena, 2016; Pazos et al., 2008; Peters, 1999). Conversely, the effectiveness of EDTA in promoting the heavy metal desorption from the solid matrices (Deng et al., 2017; Jelusic and Lestan, 2014) is mainly related to its ability to form strong complexes with the heavy metals (Dermont et al., 2008; Yoo et al., 2013).

As previous results had showed that the treatment time as not really significant in determining the process efficiency, the experiments were performed at low treatment time, ranging between 5 and 15 minutes.

All experiments were performed at both sonication frequencies.

7.2.1 Ultrasonic treatment enhanced by citric acid

The use of citric acid as enhanced agent, demonstrated a good heavy metals desorption efficiency (Figure 7.4), especially for Pb. Its desorption yield grew up to 96%, much higher than the value found in water medium that reached an average value around 47%.

The positive effects of the acid solution could be also promoted to the mechanical effect that the US may induce on the sediment particles, as indicated by the increased turbidity. Indeed, with the fragmentation of the sediment grain, there is an increase of the exposed surface that promotes the contaminant desorption (Bendicho et al., 2012).

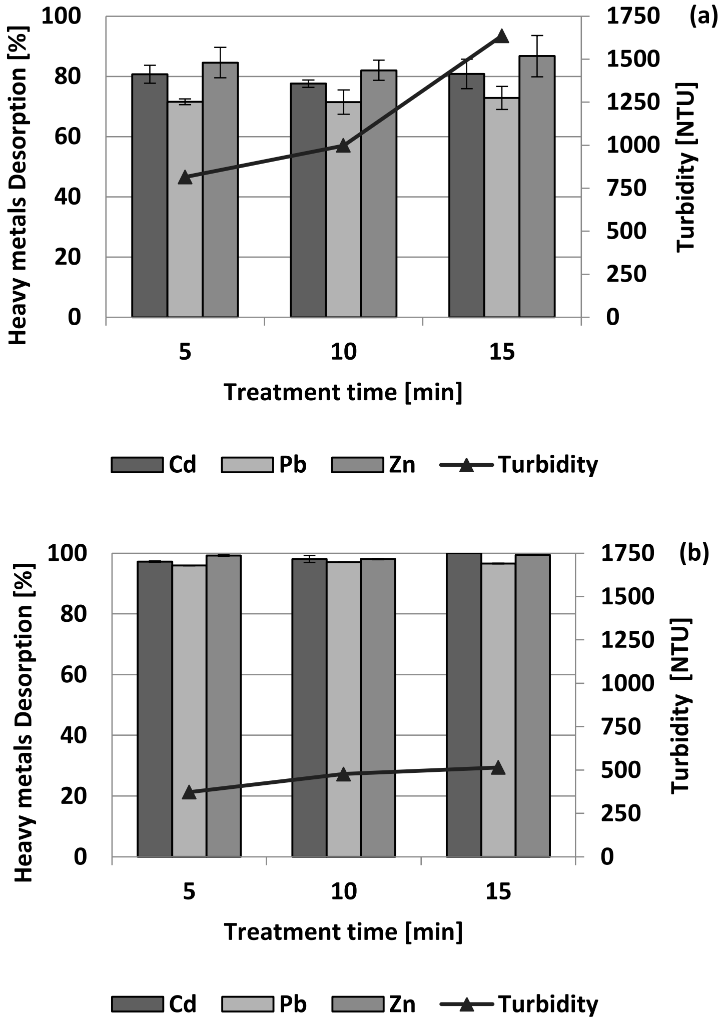


Figure 7.4 Removal percentage of heavy metals and turbidity profile after ultrasound treatment with citric acid solution (0.1 M) at 35 kHz (a) and 130 kHz (b)

Although the process enhancement mainly pursued the increase in heavy metal desorption, it is worth pointing out that the residual organic contamination was also observed to be always below the detection limit of the GC-MS (0,1 mg/l). The improvement in organic pollutant degradation could be related to the citric acid effect on the matrix. Indeed, the citric acid may lead to the erosion of the sediment mineral surface and, therefore, promote the desorption of the organic compound adhered to it (Falciglia et al., 2018; Ma et al., 2015; Mason, 1997).

The enhanced US proved to be quick and effective to remove organic and inorganic compounds in a single stage.

7.2.2 Ultrasonic treatment enhancement by EDTA

Figure 7.5 reports the results for the heavy metals removal.

The outcomes showed a comparable desorption yields for the selected inorganic contaminants. In the case of Pb, which is usually harder to desorb, a significant reduction, up to 78.98±3.75%, was observed, confirming the effectiveness of this chelating agent.

As already observed for citric acid, a slight increase of the efficiency was observed also for the organic contaminants. Nevertheless, there are no records in literature on the use of EDTA for the removal of organic contaminants. Furthermore, the effect of EDTA on the structure of the sediment is lower compared to that of strong acids (Dermont et al., 2008; Jelusic and Lestan, 2014; Wang et al., 2015). In this context, it is possible to consider that this result was mainly linked to the action of the ultrasound rather than to that of the used agent.

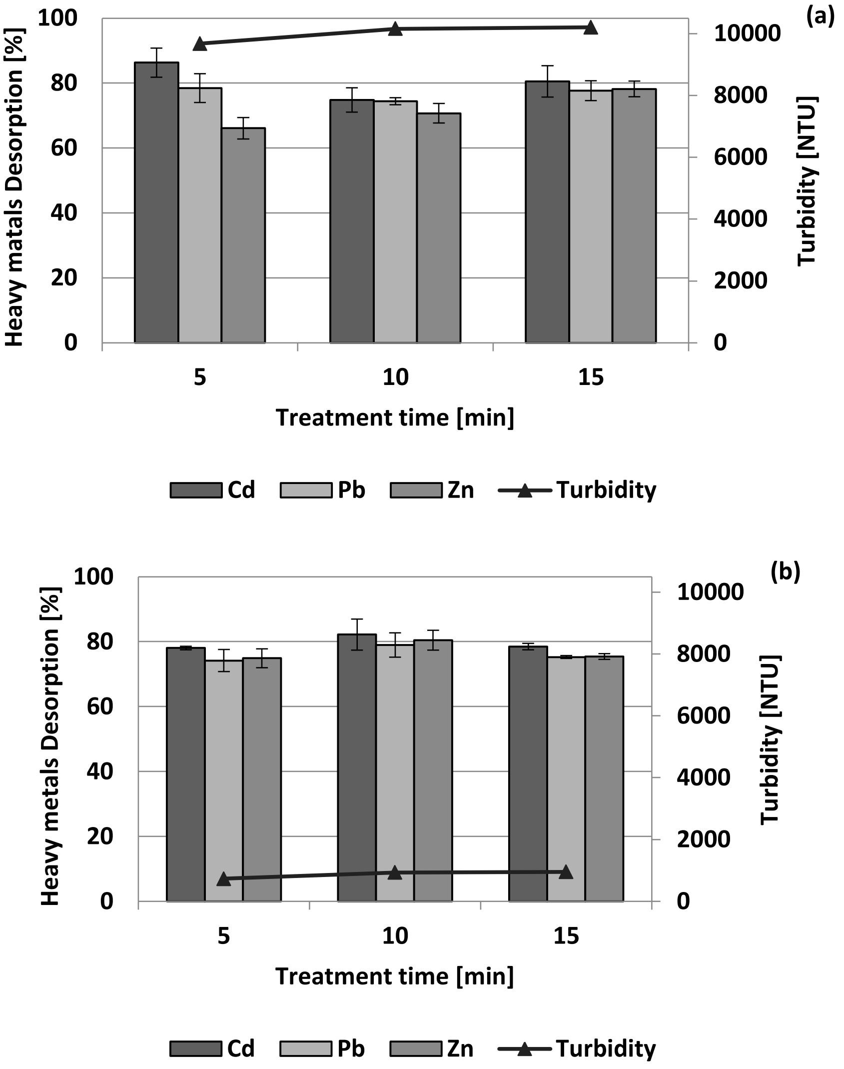


Figure 7.5 Removal percentage of heavy metals and turbidity profile after ultrasound treatment with EDTA solution (0.1 M) at 35 kHz (a) and 130 kHz (b)

7.2.3 Ultrasonic optimization

Based on the results for the enhanced US treatment, a further step was carried out in order to optimize the treatment.

Both the chelating agents used for the enhancement phase demonstrated high removal yields. However, it must be considered that the chelating agent should be (Dermont et al., 2008; Leštan et al., 2008; Nogueira et al., 2007):

- not absorbable onto the solid matrix;
- able to operate in a wide pH range;
- eco-friendly;
- cost-effective.

Taking into consideration these requirements, the citric acid may be considered more suitable agent for the heavy metals desorption. Indeed, this acid has a high biodegradability so that it is considered an eco-friendly agent. In addition, it is able to maintain a low pH to promote the solubilisation of the heavy metals, besides to form complexes with them (Ammami et al., 2014; Cameselle and Pena, 2016; Nogueira et al., 2007; Pazos et al., 2008).

Conversely, the EDTA, which is also an effective chelating agent (Leštan et al., 2008), has some disadvantages related to the narrow pH range in which is able to form complexes (Peters, 1999), and the relative high cost. Moreover, it is not biodegradable (Dermont et al., 2008) and potentially harmful to the environment (Deng et al., 2017; Voglar and Lestan, 2010).

Further tests were, thus performed using the citric acid and its effects were evaluated for shorter treatment time, since it was observed a not significant influence of this parameters on the desorption yield. The reduction in treatment time to 2.5 minutes represents a further point of strength for the use of this agent as it may result in the possibility of energy savings (dos Santos et al., 2017).

Furthermore, as the best performances were achieved at the highest frequency investigated, which allowed to reduce the particles fragmentation, the sonication frequency was set at 130 kHz.

Figure 7.6 plots the results related to these experimental conditions.

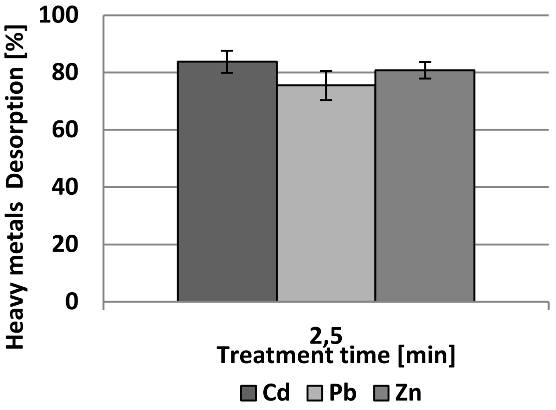


Figure 7.6 US efficiency for the optimized treatment

The desorption yields achieved for Cd, Pb and Zn were 83.74±2.73%, 75.47±0.92% and 80.77±0.70%, respectively.

These good results, obtained despite the short treatment time, could be explained by the PZC value of the sediment.

When the pH of the sediment is higher than its PZC, the surface will have a net negative charge and a greater penchant to exchange the cations. Conversely, when the pH is lower than its PZC, the surface will have a net positive charge and a greater penchant to exchange the anions (Karak et al., 2005).

As describe in the section 6.1.4, the PZC value of the sediment is 6.2. The pH value after 2.5 min of treatment resulted lower than the sediment PZC and equal to 3.45. In these conditions the surface of the sediment has a positive charge and, hence, a lower affinity with the positive ions of the heavy metals (Karak et al., 2005).

As expected, in these experimental conditions, a general decrease of about 20% was observed compared to the results obtained at higher treatment time.

However, the energy saving and the sediment structure preservation may balance the decrease of the desorption yields.

7.3 The feasibility of ultrasound as pre-treatment

In the following chapter, the results related to the removal efficiency for the EK, US+EK processes and their comparison are shown. The results are discussed in terms of heavy metals desorption.

7.3.1 Electrokinetic process

The EK was implemented as stand-alone treatment in order to compare their efficiency with that of the process with ultrasound pre-treatment (US+EK). The sample was treated for twenty days by an electrokinetic cell. After the treatment, the sample was divided into three parts, subsequently indicated as Sec.1, Sec.2 and Sec.3, from the anode to the cathode, to determinate the distribution of the contaminants in the sediment along the cell (Figure 7.7).

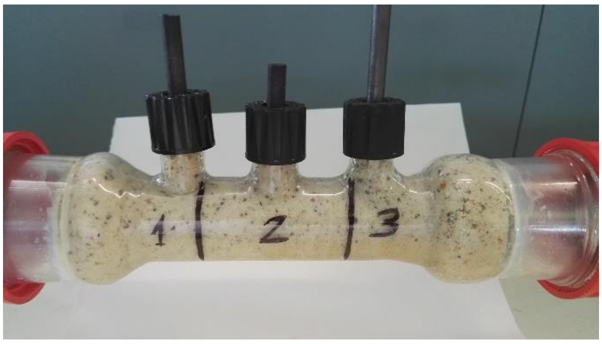


Figure 7.7 Experimental set-up: electrokinetic cell and sample sections

The results were plotted in terms of removal percentage with reference to the section of the sample in which they were determined (Figure 7.8).

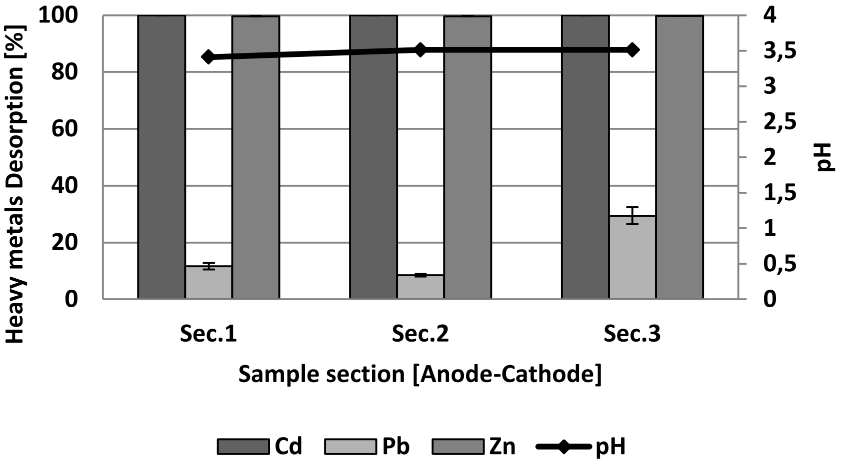


Figure 7.8 Heavy metals distribution and pH profile after EK treatment

In each section, the concentration of Cd was below the detection limit of the instrument (0.005 mg/l). High removal efficiencies were also achieved for the Zn, with peak of 99.63 ± 0.06%.

These results are in agreement with the work of Cameselle and Pena (2016), which has obtained the best efficiencies, over 70%, for Cd and Zn. These percentages are lower compared to those achieved in this work and the reason could be identified in the mineralogy of the sample. Indeed, the sediment used for the experiments is mainly composed of quartz, whereas the sample used in the work of Cameselle and Pena (2016) has a percentage of clay. This is a key factor because the clay mineral are able to retain the positive ions, like metal ions, due to their negative superficial charge (Alcántara et al., 2012).

Limited removal efficiencies were obtained for the Pb, with a maximum percentage of 29.44 ± 2.96%. This behaviour was also observed in others scientific works (Ammami et al., 2015; Cameselle and Pena, 2016). The Pb is usually more difficult to extract because of their strong links with the sediment. Moreover, the low mobility could also be due to the formation of complexes in presence of organic acids, like citric acid (Schwab et al., 2005, 2008).

After the treatment, the values of removal for Cd and Zn in each section of the sample were comparable, whereas the Pb showed a variable removal profile decreasing from the cathodic to the anodic chamber. This trend can be attributed to the formation of negative complexes and therefore to the displacement of the contaminants towards the anodic chamber (Alcántara et al., 2012; Ammami et al., 2014; Cameselle and Pena, 2016).

7.3.2 Ultrasound as pre-treatment for the electrokinetic process

Before the EK process, the sample was sonicated for 10 minutes at the ultrasonic frequency of 35 kHz (Wang et al., 2015). The ultrasonic pre-treatment allowed an initial reduction of the contaminants. In particular, the organic compounds were almost completely removed in this first step with percentages of 91.39 ± 5.29% and 97.29 ± 2.29% for benz(α)anthracene and benzo(α)pyrene, respectively. Therefore, considering the high efficiency of the ultrasound on the organic compounds removal, these compounds were not determined at the end of the whole treatment.

In the case of heavy metals, as observed in the previous paragraph for the EK, the best removal efficiency was obtained for Cd and Zn with a same removal percentage across the sample (Figure 7.9).

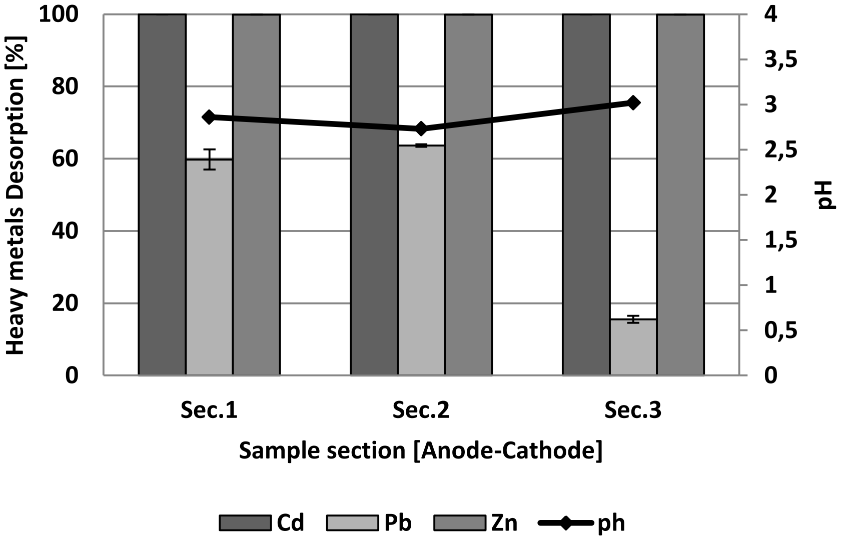


Figure 7.9 Heavy metals distribution and pH profile after the US+EK

With regard to the Pb, instead, the removal profile showed a higher efficiency in the sections 1 and 2, with percentages of 59.78 ± 2.82% and 63.64 ± 0.33%, respectively. This profile could be attributed to the pH value of the sediment along the EK cell. Indeed, even if during the treatment, an acid solution was used for both chambers and furthermore, a pH controller was installed for the cathodic chamber, there was a slight difference in the pH value across the sample. In particular, the higher efficiency occurred in the section near the anode where the pH was lower than 3. At this value of pH it was possible the formation of positive complexes (Cameselle and Pena, 2016). As showed in Figure 7.9, the removal percentage of Pb decreased from the anode to the cathode, demonstrating their migration towards the cathode.

7.3.3 Comparative analysis

In order to evaluate the effect of US pre-treatment on the contaminant removal, the EK was compared to the US+EK and the comparison was carried out with reference to the inorganic contamination.

Taking into account that during the EK process there is a movement of the contamination and then a different contaminant concentration along the sample, the comparison was carried out for the sample section, which showed the best removal, for each experiment.

The significant effect of the US pre-treatment was observed for the Pb desorption yield (Figure 7.10), which enhanced from 29.49±5.50% to 63.64±0.06%, with an increase of about 34%.

The positive effect of the US pre-treatment are in agreement with what was stated by Wang et al., (2015). In their work, US was used as pre-treatment to enhance the acid soil washing process. Wang et al. (2015) showed an increase of about 20% and 30% for Pb and Zn, respectively, using 10 min of US pre-treatment. This enhancement in the removal efficiency was related to the cavitation effect, which generate shock waves, microjets which may destroy the structure of the sediment and promote the contaminant desorption.

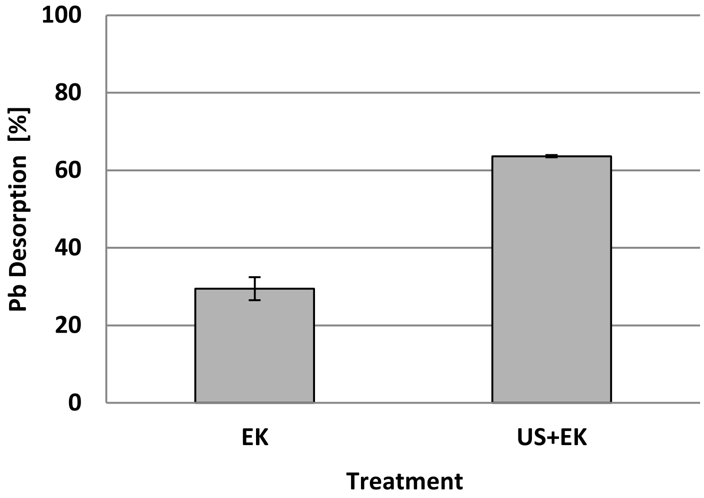


Figure 7.10 Comparison of treatment efficiency of the EK and US+EK versus Pb desorption

In particular, in the present research the percentage of 63.64 ± 0.36% refers to the total removal achieved at the end of the whole treatment US+EK. This percentage was calculated considering as the initial contamination that of the untreated sample, before the US, and as final contamination the one after the US+EK. However, this result might suggest that the final efficiency was only due to the implementation of two treatment in sequence and therefore, to the sum of their effectiveness.

In order to emphasize the real enhancement of the EK after US pre-treatment, the results were also discussed with regard to the desorption efficiency related only to the EK process following the sonication (EK after US). This removal efficiency was calculated considering as initial contaminant concentration the one achieved at downstream of the US pre-treatment.

For this purpose, in Figure 7.11 was reported the comparison of the results related to the removal efficiency of the stand-alone system EK and the EK after US, considering only the section, which has obtained the best removal efficiency in each treatment. Starting from a lower contamination, due to the US pre-treatment, the forces with which the contaminants are linked to the sediments are greater and, therefore, one would expect a lower removal efficiency (Feng and Aldrich, 2000; Flotron et al., 2005).

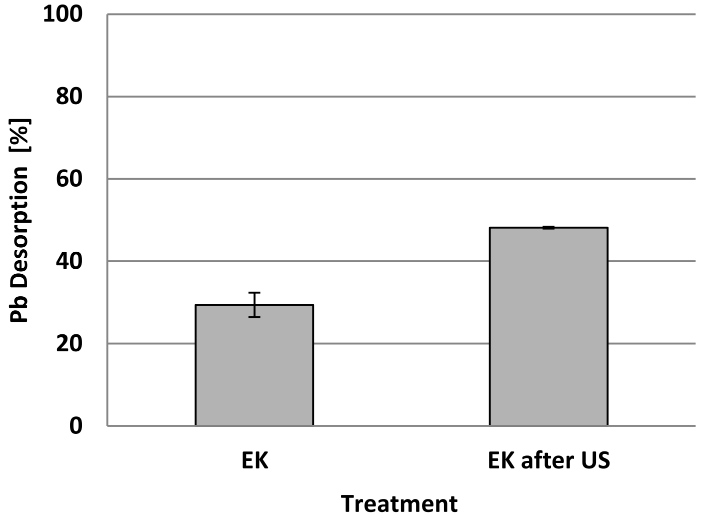


Figure 7.11 Comparison of removal efficiency between EK and EK after US versus Pb desorption

Analysing what occurred in the EK after US, instead, it was clear how there was a real improvement due to the pre-treatment. Indeed, in particular with reference to Pb, the removal efficiency has increased from 29.44 ± 2.96% to 48.15 ± 0.22%, with a final increase of about 19%.

This positive effect of the US was a synergistic effect, how is possible to see in the Figure 7.12, where the removal efficiency was plotted with reference to the US, EK and US+EK. Indeed, the synergistic effect was more evident in the case of Pb, for which were obtained removal of 29.49 ± 5.50%, 29.44 ± 2.96%, 63.64 ± 0.33% for US, EK, US+EK, respectively.

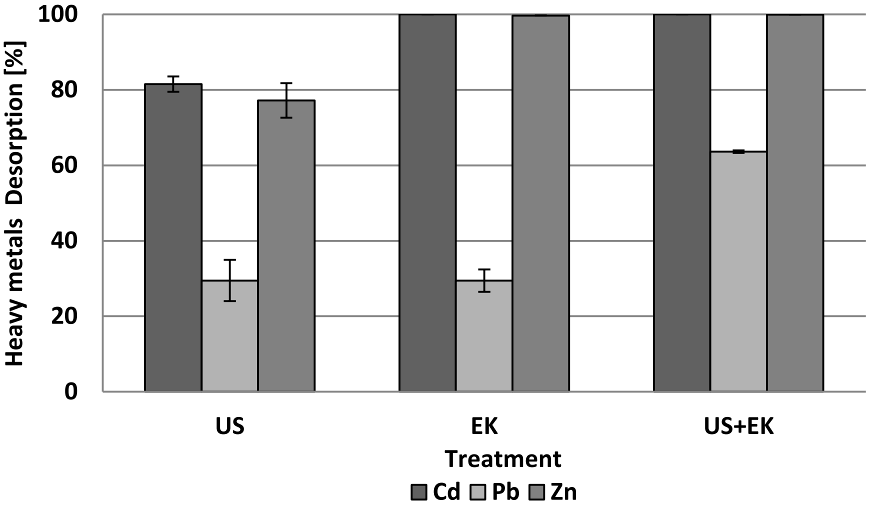


Figure 7.12 Comparison of removal efficiency among the US, EK and US+EK processes

The best results obtained after the pre-treatment, could be attributed to the mechanical effect of ultrasound, which led to the reduction of the grain size by increasing the surface in contact with the process solution (Bendicho et al., 2012; Son et al., 2011).

An additional factor to consider is the preventive removal due to the ultrasound on organic compounds. Indeed, some scientific works have shown how in the EK processes, the efficiency of the inorganic contaminants removal, is hindered by the simultaneous presence of organic contaminants. These compounds do not have an electric charge and can reduce the current intensity limiting the flow of charges, with negative effects on the process (Falciglia et al., 2017). For this reason, in the case of matrices with simultaneous contamination of organic and inorganic compounds, a sequential treatment is usually performed (Hahladakis et al., 2014; Maturi et al., 2008).

The variation of the current intensity was noted during the treatments, with lower values for the EK (Figure 7.13a).

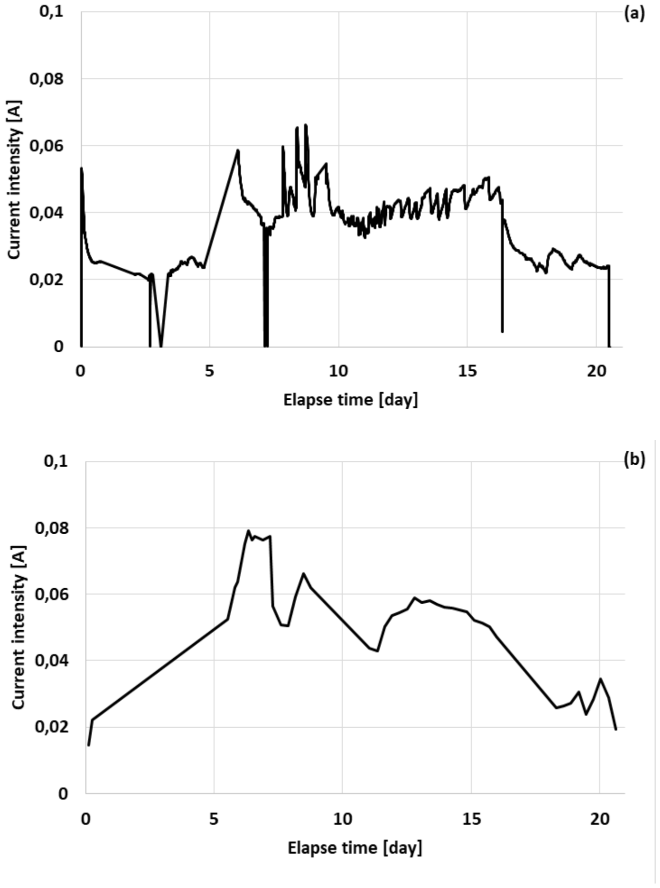


Figure 7.13 Current intensity profile during the EK (a) and the US+EK (b)

Moreover, in Figure 7.13 it is possible to notice an overall reduction of the current intensity over time, that may be related to the decrease of the ionic compounds during the treatment (Ammami et al., 2014; Missaoui et al., 2016).

It is worth pointing out that, with reference to the Cd and Zn, despite the efficiency yields obtained after EK and US+EK processes were comparable, and close to the complete desorption, the most part of these compounds were removed by US pre-treatment (Figure 7.12).

The experimental results, proved that US technology could be an effective pre-treatment to enhance the contaminant desorption.

8. Conclusion and future perspectives

In Europe about 200 million cubic meters of sediments are estimated to be annually dredged. This material is partially contaminated, as hazardous compounds tend to sorb onto the fine-grained particles of the sediments. This poses a problem related not only to the possible negative effects of the contamination on both the environment and the human health, but also for the management of the sediments themselves.

Landfill and the confined aquatic disposal are still most commonly used options for the contaminated sediments, although not sustainable. A beneficial reuse of sediments could represent a suitable alternative but, in this regard, a treatment is necessary to reduce the contaminant concentration to avoid the possible adverse effects.

Scientific literature reports different traditional soil remediation technologies, which were adapted for the contaminated sediment treatment. However, the specific characteristics of the sediments, as the low permeability, could affect the treatment yields making them ineffective.

Ultrasound (US) is recognized worldwide as an innovative, promising technology for treatment of both soil and sediments, due to its advantages over conventional remediation processes. The ultrasonic action occurs in two main steps, namely the transfer of the contaminants from the solid to the aqueous phase and the subsequent degradation of dissolved organic compounds.

As US may reduce the treatment time and prevent the use of chemicals, it is considered an environmental friendly technology.

In this context, the research discussed in this work dealt with the assessment of the effectiveness of this advanced technology for the remediation of sediments contaminated by both heavy metals (Cd, Pb and Zn) and PAHs (B(α)A and B(α)P), considered as target compounds.

For this purpose, experimental activity was structured in two main parts.

In the first part, US technology was applied as a stand-alone treatment to reduce the organic and inorganic contamination from the sediments. The treatment was carried out at batch-scale through an ultrasonic bath, operated under different sonication frequency (35-130 kHz) and treatment times (5-60 minutes).

Results demonstrated that the application of ultrasonic waves, led to an overall reduction of the contaminant concentration, which occurred already after few minutes of treatment. In particular, the best performances were achieved for the organic compounds, showing an average removal of 88% after five minutes of treatment. The heavy metals desorption was almost constant in all experiments, despite the sonication frequency as well as the treatment time. However, different results were obtained for the single inorganic contaminants: Cd and Zn reached approximately 84% and 70% desorption, respectively; Pb showed an average 47% removal. This evidence could be explained by the strong influence that the pH value has on the solubility of heavy metals. It is worth pointing out that the experiments were carried out in water, at a pH around 6, which is the preferred condition for both Cd and Zn solubilisation. Conversely, for the Pb solubilisation is necessary an acid environment.

On the basis of these results, in order to improve the desorption of heavy metals, two different solutions of 0.1 M citric acid and 0.1 M ethylenediaminetetraacetic acid (EDTA) were used as the liquid mediums for the ultrasonic treatment.

The samples were sonicated at both frequencies of 35 and 130 kHz for a maximum of 15 minutes.

A significant improvement was noted in the Pb desorption, with both solutions. However, the best performances were obtained through the use of the citric acid solution and a sonication frequency of 130 kHz. This combination led to desorption yields up to 97%. Moreover, as previously noted, the variation of the treatment times was observed to be not significant, thus a long US treatment is not justified.

Taking into account the previous results, in order to define the optimal treatment conditions, a further experiment was carried out using the citric acid solution, the higher frequency of sonication and reducing the treatment times at 2.5 minutes.

In these experimental conditions an overall decrease of about 20% was observed. However, the desorption yields were satisfactory with the lower efficiency for the Pb of 75.47±0.92%.

In the second part of the research, the US technology was evaluated as pre-treatment to an electrokinetic (EK) process, implemented by an electrokinetic cell. To this end, the combined process was compared with the remediation performances provided by the EK alone.

For Cd and Zn, the desorption percentages obtained with the combined US+EK process were found to be comparable with those achieved by EK alone; in both cases they were close to the complete removal.

Conversely, the use of the US pre-treatment was able to enhance the Pb treatment efficiency, which enhanced from 29.49±5.50% to 63.64±0.06%, with an increase of about 34%. This improvement, related to the US action, was better highlighted from the comparison of the investigated processes, namely US, EK and US+EK. Pb desorption of 29.49 ± 5.50%, 29.44 ± 2.96%, 63.64 ± 0.33% was obtained from US, EK, US+EK, respectively. It should be noted that not only there was an improvement of the treatment efficiency, but the US pre-treatment also promoted a synergistic effect.

This evidence could be related to the mechanical action of the US, which led to the reduction of the grain size by increasing the surface available for the treatment.

The results obtained from the experimental activity suggested that US technology is able to promote the degradation of organic compounds as well as the desorption of heavy metals in a single stage and short time.

Furthermore, US could be considered not only a potential alternative technology for the contaminated sediment remediation, but also an effective pre-treatment combined with other technologies.

Nevertheless the great treatment potential, the effectiveness of the US treatment was more investigated at laboratory scales, limited studies dealt with the industrial scale applications.

Moreover, also from the theoretical point of view, the mathematical models related to the diffusion of the cavitation phenomenon were mainly developed for the liquid medium. Contrary, few information are available for the heterogeneous systems. Indeed, these evidences may be necessary to optimize the geometrical configuration of the US system. In addition, the possibility to avoid further treatments and to operate in brief times, could be key factors for the diffusion of the US technology in the contaminated soil and sediment treatment at real scale.

Thus, due to the great potential of US applications for soil and sediment treatment, further detailed studies should focus on:

- the influence of the contaminated sediment characteristics, as the aging of contamination, natural organic matter content, different concentration levels and type of contaminants, on the US treatment efficiency;
- the theoretical propagation and development of the cavitation phenomenon in the heterogeneous systems;
- the investigation of US effectiveness treating real contaminated sediments;
- the investigation of different US system configurations;
- detailed analysis in terms of costs and energy balance at pilot scale;
- the US treatment implementation at larger scale for industrial applications.

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