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# Ultrasonic processes for the advanced remediation of contaminated sediments

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ABSTRACT

Sediments play a fundamental role in the aquatic environment, so that the presence of contaminants poses severe concern for the possible negative effects on both environmental and human health. Sediment remediation is thus necessary to reduce pollutant concentrations and several techniques have been studied so far. A novel approach for sediment remediation is the use of Advanced Oxidation Processes, which include ultrasound (US). This paper focuses on the study of the ultrasonic effects for the simultaneous reduction of both organic and inorganic contaminants from sediments. To this end, the US technology was investigated as a stand-alone treatment as well as in combination with an electro-kinetic (EK) process, known to be effective in the removal of heavy metals from soil and sediments. The US remediation resulted in higher organic compound degradation, with an average 88% removal, but promising desorption yields (47–84%) were achieved for heavy metals as well. The combined EK/US process was found to be particularly effective for lead. Experimental outcomes highlighted the potential of the ultrasonic technology for the remediation of contaminated sediments and addressed some considerations for the possible scale-up.

## 1. Introduction

Over the years, different polluting compounds have affected the aquatic environment because of either improper anthropogenic activities 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 [1-3], where they tend to accumulate.

Heavy metals and polycyclic aromatic hydrocarbons (PAHs) are among the most detected contaminants in the sediments, due to their high persistence in the environment [4-7]. The main concern is related to the toxic and carcinogenic effects that they can display towards the environment and the human health [8,9]. Since sediments represent a potential reservoir of contaminants, the variation of environmental conditions may promote the release of these hazardous compounds from sediments, turning them into a secondary source of contamination [10,11].

Such issue is particularly relevant during dredging operations in port areas, which are becoming more and more common either to adapt the navigation depth to the increasing maritime traffic or for remediation purposes. Bortone et al. [12] reported that about 200 million $m^3$ are moved each year and part of them is contaminated, posing the issue of their proper handling.

Traditional management strategies of dredged sediments include the replacement in water bodies or the landfill disposal, depending on the contamination level. Nevertheless, these strategies are not economically viable nor environmentally sustainable, so that in situ remediation approaches have also been proposed to avoid dredging, when not necessary for maintenance operations. Such approach relies on the use of either inert or reactive capping [13], but the wider application of in situ capping has been hindered by the uncertainties of its long-term stability under different environmental conditions.

In this context, the identification of alternative systems for the remediation of contaminated sediments has to be addressed towards sustainable solutions. Notwithstanding the advantages related to in situ remediation technologies, the treatment of dredged sediments for their possible use is particularly attracting, fitting the principles of the circular economy.

The remediation of sediments usually relies on the same technologies used for the treatment of contaminated soil [14], although the prevalence of the fine fraction and higher organic matter content in sediments can influence process yields [15,16]. Chemical methods are

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among the mostly applied techniques for sediment remediation and include the use of washing solutions as well as electro-kinetic (EK) processes [13,17]. The latter involves the direct application of low intensity electric into the sediments that, in turn, produce the electrolysis of the water, with the generation of an acid front ($H^+$) at the anode side and an alkaline one ($OH^-$) at the cathode. The process is particularly effective towards heavy metals [18] because the acid front tends to move toward the cathode thus promoting the solubilisation of the metal species and their precipitation at the cathode [19]. Several studied have also demonstrated EK effectiveness towards organic contaminants [20,21]. Nevertheless, when a multiple contamination occurs, the presence of organic compounds may results in the decrease of the electric field, which may condition the treatment efficiency [19].

A novel approach relies on the use of Advanced Oxidation Processes (AOPs). Following their successful use for the treatment of aqueous solutions [22], they have been recently considered for the treatment of contaminated solid matrices [16,23-25]. AOPs include ultrasound (US) based technologies, which are widely employed in different areas of science and technology [26,27]. In the environmental engineering field, US has been used for the treatment of different matrices, as wastewater, organic waste and sludge [28-31,58,60]. The mechanism of US treatment is based on the cavitation phenomenon, which takes place in aqueous medium and involves both chemical and physical effects [32]. 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 into less harmful compounds [33,59]. The physical effects mainly result in the fragmentation of solid particles, promoting the contaminants desorption [34-36].

The advantages of US processes against conventional treatments lay in the speed of reactions as well as in the possibility to avoid or reduce the use of chemical solvent [35,37-39]. Due to its operational features and reported advantages, the ultrasonic treatment represents a promising technique for the sediment remediation.

Although some experiences have already been reported [35,36] these mainly focus on single classes of pollutants. Nevertheless, contamination phenomena usually imply the presence of a wide range of contaminants, characterized by specific chemical-physical properties and differently bound to the sediments. Their effective remediation may thus require rather specific actions. Based on the reported versatility of the ultrasonic technology, it has been investigated both as a stand-alone process and as a treatment prior to the EK remediation for the simultaneous reduction of both organic and inorganic contaminants from the sediments.

## 2. Materials and methods

### 2.1. Sediment sample and spiking procedure

Fine silica sand was selected as model sediment and the particle size distribution was analyzed according to ASTM D422-63 (Fig. 1). Then, the samples were spiked in order to simulate a simultaneous contamination from polycyclic aromatic hydrocarbons (PAHs) and heavy metals. To this end, benzo(a)pyrene (B(a)P) and benzo(a)anthracene (B(a)A) were considered as representative PAH target compounds, whereas the selected inorganic compounds, added in the form of nitrates, were cadmium ($CdN_2O_6 + H_2O$), lead ($N_2O_6Pb$) and zinc ($ZnN_2O_6 + 6H_2O$) [7,9].

All the contaminants were purchased from Sigma Aldrich and used to prepare spiking solutions. Due to analytical requirements, the desired concentration of each compound was established as the double value of the threshold limit concentration set by the Italian legislation for contaminated soil in industrial and commercial sites.

2 mg of each selected organic contaminant were dissolved in 10 mL of dichloromethane (VWR Chemicals). The resulting solution was poured onto 100 g of dried sediment samples and the whole was mixed to obtain a final concentration of 20 mg/$kg_{DW}$. As described by Russo et al. [40], the samples were then placed under hood for three days, at ambient temperature, in darkness, in order to promote the complete evaporation of the solvent used to prepare the organic spiking solution.

The heavy metal contamination was carried out as reported in the study of Rozas and Castellote [41]. To this end, 8.22 mg of Cadmium nitrate, 320 mg of Pb nitrate and 1365 mg of Zn nitrate were dissolved into 50 mL of deionized water to reach final concentrations of 30 mg/$kg_{DW}$ of Cd, 2000 mg/$kg_{DW}$ of Pb, 3000 mg/$kg_{DW}$ of Zn, respectively.

The solution was then left in contact with the sediments for one hour and it was subsequently evaporated in the oven (Inter Continental Equipment) at 105 °C for 24 h.

### 2.2. Ultrasound treatment set up

Ultrasound (US) treatment was carried out using an ultrasonic bath (Elma TI-H 10) with a power of 200 W. The tests were performed by varying both the treatment time in the range 5–60 min and the ultrasonic frequency from 35 to 130 kHz, based on previous studies [34,36,42].

Sand slurry samples were prepared in 250 mL beaker, adding 20 gr of artificially contaminated sand to 40 mL of deionized water (w/w 1:2) (Milli-Q system from Millipore) [43]. Each sample was sonicated at 110 W/L ultrasonic density. In order to avoid overheating during the treatment, a cold-water recirculation system was realized with two peristaltic pumps (323 S/D Watson-Marlow, UK) to keep the temperature in the beaker below 30 °C.

Each test run as well as all the analytical determinations were repeated at least twice, to evaluate the reproducibility of the results. The outcomes were presented as average values.

### 2.3. Electrokinetic treatment set up

The electrokinetic (EK) process used a glass electrokinetic cell [44], composed by a central tube (100 mm length and 32 mm of internal diameter) and two electrode chambers, each with a 300 mL working volume. The central tube contained approximately 200 g (dry weight) of sample; the electrode chambers were filled with a process fluid, consisting of a solution of 0.1 M sodium sulphate ($Na_2SO_4$) (Sigma Aldrich) and 0.1 M citric acid ($C_6H_8O_7$), in order to maintain the acid environment in the cathode chamber [45,46]. Filter paper and porous stones avoided the direct contact between the process fluid and the sample. Two graphite electrodes connected with power supply (Agilent 6634b) were placed in the electrode chambers to apply a constant potential difference of 30 V [19,44]. Further three electrodes were placed in the central tube to monitor the electric field. The EK-Data software was used for the acquisition of the electrical parameters and electrodes pH over time.

The EK treatment was carried out for 20 days on samples sonicated at 35 kHz for 10 min, in accordance with the outcomes of the previous part of the work.

### 2.4. Analytical set up

In order to determine the organic contaminant concentration, a solid–liquid extraction procedure was performed in accordance with the standard method US EPA 3550b. The extracted liquid fraction was then analyzed by gas chromatography coupled with a mass selective detector (GC–MS Thermo- Finningan DSQ Trace), based on the method US EPA 8270.

For the analytical determination of heavy metals, the extraction was accomplished by microwave assisted acid digestion in accordance with the method US EPA 3051a and the concentration measurement was carried out by an inductively coupled plasma optical emission spectrometry (ICP-OES Thermo electron corporation-Icap6000 series), in accordance with the Standard Method US EPA 6020a.

After the EK treatment, each sample was divided into three section,

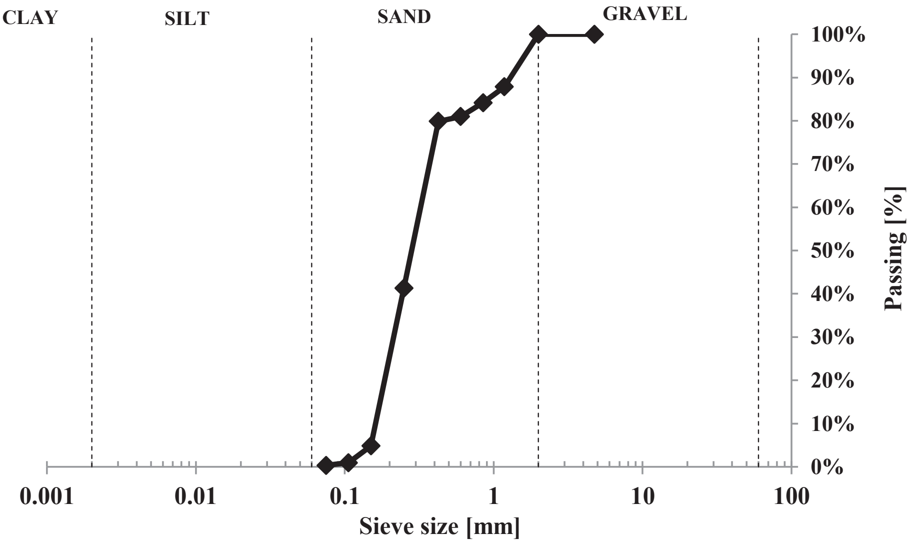

**Fig. 1.** Grading curve of the model sediment.

namely 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.

The remediation yield was evaluated in terms of contaminant removal from the solid matrix, expressed according to the following formula:

$$Removal\,(\%) = \frac{C_i - C_f}{C_i} * 100$$

where:

- $C_i$ is the initial contaminant concentration in the sediment samples;
- $C_f$ is the final contaminant concentration in the sediment samples, obtained at the end of the US treatment.

The concentration of the selected contaminant in the liquid matrix was not determined because this work focused on their removal from the solid matrix, with the main aim to propose a suitable solution for the remediation of sediments.

## 3. Results and discussion

### 3.1. US focused study

The effects of the US treatment were referred to the reduction of both organic and inorganic contaminants from the sediment samples.

Experimental results are plotted in Fig. 2. They show that US provided good performances in terms of contaminant removal, notwithstanding the sonication time and frequency.

After only 5 min of treatment, an average 88% organic contaminant removal occurred; the increase in sonication time did not result in any further degradation of the target PAHs. This outcome should be regarded in the light of the contaminant aging processes. As a spiking procedure had been applied to contaminate the samples, the sorption of the contaminants onto the sediment surface was likely weaker than the one occurring in actually contaminated samples. This condition, in turn, may have affected the degradation response under different sonication time. Several studies show that the contamination aging increases the persistence of the polluting compounds, thus reducing their availability [47,48].

The organic matter of sediment samples is another aspect influencing the removal performances of the target contaminants. Organic compounds tend to create bonds with organic matter, thus making the removal more difficult [49,50].

It is worth underlining that the negligible effect of the treatment time is in accordance with the previous study of Shrestha et al. [43] that reported the negligible effect of sonication time on the removal percentage of hexachlorobenzene and phenanthrene from natural soil samples.

In most cases, the lower frequency was slightly more effective. This behavior can be explained with the prevalent mechanical effects occurring at low frequencies, as confirmed by several scientific works [35,38]. Such effects promote indeed the desorption of the contaminants from the solid surface of sediments making them more easily available for further degradation through hydroxyl radicals in the liquid matrix [36,51].

Promising results were also obtained in terms of heavy metal desorption. Frequency and sonication time did not show to influence significantly the treatment effects, whereas different desorption yields were reached for single inorganic compounds (Fig. 3). Cd and Zn showed the best desorption yields with average values around 84% and 71%, respectively. Pb desorption was observed to reach average values

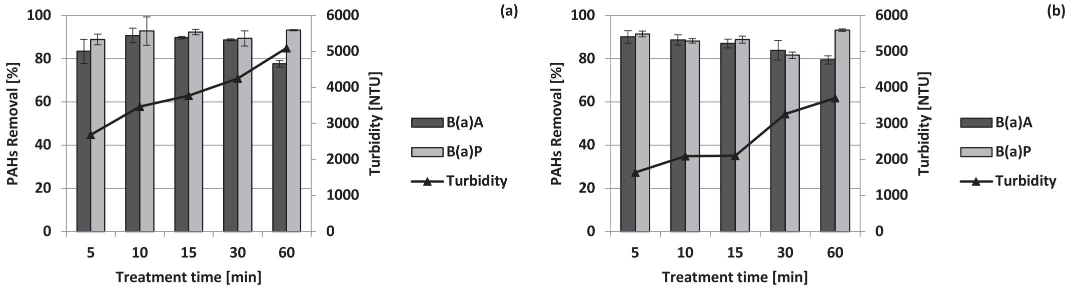

**Fig. 2.** Removal percentage of PAHs after treatment at 35 kHz (a) and 130 kHz (b).

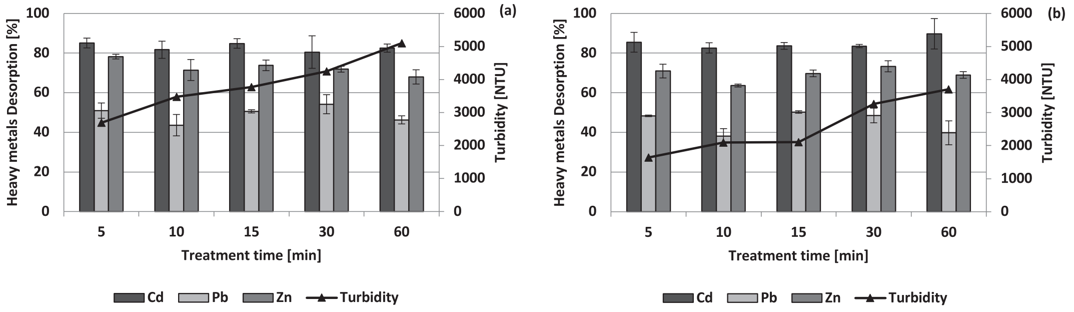

**Fig. 3.** Desorption percentage of heavy metals after treatment at 35 kHz (a) and 130 kHz (b).

of 49% (Fig. 3 a) and 45% (Fig. 3 b) for the treatment at 35 kHz and 130 kHz, respectively.

The behavior of each heavy metal should be regarded in the light of the strong influence of pH [52]. It is worth pointing out that the experiments were carried out in deionized water, at a pH around 6, which is the preferred condition for both Cd and Zn solubilisation. Conversely, Pb mobilization from solid to liquid matrices is promoted by acidic conditions [53]. US waves applied in the aqueous medium do not allow the development of $H^+$ or $OH^-$ ions [43] and the consequent change of pH, that in this case could have been useful to enhance heavy metal desorption.

These outcomes pointed out that ultrasound is potentially effective for the treatment of contaminated sediments, allowing the reduction of compounds of different nature in a sole stage. For both organic and inorganic contaminants, experimental results showed that both lower frequency and short sonication time can be effective, suggesting the possibility to limit the energy consumption for US generation. This aspect is of particular importance when considering the process scale-up, since the implementation of a technological solution should pursue both its technical and economic feasibility.

This study represents a first attempt highlighting the effectiveness of US treatment towards a multiple contamination of sediment samples as well as the possibility to pursue relevant removal yields with a relatively low energy input, posing US as a promising technology for sediment remediation.

### *3.2. US as pretreatment for the EK remediation*

The EK process is well known to be effective towards metal species; conversely as PAH are non-polar species they are not involved in electro-migration mechanisms. EK application to untreated control samples was thus used to depict its remediation yields towards heavy metals, in order to better understand the contribution of the US pretreatment on the sole target inorganic contaminants.

The EK treatment of untreated samples reduced Cd concentration below the instrumental detection limit (0.005 mg/l) and provided a Zn removal as high as 99.63 ± 0.06%. (Fig. 4a).

These results are in good agreement with the work of Camesselle et al. [54], reporting the best EK efficiencies for Cd and Zn. In their study, the authors estimated an average 70% removal, lower than the one observed in the present work, likely due to the presence of clay in the sediments. As indicated by Alcántara et al. [20], the clay negative superficial charge is able to retain positive ions, like the metal ones, playing a key role in determining remediation results.

Different consideration raises for Pb, as the EK process resulted in increasing desorption profile across the sample, with an efficiency as high as 29.44 ± 2.96% obtained in section 3. The acid process fluid used to keep pH below 4 at the cathode, mobilized the metal at the cathode side, likely forming negative complexes that migrated towards the anode [54]. Such mechanism could explain the higher desorption efficiency at the cathode (Fig. 4a).

The US treatment of the samples prior to EK was particularly effective on the organic compounds, which were almost completely removed, with percentages of 91.39 ± 5.29% and 97.29 ± 2.29% for benzo(a)anthracene and benzo(a)pyrene, respectively. Therefore, the subsequent EK treatment was evaluated with reference to heavy metal desorption. After the EK treatment, the best removal efficiency was obtained again for Cd and Zn, with the same removal percentages across the sample (Fig. 4b). Conversely, Pb final concentration decreased across the sonicated sample sections in the EK cell, when moving from the anode to the cathode, with overall removal yields of 59.78 ± 2.82% and 63.64 ± 0.33% in section 1 and 2, respectively. When considering the Pb concentration after the US pretreatment, it is possible to estimate the contribution of the sole EK, which further increased Pb desorption yields by approximately 19%.

The Pb desorption profile is in good agreement with the slight different pH values across the sediment sample (Fig. 4b): the higher efficiencies were, indeed, observed in the sections closer to the anode, where the pH was lower than 3 and the formation of positive complexes likely occurred [54].

It is worth pointing out that the average pH values in sonicated sample sections is below 3, whereas those observed for the untreated sample sections are slightly higher. As the tests were performed under the same operating conditions, this evidence accounts for the US

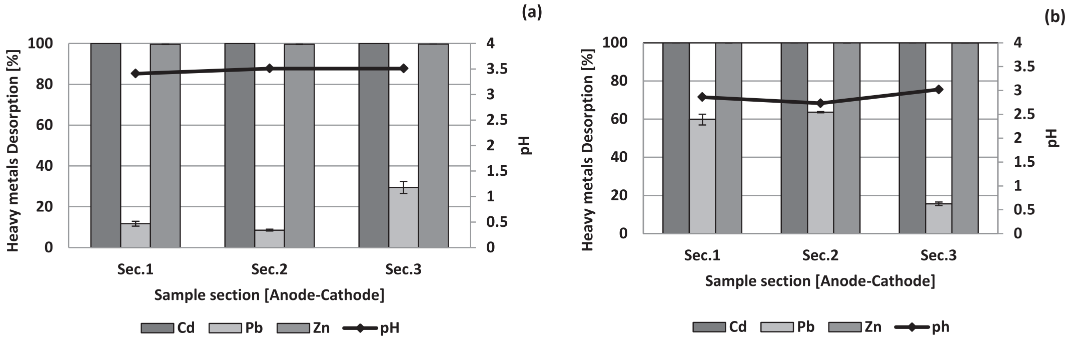

**Fig. 4.** Desorption percentage of heavy metals and pH profile after the EK treatment of untreated (a) and sonicated (35 kHz, 10 min) samples (b).

pretreatment effect on the samples. US action mechanisms are based on the cavitation phenomena, which generate shock waves and microjets, which may destroy the structure of the sediment and promote the contaminant desorption. Notwithstanding the partial desorption provided by US, its mechanical effects led to the reduction of the grain size and to the increase of the surface area in contact with the process solution [55]. The US induced homogenization of the sample further promoted the circulation of the process fluid, which results in the overall improvement of the contact between the contaminated sediments and the acid solution, with a consequent enhancement of metal desorption. In this view, Wang et al. [56] found that a 10 min US pretreatment enhanced acid soil washing by about 20% and 30% for Pb and Zn, respectively. The hypothesis of a uniform acidification of the sample may also influence the EK mechanisms, thus justifying the decreasing trend of Pb removal yield across the sample sections with regard to the increasing one observed for untreated samples.

An additional aspect that contributed to the effectiveness of US as pretreatment of EK lays in the removal of the organic compounds, whose presence may hinder EK remediation results. For this reason, in the case of matrices with simultaneous contamination of organic and inorganic compounds, a sequential treatment is desirable [57].

## 4. Conclusions

This study considered the potential of ultrasound application for the simultaneous reduction of the concentration of both organic and inorganic compounds from contaminated sediments. To this end, the US technology was tested as stand-alone treatment as well as in combination with an electro-kinetic (EK) process.

US proved to be particularly effective towards organic compounds. Average removal of 88% was obtained after only 5 min of sonication and increasing treatment time up to 10 min, an almost complete removal was observed. Under the same experimental conditions, desorption yields of 84%, 47% and 71% were achieved for Cd, Pb and Zn, respectively. The lower average value observed for lead should be attributed to the neutrality of the aqueous medium, which does not promote the solubilisation of this metal, usually occurring in acid condition. The percentage of heavy metal desorption was almost constant in all experiments, despite the sonication frequency as well as the treatment time.

Based on these outcomes, 10 min, low frequency US treatment was applied prior to an EK process. Experimental results suggest that the removal of the organic compound as well as the homogenization of the sediment samples provided by US accounted for the high metal removal efficiencies obtained after the EK of sonicated samples. The average desorption yield of lead increased from 29.44% to 63.64% when applying the EK on untreated and sonicated samples, respectively.

The application of ultrasonic waves led to a considerable reduction of different polluting compounds from the sediments, with relatively low energy input, that need to be optimized and probably further reduced when US technologies are combined with EK processes. Further tests are necessary to characterize the degradation kinetics for both organic and inorganic contaminants: mass balances should be provided for each selected contaminant to quantify its distribution between the liquid and the solid phase. The optimization of operating conditions for the process scale-up could be then better addressed. Nevertheless, experimental outcomes clearly point out the potential of US for the remediation of sediments characterized by multiple contamination.

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