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Microwave heating coupled with UV-A irradiation for PAH removal from highly contaminated marine sediments and subsequent photo-degradation of the generated vaporized organic compounds

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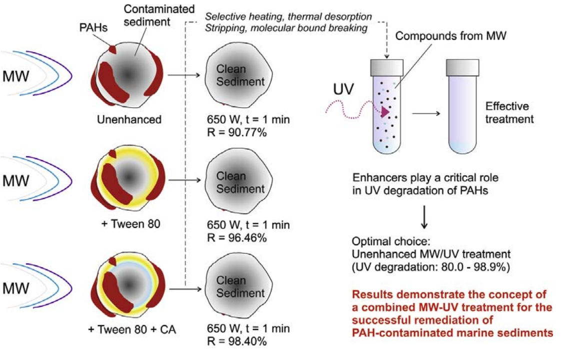
GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work was to demonstrate the concept of a combined MW-UV-A treatment for the successful remediation of PAH-contaminated marine sediments and the successive photo-degradation of the generated vaporized organic compounds, entrapped in the exhaust gas line. The role of Tween 80 and citric acid as degradation enhancers was also investigated, considering variable MW/UV operating conditions and irradiation times. Main results revealed a very rapid sediment temperature increase during MW heating (up to ~380 °C), due to the dielectric properties of both sediment minerals and adsorbed PAHs, which highlighted their great ability to passively convert MWs into heat and in turn allow a very effective PAH-decontamination. PAH removal was higher than 85% after 1-min MW irradiation mainly due to "selective heating" and contaminant stripping removal mechanisms. Longer times led to the total removal of the contaminants. The addition of enhancing agents showed an improvement of the MW performance in the order: MW < MW + Tween 80 < MW + Tween 80 + citric acid. UV light irradiation of condensate from the unenhanced MW treatment resulted in an effective PAH-photo-removal in 34 min, with maximum values in the range 80.0–98.9%. However, the presence of enhancers in the sediments before MW irradiation lowered the contaminant removals (56.0–91.7%) by UV-A. The fate of PAH and their by-(photo)-products during UV irradiation, suggested molecular bond breaking as further contaminant removal mechanism. Overall, obtained data demonstrated the concept of the combined MW-UV-A

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treatment and the critical role of the enhancers in the photo-degradation, which elected unenhanced MW as the best choice.

1. Introduction

Marine sediments act as a major sink for a wide variety of hydrophobic organic compounds (HOCs) and inorganics released, especially in industrial areas [1], consequently posing high risks to aquatic life and humans, which makes dredging activities a necessary strategy to control pollution phenomena. In Europe, about 200 million cubic meters of contaminated sediments are dredged annually and they are classified as waste, which poses serious logistical, economic and environmental problems [2]. Among pollutants affecting marine sediments, a special concern is given to Polycyclic Aromatic Hydrocarbons (PAHs). PAHs are a large group of HOCs with two or more fused aromatic rings of carbons and hydrogen atoms, mainly formed by the incomplete combustion or pyrolysis of organic matter. They are strongly adsorbed on sediment grains and organic matter with a rather long-term persistence and are able to cause long-term effects like mutagenic, carcinogenic and teratogenic potentials to human health [3]. In addition, adsorbed PAHs can also be converted into other organic compounds that are more carcinogenic than PAHs even at much lower concentrations than their parent compounds [4].

A large amount of bottom sediments contaminated with HOCs, among which PAHs, are currently present in Augusta bay (East coast of Sicily, Italy) due to different industrial and chemical activities, which have been operating since the 50's [5]. Traditional management strategies of PAH-contaminated marine sediments generally include disposal in long-shore confined facilities or landfills, whereas the European policy encourages the revaluation of dredged sediments by means of clean-up activities [6]. This makes the possibility to successfully remedy PAH-contaminated sediments a key factor in terms of human safety and social sustainability. However, the poor biodegradability of PAHs and low solubility in water, jointly with the marine sediment features (fine texture with low permeability and high salt, organic content and humidity) make most of the remediation techniques inappropriate or ineffective [7]. Despite the continuous progress in experimental researches, recent studies on bio-treatments still report a successful applicability only in the case of very low contaminant levels or single PAH contaminations, not-satisfying the PAH removal targets and/or requiring remediation times, which are too long [2,8]. In fact, PAH high affinity for organic matter and low solubility make them poorly available to microorganisms, especially when subjected to adsorption onto sediment particles and diffusion phenomena into micropores [3].

Relatively low performances have also been observed by using retrievable activated carbons to treat sediment contaminated with PAHs. Recent studies showed that the feasibility of the sediment treatment has been challenged by low magnetic particle collection efficiency (50–60%) [9]. Electrokinetic (EK) decontamination has been shown as a suitable technique for fine-grain materials such as marine sediments, but recent studies again revealed a limitation in PAH removal ($< 60\%$) jointly with high costs, especially in the presence of high contaminant levels [10–12]. Higher removals can be achieved using chemical oxidation [13] or extraction processes [14] but, in this case, expensive applications are required. Consequently, the successful application of a rapid and cost-effective technique is very desirable but, at the same time, it represents a great challenge for the scientific and technical communities [15].

In recent years, microwave (MW) technology has been exploited as a powerful tool in treating HOC-contaminated soils [16–19], aquifers [20] and wastewater [21]. It showed a great ability to combine a rapid and effective contaminant removal with high flexibility and low costs [22]. The application is based on dielectric heating of MW [23]. Recent investigations demonstrated that contaminant and/or contaminated matrix dielectric features (polarity) significantly influence the effectiveness of the treatment, resulting in different removal mechanisms. When contaminant dielectric constants are significantly higher than their adsorption support (mineral grains), selective heating was shown as main removal mechanisms [19]. On the other hand, for low-dielectric contaminant, polarity of the support matrix (mineralogical composition and water content) play the major role in heating/removal process [24]. The coastal marine sediment mineralogical features and PAH polarity could make MW a much more effective and rapid remedial tool. This needs to be investigated. The addition of enhancing agents has been shown as being strictly required [24]. The knowledge of the volatile organic by-products generated during the thermal application, also in the presence of additional agents, and the subsequent treatment of the produced wastewater are of critical importance.

Photo-degradation using UV radiation might be an efficient way to eliminate PAHs from the contaminated solutions generated by MW application [25]. Main photo-degradation mechanisms include:

(1) direct photoionization or photolysis;
(2) energy transfer from an excited PAH triplet state to molecular oxygen;
(3) charge or electron transfer from an excited singlet or triplet PAH state to molecular oxygen.

Despite some works reporting the pathway (1) as primary mechanisms, recent studies suggested (2) and (3) as dominant routes [26]. These mechanisms were also shown to be affected by wastewater features [27–29]. Consequently, wastewater produced during different sediment MW treatments, especially in the presence of the vaporized enhancing agents, could significantly affect the degradation effectiveness. This could make the final result of the combined application of MW coupled with UV irradiation uncertain. Furthermore, as regards the possibility to achieve a global application, the knowledge of the final fate of the irradiated PAHs is another crucial point that should be addressed. These aspects need appropriate further investigations. Desired achievements will help reduce the energy requirements, CO_2 footprints and costs, jointly with minimisation of by-product waste, which needs expensive and un-safe disposal in landfill.

In the present study, experimental lab-scale approaches were developed to understand the applicability of a two-step treatment, including MW coupled with UV irradiation, for the simultaneous removal of PAHs from marine sediments and the subsequent degradation of the generated products. Main objectives were: (i) to assess the single PAH removal kinetics of MW treatments also by using enhancing agents; (ii) to investigate the UV irradiation ability to degrade the PAHs collected in the exhaust-gas line at the end of the heating process; (iii) to know the fate of PAHs after their MW irradiation and the final fate after UV photo-degradation. Investigated removal mechanisms and kinetics can serve as a foundation for future scaling-up studies and for the development of further innovative techniques aimed at PAH removing from sediments.

2. Materials and methods

2.1. Sediment sampling and characterization

The coastal sediment samples used for the experiments were collected from the southern part of Augusta Bay (Site of National Interest of Priolo, Italy) and immediately stored at a temperature of $-4\,^{\circ}C$ for their transport to the laboratory. Then, they were air-dried for 72 h,