



Enhanced remediation of a real HCH-polluted soil by the synergetic alkaline and ultrasonic activation of persulfate

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ABSTRACT

The desorption of hydrophobic organic compounds (HOCs) and limited mass transfer in soil systems is a significant challenge for efficient soil remediation by oxidation treatments. The utilization of sonochemistry is a promising technology to enhance the decontamination of HOCs-polluted soils. In this work, ultrasound (US) was coupled to NaOH for activating persulfate (PS) to enhance the remediation of a real soil polluted with hexachlorocyclohexanes (HCHs) ($\Sigma_{\text{HCHs}} = 404 \text{ mg kg}^{-1}$). Batch experiments (mass aqueous/soil ratio, $V_L/W_S = 2$) were performed to evaluate the effect of US on HOCs desorption and oxidation. Moreover, the influence of US power (0–245 W, corresponding to 0–91 W L^{-1} of US power density) and the initial oxidant concentration ($C_{\text{PS}} = 10\text{--}60 \text{ g L}^{-1}$) on pollutants abatement, dechlorination degree, and oxidant consumption have been studied. Scanning electron microscopy (SEM) images verified that the US facilitates the breakdown of soil aggregates, enhancing the desorption of trichlorobenzenes (TCBs) (generated from HCHs alkaline hydrolysis) from the soil. Moreover, their subsequent oxidation is favouring because of higher radical species concentrations and the temperature rise. An increase in the US power up to 165 W accelerates the production rate of radicals, improving the pollutants' degradation. The difference between pollutant oxidation and dechlorination decreases with increasing US power, associated with a lower concentration of intermediate chlorinated compounds. In the same way, the initial oxidant concentration plays a fundamental role in the remediation treatment. At the selected operating conditions ($C_{\text{PS}} = 60 \text{ g L}^{-1}$, $\text{NaOH/PS} = 2$, 165 W), a pollutants degradation and dechlorination of 0.94 and 0.74, respectively, were achieved in just 3 h of reaction time.

1. Introduction

Among soil contaminants, persistent organic pollutants (POPs) are of particular concern because of their long half-life in the environment and high toxicity [1]. Recently, some hexachlorocyclohexane (HCH) isomers (α -, β -, and γ -HCH) have been added to the POPs list, regulated by the Stockholm Convention [2]. γ -HCH, also known as lindane, has been extensively used as a wide-spectrum pesticide during the last 5 decades, resulting in global environmental contamination. Regrettably, lindane production entailed the generation of other HCH isomers (α -, β -, ϵ -, and δ -HCH) without insecticidal properties, representing around 85–90% of the total volume [3]. Usually, these compounds were uncontrollably dumped near the production sites, becoming hazardous wastes [4]. HCHs are hydrophobic organic contaminants (HOCs) that have high

persistence in soil and water systems and are considered toxic and carcinogenic compounds [5]. Although lindane production and use have been banned in most countries, many sites around the planet remain contaminated by its wastes nowadays. Thus, to ensure the protection of human health and the environment, there is an urgent need for further assessments and remediation of HCH-polluted sites. The lindane legacy is of great significance in Europe, where most of HCHs waste (63%) is concentrated [2]. One of the most relevant cases is found in Sabinánigo (Huesca, Spain), where the Sardas and Bailín landfills are located. On this site, the company INQUINOSA discharged >7,000 tons of HCH-solid waste per year, generating large quantities of superficial soil pollution [4]. This solid waste was mainly constituted by α -, β -, δ -, and ϵ -HCH isomers (lindane was separated by distillation from the other HCH isomers for its commercialization) [4].

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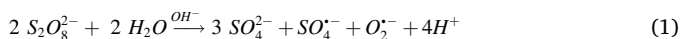
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Advanced oxidation processes (AOPs), such as Fenton, and different activations of persulfate (PS, $S_2O_8^{2-}$), have been tested to degrade HCHs in soil systems [6–10]. Among them, the use of PS led to better results [6,7] due to its high aqueous solubility, higher stability than H_2O_2 , and relatively low cost [11,12]. Different PS activation methods such as i) Fe (III)-EDTA [8], ii) temperature [8,9], iii) alkali [6,10], and iv) synergetic activation with alkali and temperature [6,10] have already been studied for the remediation of HCH-polluted soils. The main limitations when treating HCHs-polluted soils come from their slow desorption from the soil [8] and their low solubility in the aqueous phase [13] (where the oxidation process is most effective) [10]. Among the treatments already studied, the alkaline activation of PS intensified by temperature (PS/NaOH/T), which is a novel and promising treatment, led to the most interesting results [10]. In the PS/NaOH/T system ($C_{PS} = 40 \text{ g L}^{-1}$, $NaOH/PS = 2$, $T = 50^\circ\text{C}$), a pool of radical species is generated (sulfate, superoxide, and hydroxyl radicals, Eqs. (1) and (2)), achieving 94% of chlorinated organic compounds (COCs) conversion in 3 days of treatment [10].



At alkaline conditions ($pH > 12$), TCBs are generated from HCHs hydrolysis [6,13,14]. Although these compounds have a higher solubility than the parent pollutants [6,10,13,14], their desorption still has diffusional limitations as there is a delay between their generation (as an organic phase adsorbed onto the soil) and their desorption to the aqueous phase [10]. Among the HCH isomers, β -HCH degradation is the limiting step in the PS/NaOH/T system (slower hydrolysis rate, lower solubility, and higher refractoriness towards oxidation). Thus, relatively high reaction times were required to achieve acceptable pollutant conversions (3 days) [10]. To overcome these inconveniences, ultrasound (US) can be used to enhance pollutant desorption [15] and to activate PS via cavitation and thermal activation [16,17], which would result in a reduction of the reaction time required. Eqs. (3)–(5) show the main reactions involved in the US-activated PS system, where “)))” refers to US irradiation [18]. US application involves the production of localized hot spots, reaching temperatures and pressures above 5000 K and 500 atm, respectively [19,20]. These extreme conditions result in water thermolysis, generating radical species such as $OH^\bullet$ and $H^\bullet$ (Eq. (3)) [18]. At these conditions, PS can be effectively activated by US to generate sulfate radicals ($SO_4^{\bullet-}$) (Eq. (4)). Moreover, the rapid rise of temperature generated by the breakage of the cavitation bubbles enhances the thermal activation of PS generating sulfate radicals (Eq. (5)).



Hence, the pollutants could be directly degraded via pyrolysis near the cavitation bubbles or indirectly via oxidation by the radicals generated [17]. In this line, the US activation of PS has recently gained increasing attention when treating soils contaminated with different organic pollutants, such as phenanthrene [21], total petroleum hydrocarbons (TPHs) [16,17,22], polychlorinated biphenyls (PCBs) [23], and per- and polyfluoroalkyl substances (PFAS) [24], among others. However, these studies are scarce in the literature and are mostly focused on the remediation of artificially contaminated soils [16,21–23]. Thus, the effect of US on pollutants desorption and soil structure and the pollutant degradation mechanism in the PS/US system, need to be further studied, especially in the case of real polluted soils. Besides, although the effect of pH has been considered in some of the above-mentioned papers [16,22,24], the maximum pH evaluated was 11 [16], insufficient for the

alkaline activation of PS ($pH > 12$). Thus, to the best of our knowledge, the application of the PS/NaOH/US approach has not been previously investigated in the literature. In addition, the use of real HCH-polluted soils (with contamination in the form of particulate matter and adsorbed onto the soil) would provide valuable information for a potential remediation treatment. The worst-case conditions have been selected to carry out the remediation experiments, in which the smallest soil fraction with a high proportion of β -HCH is present (implying a high proportion of adsorbed contamination [9,10]).

Therefore, the current work aims to investigate the on-site application of the PS/NaOH/US system for the remediation of a real HCH-polluted surface soil (hotspot), which is expected to reduce the reaction times required in previous work [10]. The efficiency of the process will depend on soil type, aqueous/soil ratio, initial oxidant concentration, irradiation duration, frequency, and power, among others. Thus, once the effect of US application on the pollutant desorption has been determined, the most decisive variables: the US power and the temperature increases associated, as well as the initial PS concentration, will be systematically evaluated to find the most convenient operating conditions. Likewise, the possible modifications in the soil structure after the remediation treatment will be studied.

2. Material and methods

2.1. Chemicals

The reagents used were of analytical grade. The oxidant (sodium persulfate (PS, $Na_2S_2O_8$)) was provided by Sigma-Aldrich. Potassium iodide (KI) and sodium hydrogen carbonate ($NaHCO_3$), used for its colorimetric quantification, were provided by Fisher and Panreac, respectively. Sodium hydroxide (NaOH), purchased from Riedel-de Haën, was used for the alkaline activation of PS. Methanol (CH_3OH) and n-hexane (C_6H_{14}), provided by Honeywell and Fisher, respectively, were used for the extraction of chlorinated organic compounds (COCs) from the solid and aqueous phases, respectively. Working standard solutions of the studied COCs, consisting of HCHs (α -HCH, β -HCH, γ -HCH, δ -HCH, and ϵ -HCH) and trichlorobenzenes (TCBs; 1,2,4-TCB, 1,2,3-TCB, and 1,3,5-TCB), were prepared with commercial compounds (Sigma-Aldrich). Tetrachloroethane ($C_2H_2Cl_4$) and butyl cyclohexane ($C_{10}H_{20}$), provided by Sigma-Aldrich, were used as internal standard compounds (ISTD) for COCs quantification. Sodium carbonate anhydrous (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$), provided by Panreac, were used in the mobile phase for ion chromatography (IC). The regenerating solution for IC analyses was prepared with sulfuric acid (H_2SO_4 , Fisher), acetone (C_3H_6O , Fisher), and oxalic acid ($C_2H_2O_4$, Riedel-de Haën). Sodium chloride (NaCl, Sigma-Aldrich) was used for chlorides calibration by IC. The stock solutions and dilutions were prepared with high-purity water from a Millipore Direct-Q system with resistivity $> 18 \text{ M}\Omega \text{ cm}$ (25°C).

2.2. Polluted soil

This study deals with the on-site treatment of surface HCHs-polluted soils from a limited contaminated area (hotspot). The polluted soil was supplied by SARGA (*Sociedad Aragonesa de Gestión Agroambiental*). It was collected from the surface of Bailín's landfill (0–30 cm), located in the vicinity of an old lindane factory (INQUINOSA) in the town of Sabinánigo (Huesca, Spain). As explained in the introduction section, the pollution of this soil mainly comes from the disposal of HCH-solid waste. Although most of the solid HCH-waste was transferred to secure cells in the last years, the surface soils of this unlined landfill are still polluted. The soil sample was crushed in the landfill facilities, and it was homogeneously mixed and sieved with an electromagnetic sieve shaker (BA-200-N) in our labs. The majority fraction, with a particle diameter between 0.02 and 0.25 mm, which was also the one presenting the highest proportion of β -HCH [9] was selected for the current study.

The COCs concentration of the initial polluted soil was obtained by the mean value of 10 replicates (measured under the same conditions and following the same extraction process). A deviation below 5% was obtained in the COCs concentration of the GC analyses. Moreover, a sample of untreated soil was remeasured as a control before each test.

The chemical characterization of a superficial soil sampled in the same location was reported in a previous study, including the concentration of metals (Fe, Mg, Al, etc.) and the inorganic (IC) and total organic carbon (TOC) content. [6]. The pH of the polluted soil was measured from a soil–water suspension (mass ratio between the aqueous and soil phases, $V_L/W_S = 2$) using a Basic 20-CRISON pH electrode.

2.3. Experimental design

The experiments were carried out in PTFE well-mixed batch reactors, using a 40 mL PTFE centrifuge tube with PTFE screw caps. Each reactor was filled with 15 g of soil (W_S) and 30 mL (V_L) of the reagents (NaOH or NaOH-PS, from concentrated stock solutions, and milli-Q water). The mass ratio V_L/W_S value ($=2$) was selected according to the results obtained in previous works [6,10]. The experiments were performed in duplicate, being the standard deviation $<10\%$.

2.3.1. Desorption experiments

The positive effect of US application on pollutants desorption has been determined in the absence of oxidant by placing the reactors in a US bath (Power sonic 505, 40 kHz, 350 W, 6 h, without temperature control) (D2). The water level inside the bath (volume of 2.5 L) was adjusted to cover the volume occupied by the soil–aqueous phase suspension of the Teflon reactors (2 reactors of 30 mL each one), giving a total sonicated volume of 2.56 L. The results obtained in run D2 were compared with an equivalent one but without US application (6 h, 22 °C) (D1). Considering that COCs distribution changes at $\text{pH} \geq 12$ due to HCHs hydrolysis [10,14], desorption experiments were carried out at alkaline conditions (pH used in the oxidation experiments, $C_{\text{NaOH}} = 13.5 \text{ g L}^{-1}$). These results were compared with those obtained at equilibrium conditions (24 h, 22 °C, rotatory agitation, 30 rpm) (D_{eq}). The experimental conditions of the desorption experiments have been summarized in Table S1 of the Supplementary Material.

2.3.2. Oxidation experiments

The oxidation runs were carried out by simultaneously adding to the polluted soil the required volume of the oxidant (PS) and activator (NaOH). Moreover, unpolluted soil (with similar physicochemical characteristics to the polluted soil but collected in a non-contaminated area at the Bailín landfill) was also used to evaluate the unproductive consumption of PS. The molar NaOH/PS ratio was fixed at 2, a value commonly found in literature, ensuring a $\text{pH} > 12$ during reaction [6,14]. Samples were analysed at 0, 1, and 3 h (to simplify the analysis of the results obtained, only those corresponding to 3 h will be shown). At the selected reaction times, the corresponding vial was sacrificed. The reactors were refrigerated using an ice bath to stop the oxidation reaction and avoid the possible loss of pollutants by volatilization. After that, the slurry was centrifuged and decanted to separate the aqueous solution from the solid phase.

The conditions selected in the oxidation experiments are listed in Table 1. This table contains the objectives studied, the run number (R1–R18), the type of soil used (polluted (P) or unpolluted (U)), the initial oxidant concentration (C_{PS}), the US power (b), the corresponding power density (energy input per unit volume), considering the total volume sonicated (bath (2.5 L) + 6 reactors (30 mL each one), giving a total volume of 2.68 L), and whether isothermal conditions (or not) were maintained during the reaction time. Experiments without US application but reproducing the temperature ramp associated with each US power have been included for comparison (a). The variable studied in each set of runs has been highlighted in blue color and bold type.

First, to evaluate the effect of the US application, an experiment was

Table 1

Oxidation runs experimental conditions ($\Sigma C_{\text{HCHs},0} = 404 \text{ mg kg}^{-1}$, $V_L = 30 \text{ mL}$, $V_L/W_S = 2$, NaOH/PS = 2, P = polluted soil, U = unpolluted soil).

Objective	Run	Soil Type	C_{PS} (g L ⁻¹)	US Power (W)	US Power density (W L ⁻¹)	Isothermal conditions
Synergetic influence of US application and induced T	R1	P	40	0	0	Yes (22 °C)
	R2	P	40	350^{a,c}	137	Yes (22 °C)
Influence of US power	R3	U	40	0	0	No
	R4	P				
	R5	U	40	0^a/20^b	0/7	No
	R6	P				
	R7	U	40	0^a/65^b	0/24	No
	R8	P				
	R9	U	40	0^a/	0/62	No
	R10	P		165^b		
	R11	U	40	0^a/	0/91	No
	R12	P		245^b		
Influence of C_{PS}	R13	U	10	0^a/165^b	0/62	No
	R14	P				
	R15	U	20	0^a/165^b	0/62	No
	R16	P				
	R9	U	40	0^a/165^b	0/62	No
	R10	P				
	R17	U	60	0^a/165^b	0/62	No
	R18	P				

^a Without US application but reproducing the temperature ramp associated with each US power.

^b US bath (40 kHz, 2.56 L).

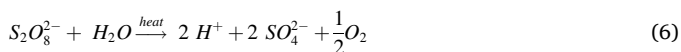
^c US application (US probe, 20 kHz, 2.68 L).

carried out at isothermal conditions ($22 \pm 2^\circ \text{C}$) using a US bath (Power sonic 505, 40 kHz, 2.56 L, 350 W, 137 W L⁻¹) (R2), and the results obtained were compared with those obtained without US application (R1). A circulatory water bath was used to maintain the reaction at an assigned temperature. After that, the effect of US power and initial PS concentration have been studied by using a US probe, which provides greater versatility. The ultrasonic processor used was a Branson Digital Sonifier SFX 550 with a 3/4" diameter ultrasonic horn operating at 20 kHz with a maximum power intensity of 550 W. The sonicator was operated using the pulse mode of 4 s "on" and 1 s "off". The ultrasonic horn was immersed in a bath (2.5 L of water), and 6 reactors (blank, unpolluted, and polluted soil at two reaction times (1 and 3 h)) were homogeneously placed around the horn at 2 cm distance (total sonicated volume of 2.68 L). The schematic diagram of the experimental setup can be found in the Supplementary Material (Figure S1). It should be noted that the experimental device was acoustically and thermally isolated. The solution temperature of the water bath (equivalent to that of the slurry inside the Teflon reactors) was monitored by a thermocouple thermometer (DeltaOHM HD 2108.2).

In the set of experiments carried out to study the effect of the US power in the presence of polluted soil (P), the reactors were subjected to a power input of 0, 20, 65, 165, and 245 W, using a PS concentration of 40 g L⁻¹ (R4, R6^b, R8^b, R10^b, R12^b, Table 1). The unproductive consumption of PS (conversion of oxidant not associated to pollutant abatement) was evaluated by carrying out equivalent runs but using unpolluted soil (U) (R3, R5^b, R7^b, R9^b, R11^b, Table 1). The effect of the initial oxidant concentration (10, 20, 40, and 60 g L⁻¹) was tested by applying a US power of 165 W (R14^b, R16^b, R10^b, R18^b, Table 1). Similarly, the unproductive consumption of PS (using the same initial C_{PS} values) has been evaluated in the presence of unpolluted soil (R13^b, R15^b, R9^b, R17^b, Table 1).

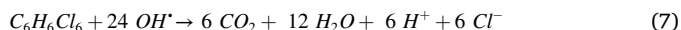
The US activation of PS generates radical species (Eq. (4)), increasing the consumption of this reagent. It should be noted that the application of US increases the temperature of the reaction medium [21]. Here, PS

conversion can also be increased by temperature effect following Eq. (5) (productive consumption) and Eq. (6) (unproductive consumption) [25,26].



The contribution of each effect (US and temperature) has been evaluated by carrying out additional experiments without the application of US but simulating the temperature ramp associated with each US power under study. For that purpose, the reactors were placed in a beaker (with the same volume that the US bath) on a temperature-controlled stir plate (IKA RCT Basic). These experiments have been assigned with the same number as the corresponding experiments carried out with US application, but with the superscript ^(a) (see Table 1).

Both $OH^\bullet$ and $SO_4^{\bullet-}$ radicals contribute as oxidizing agents in the US/PS system [27]. At $pH > 12$, due to base-catalysed hydrolysis of $SO_4^{\bullet-}$, suppression of this radical by rapid transformation into $OH^\bullet$ is produced (Eq. (2)) [28]. Thus the proportion of $OH^\bullet$ (to the detriment of $SO_4^{\bullet-}$) increases with pH , becoming the dominant radical in the PS/NaOH/US system [19]. Considering this point, the stoichiometry of the HCHs ($C_6H_6Cl_6$) oxidation is the following (Eq. (7)):



Therefore, the stoichiometric concentration of PS required for the mineralization of the HCHs present in the soil ($C_{PS, \text{stg}} = 8 \text{ g L}^{-1}$) has been calculated considering the moles of $OH^\bullet$ generated per mol of PS by alkaline activation (Eqs. (1) and (2)) and the aqueous to solid phase ratio used in the oxidation experiments ($V_L/W_S = 2$). The concentration of oxidant used was always higher than the stoichiometric amount (between 1.3 and 7.6 times the stoichiometric concentration, values usually found in the bibliography for the activation of PS in aqueous and soil systems to decrease the reaction times required [6,29–32]).

2.4. Analytical techniques

Soil and aqueous phases were separated by centrifugation (MED-TRONIC-BL-S, JP SELECTA®, 10 min, 9000 rpm) at the selected reaction times. The COCs concentration in the soil phase (polluted or treated soils separated from the aqueous phase) was determined after ultrasonic organic solvent (methanol) extraction. For this purpose, 15 g of soil were mixed with 30 mL of methanol and introduced into an ultrasonication bath (Power sonic 505, 180 min, 45 °C) [10,33,34]. By separating the aqueous phase, most of the remaining PS is removed from the soil phase, assuring the reaction stops. After the extraction process, the PTFE vials (containing MeOH and soil) were cooled in an ice bath and centrifuged. COCs concentration in the organic phase was quantified by GC coupled with Flame Ionization and Electron Capture Detectors (FID and ECD, respectively) (GC, Agilent 6890) using an HP-5-MS column (30 m $\times$ 0.25 mm i.d., 5% phenyl methyl siloxane). Butyl cyclohexane and tetrachloroethane were added to the organic samples as internal standards (ISTDs) for FID and ECD analyses, respectively, to minimize experimental errors in COCs quantification. Detailed information about the chromatographic method can be found in previous works [6,35,36]. Before and after the desorption and oxidation treatments, the soil morphology was characterized by scanning electron microscopy (SEM) (JEOL JSM 6335F INT). Moreover, a qualitative elemental energy dispersive analysis (EDS) was also performed (Oxford Instruments, model: X-Max 80 mm²). Analyses and imaging were done at 20 kV. Due to the non-conductive nature of samples, graphite coating (also compatible with EDS analysis) was applied. SEM and EDS analysis were carried out at the Spanish National Centre for Electron Microscopy (ICTS).

The aqueous phase (separated from the soil by centrifugation) was extracted with an organic solvent (hexane, 1/1 mass ratio). The biphasic mixture was vigorously agitated, and the organic supernatant was analysed by GC-FID and GC-ECD (method previously described). PS

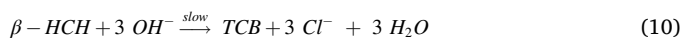
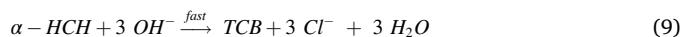
concentration, was determined by a colorimetric method at 352 nm [37], using a BOECO S-20 UV–VIS spectrophotometer. The pollutants dechlorination degree was evaluated by measuring the concentration of chlorides released to the liquid phase by ion chromatography (Metrohm 761 Compact IC). The stationary phase consisted of a metosep A SUPP5 5–250 column and the mobile one, in an aqueous solution of $NaHCO_3$ (1 mM) and Na_2CO_3 (3.2 mM). A solution of acetone, sulfuric (500 mM) and oxalic (100 mM) acids was used to regenerate the ionic resins. The pH was measured by using a Basic 20-CRISON pH electrode.

3. Results and discussion

The efficiency of the remediation treatment has been evaluated considering the pollutants and oxidant conversions (Eq. (8) where i refers to the compound under study: α -HCH, β -HCH, COCs or PS, and t , to the reaction time).

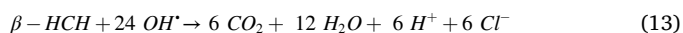
$$X_{i,t} = \frac{C_{i,0} - C_{i,t}}{C_{i,0}} \quad (8)$$

As described in previous works, the alkaline activation of PS ($pH > 12$) causes the dehydrochlorination of HCHs to TCBs [6,10], being the predominant isomer 1,2,4-TCB ($\approx 85\%$). However, the hydrolysis rate of the HCH isomers is not the same, α -, γ -, δ - and ϵ -HCH were almost instantly dehydrochlorinated to TCBs (Eq. (9)). In this equation, the hydrolysis of the α -HCH isomer, the most representative one (Fig. 1), has been represented. Contrarily, the hydrolysis rate of β -HCH (Eq. (10)) is much slower, being the limiting step of the remediation process [10]. Therefore, considering the HCHs hydrolysis, the total concentration of COCs (as mmol kg^{-1}) at alkaline conditions ($pH > 12$) is determined by Eq. (11), considering the sum of the remaining HCHs (mainly β -HCH) and the TCBs generated from HCHs hydrolysis. The molar fraction of the remaining TCBs (TCBs/HCH₀) has also been determined.



$$\text{COCs} = \text{HCHs} + \text{TCBs} \quad (11)$$

Subsequently, the pollutants (TCBs ($C_6H_3Cl_3$) generated and the remaining β -HCH (β - $C_6H_6Cl_6$), which continues slowly hydrolysing to TCBs) are oxidized by the hydroxyl radicals following Eqs. (12) and (13), respectively [10].



The hydrolysis of HCHs to TCBs releases chlorides to the aqueous phase (Eq. (9) and (10)). Moreover, the COCs oxidation could generate dechlorinated compounds as short organics acids and eventually carbon dioxide, water, and chlorides (Eqs. (12) and (13)). Thus, the dechlorination degree (Cl^-/Cl_0) achieved has been determined by Eq. (14), considering the concentration of chlorides released to the aqueous phase (C_{Cl^-}), the V_L/W_S ratio and the initial concentration of chlorine ($C_{Cl, \text{HCHO soil}}$) (calculated from the initial concentration of HCHs in the polluted soil). Finally, the chlorine balance has been calculated by Eq. (15), considering the concentration of chlorides released to the aqueous phase, the chlorine concentration of the COCs solubilized in the aqueous and the COCs remaining in the soil phase ($C_{Cl, \text{COCs aq. phase}}$ and $C_{Cl, \text{COCs soil}}$, respectively), and the V_L/W_S used. When calculating the Cl^- concentration, the soil contribution (C_{Cl^-} released from the soil to the aqueous phase ($0.73 \pm 0.06 \text{ mmol L}^{-1}$) in equivalent conditions ($V_L/W_S = 2$, 24 h)) was subtracted.

$$\text{Dechlorination degree } (Cl^-/Cl_0) = \frac{C_{Cl^-}}{C_{Cl, \text{HCHO soil}}} \cdot \frac{V_L}{W_S} \quad (14)$$

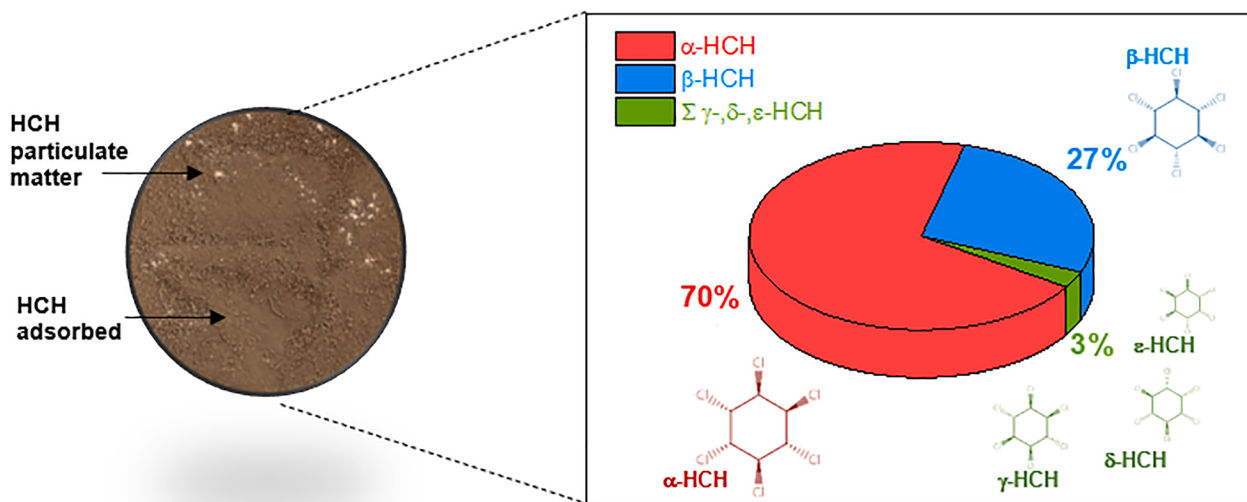


Fig. 1. Photograph of contaminated soil and HCHs distribution ($\Sigma C_{HCHs,0} = 404 \pm 20 \text{ mg kg}^{-1}$, $d_p = 0.02\text{--}0.25 \text{ mm}$).

$$\text{Chlorine balance} = \frac{(C_{Cl-} + C_{Cl, COCs \text{ aq. phase}}) \frac{V_L}{W_S} + C_{Cl, COCs \text{ soil}}}{C_{Cl, HCH0 \text{ soil}}} \quad (15)$$

3.1. Polluted soil characterization

The soil treated in the current work presents equivalent physico-chemical characteristics to the one analysed in a previous investigation [6]. It should be noted the high carbonate content (>38%) and the significant presence of some metals: iron (21.1 g kg^{-1}), magnesium (11.7 g kg^{-1}), and aluminium (17.1 g kg^{-1}). The content of inorganic carbon (IC) and total organic carbon (TOC) was 4.6 and 1.5 %, respectively.

As indicated in Fig. 1, the pollution is found as i) particulate matter of HCHs (the solid residue of the lindane production) and ii) adsorbed onto the soil [6]. The smallest soil fraction (0.02–0.25 mm) with a high proportion of β -HCH, implying a high proportion of adsorbed contamination [9,10] (worst-case conditions), has been selected to carry out the remediation experiments. The GC analyses showed that the soil was mainly polluted with HCHs with a total concentration of $404 \pm 20 \text{ mg kg}^{-1}$ ($1.39 \pm 0.07 \text{ mmol kg}^{-1}$). The HCH isomers present in a higher proportion were α -HCH (70 %) and β -HCH (27 %), with concentrations of 282 mg kg^{-1} and 110 mg kg^{-1} , respectively (Fig. 1). Low

concentrations of the other HCH isomers were also detected ($\Sigma \gamma, \delta, \epsilon\text{-HCH} = 11.8 \text{ mg kg}^{-1}$).

3.2. Influence of US application on pollutants desorption and degradation

As stated, HCHs-polluted soils remediation is usually limited by their slow desorption from the soil to the aqueous phase [8] and their low aqueous solubility. In this context, the global degradation rate is expected to increase by applying alkaline conditions (the TCBs generated from the HCHs hydrolysis have higher solubility than the parent compounds) and by favouring the pollutants desorption (US application). To confirm this hypothesis, the application of US on COCs desorption (mainly the TCBs generated) from the soil to the aqueous phase has been evaluated. The concentration of COCs (mmol L^{-1}) solubilized to the aqueous phase with US application (D2) has been compared with those obtained in the absence of US (D1) (Fig. 2-a). As a reference, the concentration of COCs solubilized in the aqueous phase at equilibrium conditions (D_{eq}) has been included in this figure (blue line). The time required to achieve the equilibrium between both phases was previously evaluated by measuring the evolution of COCs concentration in the aqueous phase up to 48 h, and an asymptotic value was obtained from 24 h (data not shown). It should be noted that the temperature increase associated with US application can also favour the desorption process

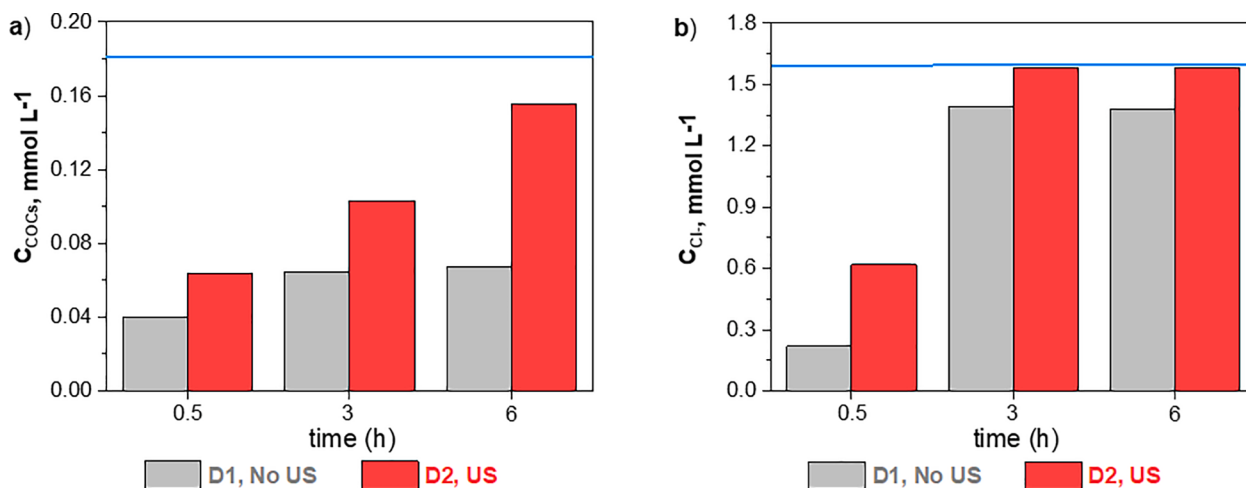


Figure 2. Effect of the application of US on the desorption of COCs (a) and Cl^- (b) to the aqueous phase. Blue line represents the experimental value obtained at equilibrium conditions (D_{eq} , $\text{pH} > 12$, $t \geq 24 \text{ h}$). Operational conditions summarized in Table S1.

[21]. These tests have been carried out without temperature control to take advantage of this fact, reaching temperatures of 60 °C after 6 h (Figure S2).

COCs (mainly TCBs, pH > 12) desorption rate from the soil to the aqueous phase is notably increased when US irradiation was applied (and the induced temperature increase) (Fig. 2-a). Hamdaoui et al. [38] studied the effects of US on the desorption of *p*-chlorophenol from granular activated carbon, reporting that the desorption rates were favoured by increasing US intensity, temperature, and NaOH addition. Moreover, the chlorides concentration released to the aqueous phase with and without US application has been compared (Fig. 2-b). As can be seen, the chlorides generated by HCHs hydrolysis and subsequently desorbed, is highly limited at short reaction times. The Cl⁻ concentration increased with the US application and reaction time, reaching the value obtained in equilibrium conditions (24 h, blue line, 1.61 mmol L⁻¹) from only 3 h of US application. From these results, it can be concluded that i) US application enhances COCs desorption from the soil to the aqueous phase and ii) the solubilisation rate of COCs is more hindered than the release of chlorides.

SEM analysis showed that US application facilitates the breakdown of soil aggregates, decreasing the soil particle size (Figure S3-a vs. Fig. S3-c) without noticeable changes in particle morphology (Figure S3-b vs. Fig. S3-d). These results are consistent with previous studies in which the effect of US on soil structure was evaluated [17,23,39]. Thus, the US application increases the surface area of the soil, allowing higher desorption of TCBs from soil to the aqueous phase. Besides, in these conditions, an enhancement in the contact between pollutants and the oxidant is expected. The US effect on pollutant degradation has been evaluated to confirm the above hypothesis. As previously stated, the US application produces a temperature increase [21,24]. Moreover, considering the positive effect of temperature in the alkaline activation of PS [6,10], results obtained with US application at isothermal conditions (R2) were compared with the equivalent without US application (R1) (Fig. 3). The conversion of α -HCH was complete in both experiments due to its almost instantaneous dehydrochlorination. The degradation of COCs at ambient temperature and absence of US (R1) was low ($X_{\text{COCs}} = 0.34$). This value was slightly increased with US application ($X_{\text{COCs}} = 0.42$), according to the higher β -HCH conversion and lower concentration of remaining TCBs. Higher differences were obtained concerning the dechlorination degree achieved in these experiments, which could be in part associated with a greater concentration of COCs in the liquid phase with US application, and therefore, a greater oxidant consumption. On the other side, it should be noted that the dechlorination degree achieved is even lower than the dechlorination degree

expected only by the HCH isomers instantaneously hydrolysed (α -, γ -, δ -, ε -HCH), considering that i) β -HCH hydrolysis is negligible at these reaction times, and ii) there is no degradation of the generated TCBs ($\text{Cl}/\text{Cl}_0 = 0.36$, Eqs. (9) and (14)). This aspect can be explained attending to diffusional problems in the desorption of chlorides from the soil phase (where they are generated) to the aqueous one (where they are measured), as previously reported.

The improvements obtained in COCs degradation and dechlorination are considered insufficient to justify the use of US under these conditions (room temperature), which is consistent with the results reported by other authors [18,24]. The heat-induced by US application is expected to significantly improve the process, playing a critical role in the i) desorption of pollutants from the soil phase [8] ii) thermal activation of PS, generating sulfate radicals (Eq. (5)) [9], that, at these conditions (pH ≥ 12), evolve to hydroxyl radicals (Eq. (2)), and finally, iii) content of dissolved oxygen, that decreases at elevated temperature [16], also favouring the production of hydroxyl radicals (Eq. (18)) to the detriment of hydroperoxyl and superoxide radicals (Eqs. (16) and (17), respectively) [27]. Consequently, there is a threshold value of temperature in the PS/NaOH/US system required to generate radicals, and an elevated temperature could affect the efficiency of HCHs dechlorination.



The temperature increase depends on different parameters such as the frequency, the US power, and the solution volume. As expected, the temperature of the aqueous medium increased because of the US application. The isolation of the experimental device also favoured temperature increase, which was proportional to the US power (Fig. 4).

Thus, once it has been demonstrated: i) the positive effect of US on pollutant desorption (which will also favour the subsequent oxidation of pollutants and overall kinetics) and ii) the slight positive effect of US on pollutants oxidation at ambient temperature, the combined effect of US with the associated temperature increase will be further studied. For this purpose, the effect of the two most relevant variables will be evaluated: US power and initial PS concentration (carried out without temperature control).

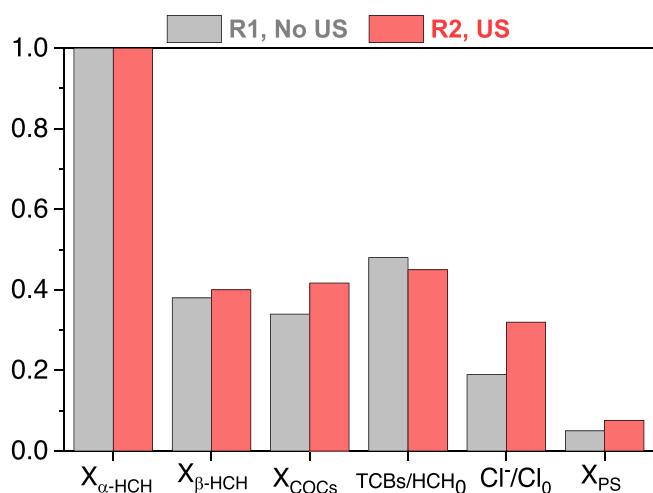


Fig. 3. Effect of US application at isothermal conditions. Operational conditions summarized in Table 1.

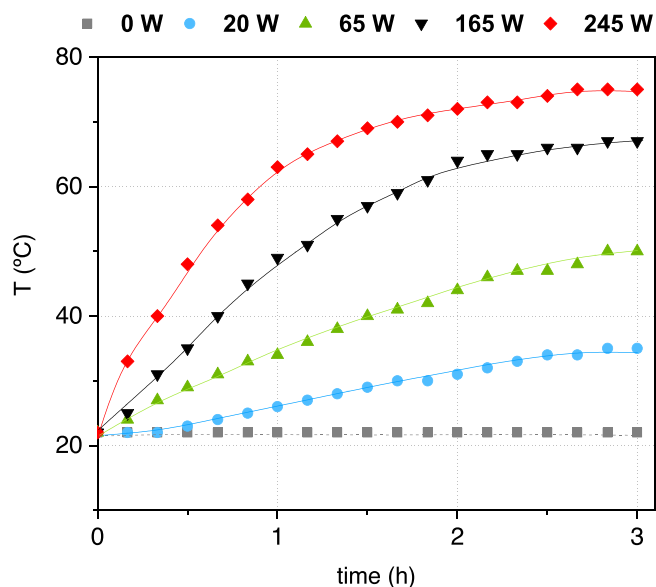


Fig. 4. Temperature increase as a function of US power (0–245 W, corresponding to 0–91 W L⁻¹) (US probe, 20 kHz, 2.68 L).

3.3. Influence of US power

This parameter was evaluated from 0 to 245 W (corresponding to a power density of 0–91 W L⁻¹), maintaining the other operating conditions unaltered (C_{PS} = 40 g L⁻¹, NaOH/PS = 2, V_L/V_S = 2, US probe (20 kHz), total sonicated volume of 2.68 L). The US power density range used in the current work is below the usually found for soils remediation using PS activated by US [16,21]. Blank experiments (without oxidant addition) were carried out, discarding COCs volatilization (data not shown). The influence of US power on oxidant consumption, pollutants degradation, and dechlorination degree has been evaluated. Samples were analysed at 0, 1, and 3 h. It should be noted that at the end of all the experiments (3 h), a pH > 12 was maintained, ensuring the alkaline activation of the PS throughout the reaction time.

3.3.1. Oxidant consumption

The consumption of PS is the result of i) COCs oxidation (Eqs. (12) and (13)) and ii) its unproductive consumption (Eq. (6)) [25,26]. Therefore, to determine the cause of oxidant consumption, the results of PS conversion obtained at 3 h in the presence of polluted soil (P, no-striped, red bars) at the different powers applied (R6^b, R8^b, R10^b, R12^b) have been compared with those obtained using unpolluted soil (U, striped, red bars) (R5^b, R7^b, R9^b, R11^b). Moreover, to determine whether the consumption of PS is due to the US or the associated temperature increase, the results obtained with US (0 W) application have been compared with those obtained without US (0 W) but reproducing the same temperature ramp associated with each US power. This comparison has been carried out using both polluted (P, no-striped, grey bars) (R6^a, R8^a, R10^a, R12^a) and unpolluted (U, striped, grey bars) (R5^a, R7^a, R9^a, R11^a) soils. The results obtained have been depicted in Fig. 5 (the temperature reached at the end of these runs, T_{3h}, has been included).

As expected, the higher the US power, the higher the PS conversion in the presence of both P and U soil (no-striped and striped, red bars). However, this increase is more pronounced in the case of P soil. Around 0.03, 0.04, 0.10, and 0.20 of PS conversions were achieved in the presence of U soil at 20, 65, 165, and 245 W, respectively, which increased up to 0.07, 0.09, 0.24, and 0.38 when P soil was treated, suggesting that PS is consumed in the oxidation of COCs. On the other hand, the difference between PS conversion achieved in the experiments carried out with P and U soils with US application is higher than those obtained without US (red and grey bars, respectively, Fig. 5). These differences increase with the US power, indicating that US favours an efficient use of PS.

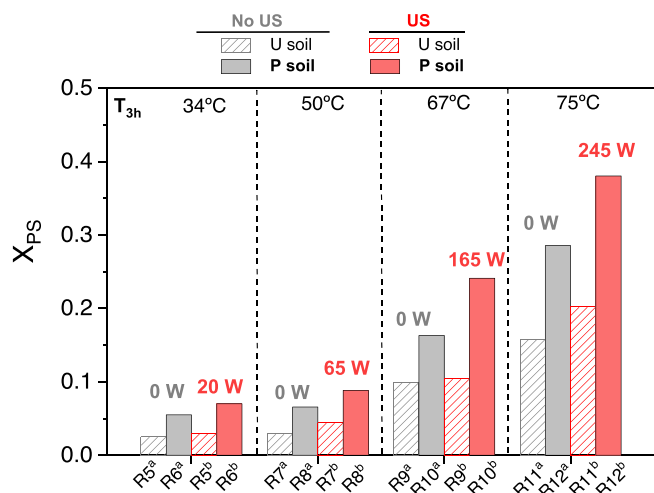


Fig. 5. Effect of US power on PS conversion. T_{3h} = temperature reached at final reaction time. Operational conditions summarized in Table 1.

3.3.2. Pollutants degradation and dechlorination degree

The influence of US power input on the conversion of α-HCH and β-HCH and the molar fraction of TCBs generated and not oxidized (TCBs/HCH₀) after 3 h of reaction time is shown in Fig. 6-a (the temperature reached has been included, the temperature ramp can be seen in Fig. 4). Regardless of the US power applied, α-HCH conversion was complete in all runs at 1 h of reaction time (Eq. (9)), confirming the almost instantaneous hydrolysis of this compound (data not shown). The hydroxyl radicals generated oxidize the organic compounds (Eqs. (12) and (13)) mainly through addition reactions and hydrogen abstraction [40]. The abatement of β-HCH is the limiting step of the remediation treatment due to its slow hydrolysis rate (Eq. (10)) and its high refractoriness toward oxidation [7,10]. The degradation of this compound is highly favoured by the increase in US power and reaction time, reaching a maximum conversion of 0.74 at 3 h when using US power ≥ 165 W (62 W L⁻¹). In the same line, the molar fraction of generated and non-oxidized TCBs (TCBs/HCH₀) decreased notably with US power. When comparing the results obtained with and without US application under the same temperature conditions (Figure S4), a remarkable increase (approximately 20%) in the removal of β-HCH (the most refractory towards oxidation) was achieved under US application. Consequently, the conversion of COCs also increases (especially in the case of low power densities), although this increase is less significant because α-HCH (majority isomer) conversion is 100% in all cases due to its fast hydrolysis. Likewise, the dechlorination degree and the chlorine balance are moderately increased when US is applied (data not shown), indicating greater mineralization and lower concentration of chlorinated intermediate compounds at these conditions.

As expected, higher US power resulted in higher COCs conversion (Fig. 6-b), demonstrating the key role of this variable in the remediation process. These results agree with those reported in the literature concerning the degradation of per- and polyfluoroalkyl substances (PFAS) [24], total petroleum hydrocarbons (TPHs) [17,41], and phenanthrene [42]. Two reasons could explain this improvement i) increased US power generates more cavitation bubbles and heat, leading to a higher production of radical species (Eqs. (4)-(5)) [17,27]; and ii) increased cavitation bubble collapse could produce stronger turbulence and desorption of pollutants (Fig. 2), facilitating the convection and mass transportation rate between the oxidant and the contaminants [16,17]. However, it is worth noting that no significant improvement in COCs conversion was observed when applying US power levels above 165 W, which corresponds to 62 W L⁻¹. Two facts can explain this: i) the tiny bubbles formed could coalesce to form larger ones reducing cavitation [33], and ii) the dual nature of the soil pollution: HCHs in the form of particulate matter and adsorbed to the soil. The fraction of β-HCH (the most resistant HCH isomer towards oxidation) in the form of particulate matter is more easily oxidable than that adsorbed onto the soil. The last one is probably too retained (aged contamination) and, consequently, its solubilization (and further oxidation) is highly hindered. Thus, it seems that 165 W is sufficient to degrade the fraction of β-HCH corresponding to particulate matter (its degradation rate increases proportionally with the US power). In contrast, the adsorbed fraction (around 25% of the total) cannot be solubilized (and therefore, degraded), even when using higher US powers (Fig. 6-a). This fact results in a stagnation of COCs conversion from 165 W.

Additionally, the positive effect of US power is reflected in the dechlorination degree and chlorine balance (Fig. 6-b). It should be noted that low dechlorination values, even below the expected one due to the HCHs hydrolysis, were obtained at low US power (Fig. 6-b). This may be due to chloride diffusional problems from the soil to the aqueous phase (Fig. 2). Chloride ions adsorbed into the soil cannot be quantified, leading also to a mismatch in the chlorine balance at low US power. At the highest US power (245 W, 91 W L⁻¹), >90% of the total chlorine balance is accomplished. On the other side, a linear relationship between the chlorine balance and the dechlorination degree was obtained (Figure S5), indicating that as HCHs dechlorination increases, the

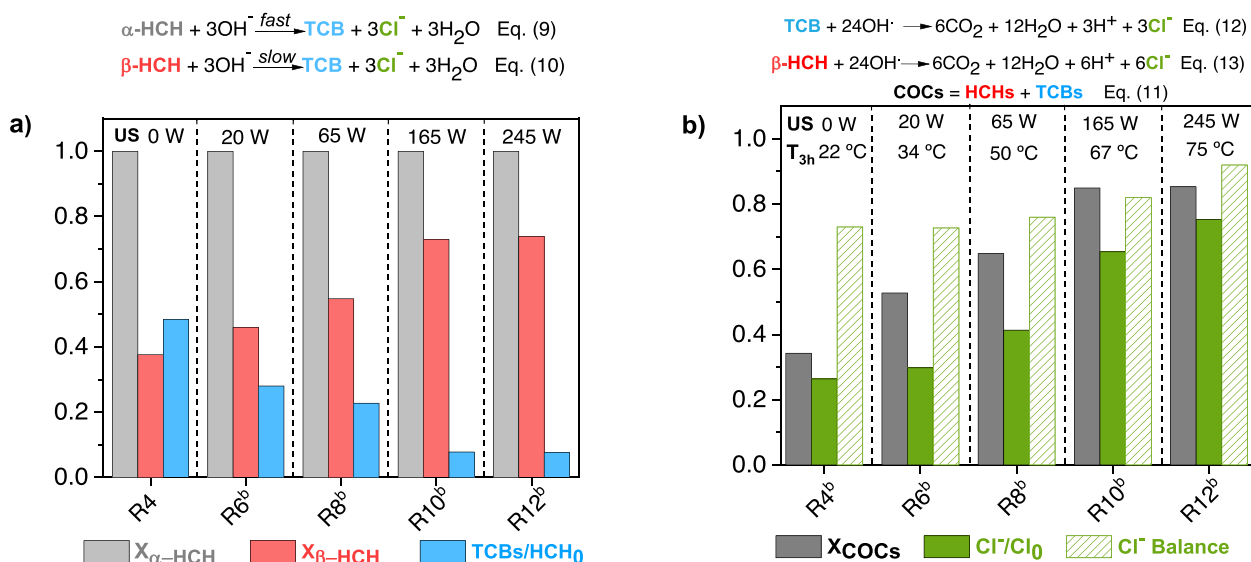


Fig. 6. Influence of US power on (a) α -HCH and β -HCH conversion and TCBs/HCH₀ ratio and (b) COCs conversion, dechlorination degree (Cl[−]/Cl₀) and chlorine balance. T_{3h} = temperature reached at final reaction time. Operational conditions summarized in Table 1.

percentage of unidentified chlorinated compounds decreases (the chlorine balance is accomplished by >90% when 80% of pollutants dechlorination is achieved). Moreover, the differences between the dechlorination degree and COCs conversion decrease as the US power increases, suggesting that lower concentrations of intermediate chlorinated compounds remain in the reaction medium when increasing this variable.

Finally, SEM images showed a decrease in particle size after the selected treatment (Figure S3-a (initial soil before treatment) vs. Fig. S3-d (soil after treatment R10^b)) without noticeable changes in particle morphology (Figure S3-b vs. Fig. S3-f). Thus, it is confirmed that the contact between COCs and oxidant (PS) is enhanced by US. On the other side, it should be noted that the Na concentration increased in the soils treated (the Na percentage determined by EDS analyses was < 0.1, 0.8 and 1.2% for the untreated, desorption (D2) and oxidation (R10^b) soils, respectively, probably in the form of sodium salts (NaOH and Na₂CO₃)). This increase in Na concentration can be related to the high alkaline conditions during experiments.

3.4. Influence of initial oxidant concentration

Once 165 W (62 W L^{−1}) has been selected as the most appropriate power, the effect of the initial PS concentration (10, 20, 40 and 60 g L^{−1}) has been studied. The influence of this variable on oxidant consumption, COCs degradation and dechlorination degree has been investigated. In these experiments, it was also determined that the final pH (3 h) was above 12, ensuring the alkaline activation of the PS throughout the reaction time.

3.4.1. Oxidant consumption

The PS conversion at 3 h of reaction time, when working with different initial concentrations of this reagent, is shown in Fig. 7. The results obtained in the presence of P soil (no-striped, red bars) at the different PS concentrations (R14^b, R16^b, R10^b, R18^b) have been compared with those obtained using U soil (striped, red bars) (R13^b, R15^b, R9^b, R17^b). Moreover, to analyse the cause of PS consumption, the results obtained with US (^b) application have been compared with those obtained without US (0 W) but reproducing the same temperature ramp. This comparison has been carried out using both, polluted (P, no-striped, grey bars) (R14^a, R16^a, R10^a, R18^a) and unpolluted (U, striped, grey bars) (R13^a, R15^a, R9^a, R17^a) soils.

As shown in Fig. 7, in the case of P soil, the conversion of PS

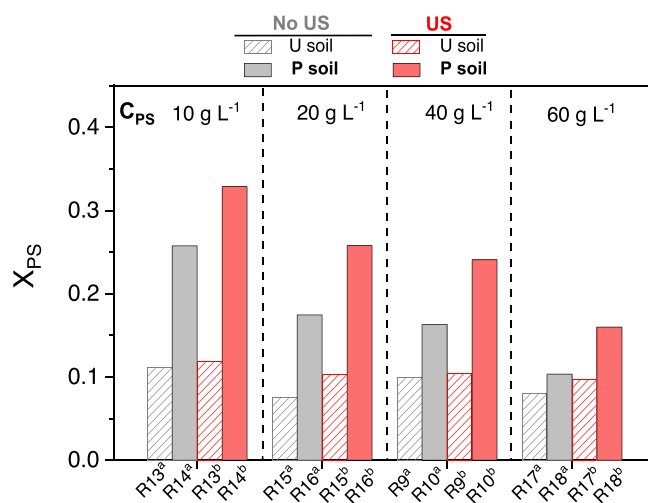


Fig. 7. Influence of initial C_{PS} on PS conversion. Temperature at final reaction time (3 h), 67 °C.

decreases when the initial concentration of this reagent increases regardless of the application of US. On the other hand, the unproductive consumption of PS with U soil remained constant at the different initial PS concentrations tested, following first order-kinetics [43–46]. Considering that COCs degradation increased when increasing the oxidant concentration (Fig. 8-a and -b, further detailed in the next subsection), the consumption of PS is mainly attributable to the oxidation of these pollutants. Moreover, the low PS conversion reached at C_{PS} = 60 g L^{−1} and 165 W (X_{PS} < 0.2) would allow the reuse of the supernatant solution to treat a new batch of HCH-polluted soil, lowering the costs associated with the remediation treatment.

3.4.2. Pollutants degradation and dechlorination degree

Fig. 8-a shows the influence of initial PS concentration (from 10 to 60 g L^{−1}) on the conversion of α -HCH and β -HCH and the molar fraction of TCBs generated and not oxidized (TCBs/HCH₀). As can be seen, β -HCH and TCBs conversion was enhanced as the initial PS concentration increased. Similarly, the COCs conversion, and the dechlorination degree increased when the oxidant concentrations increased (Fig. 8-b).

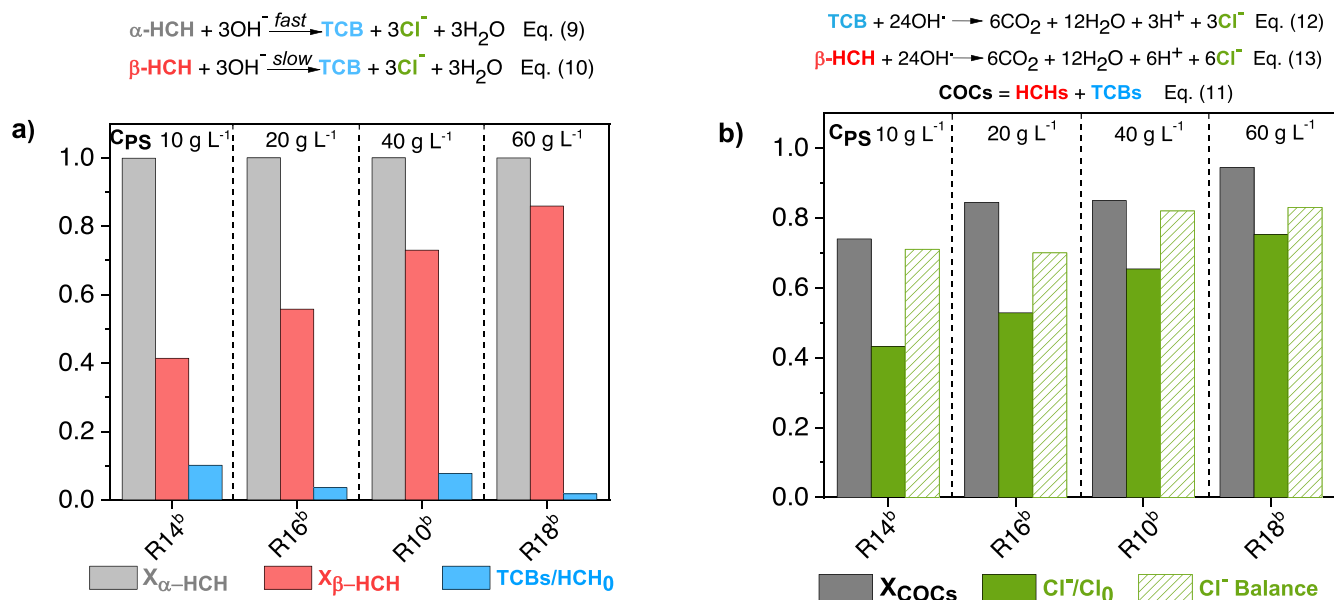


Fig. 8. Influence of initial PS concentration on α -HCH and β -HCH conversion and TCBs/ HCH_0 degradation (a) and COCs conversion and dechlorination degree (Cl^-/Cl_0) (b). T_{3h} = temperature reached at final reaction time, 67 °C.

In this line, the difference between the conversion of COCs and the dechlorination degree achieved also decreased with increasing the concentration of PS, which indicates a lower concentration of intermediate chlorinated compounds (at these conditions, 83% of the chlorine balance was accomplished). This is probably associated with the increased active radicals ($\text{OH}^\bullet$ (mainly) and $\text{SO}_4^{\bullet-}$) yield [17,24]. Thus, it has been demonstrated that the treatment PS/ NaOH /US may offer a promising on-site treatment option for source zones with high levels of HCHs, considerably reducing the reaction time required for their degradation (3 h) in comparison with the results obtained without US application: PS/T system (9 days) [9] and PS/ NaOH /T system (3 days) [10].

4. Conclusions

The intensification of the alkaline activation of PS by US increases the efficiency of the remediation of HCH-polluted soils due to i) the enhanced desorption of the pollutants from the soil to the aqueous phase (according to SEM images, US application breaks the soil aggregates), ii) the increase in the radical's production, and iii) the improved oxidation kinetics. The application of US leads to an increase in the reaction temperature (induced thermal PS activation), which is also beneficial for the remediation process. Increasing the US power (0–165 W, corresponding to 0–62 W L⁻¹ of US power density) and the initial concentration of PS (from 10 to 60 g L⁻¹), the degradation of HCHs and the hydrolysis products (TCBs) increases. Moreover, the dechlorination of HCHs is also favoured, decreasing the concentration of chlorinated intermediate compounds. No aromatic or non-oxygenated chlorinated compounds were detected in any case. At selected operating conditions ($V_L/W_S = 2$, $C_{PS} = 60$ g L⁻¹, $\text{NaOH}/\text{PS} = 2$, 165 W), a conversion and dechlorination degree of pollutants of 0.94 and 0.74 were achieved in only 3 h of reaction time, respectively. At these conditions, a chlorine balance of 83% was reached. Therefore, it has been demonstrated that the application of US significantly reduces the required reaction time to efficiently remediate HCHs-polluted soils. This work provides practical information for the design of a future US activated PS treatment for the on-site remediation of surface polluted soils. However, pilot studies using large-scale ultrasonic reactors need to be performed to scale up this treatment for field applications, considering the locations and power density of US probes, the energy consumption, and the geometry

of the reactors, among others.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2022.135901>.

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