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Novel Oxidation Strategies for the In Situ Remediation of Chlorinated Solvents from Groundwater—A Bench-Scale Study

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Abstract: Industrial chlorinated solvents continue to be among the most significant issues in groundwater (GW) pollution worldwide. This study assesses the effectiveness of eight novel oxidation treatments, including persulfate (PS), ferrous sulfate, sulfidated nano-zero valent iron (S-nZVI), and potassium ferrate, along with their combinations, for the potential in situ remediation of GW polluted with chlorinated solvents (1,2-dichloroethylene, trichloroethylene, and tetrachloroethylene). Our bench-scale results reveal that the combined addition of PS and S-nZVI can effectively eliminate trichloroethylene (10 µg/L), achieving removal rates of up to 80% and 92% within 1 h, respectively, when using synthetic GW. In the case of real GW, this combination achieved removal rates of 69, 99, and 92% for cis-1,2-dichloroethylene, trichloroethylene, and tetrachloroethylene, respectively, within 24 h. Therefore, this proposed remediation solution resulted in a significant reduction in the environmental risk quotient, shifting it from a high-risk (1.1) to a low-risk (0.2) scenario. Furthermore, the absence of transformation products, such as vinyl chloride, suggests the suitability of employing this solution for the in situ remediation of GW polluted with chlorinated solvents.

Keywords: groundwater; remediation; industry; S-nZVI; chlorinated solvents; risk assessment

1. Introduction

Groundwater (GW) is a vital and consistent freshwater source, crucial for ecosystem health and human drinking water [1]. It is, however, highly sensitive and prone to pollution from various sources, retaining certain compounds for a long time [2]. Concerns arise about the contamination of GW with organic compounds due to their potential to reach aquifers through various pathways [1,2]. Specifically, GWs from industrial areas have been described as heavily impacted by organic compounds such as per- and polyfluoroalkyl substances (PFASs), volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons or other industrial compounds [1–4], posing a risk to human and ecosystem health [5]. Among the VOCs, chlorinated solvents are widely studied due to their extensive use in industry from the 1960s onwards. These organic chemicals are very mobile in nature and are persistent enough to maintain their structure through different environmental compartments [6]. Even though they are well-known contaminants, chlorinated solvents are still a real environmental issue, as they are a large family of compounds and one of the most prevalent organic contaminants found in GW [7]. Some of these chlorinated solvents are known

to be potential human carcinogens: trichloroethylene (TCE; a metallurgic-industry solvent) [6,8], tetrachloroethylene (perchloroethylene, PCE; a metallurgic-industry solvent) [9], and cis-1,2-dichloroethylene (DCE; a petrol-industry solvent) [7,10]. As a consequence, chlorinated solvents have been classified as persistent, mobile, and toxic (PMT) and very persistent and very mobile (vPvM) substances, as dictated by REACH [11]. Recently, a European Directive from 2020 has established maximum levels for some chlorinated solvents in tap water intended for human consumption, according to their risk assessment [12]. Within this framework, the sum of TCE and PCE has been limited to 10 μg/L.

The study of advanced treatment methods for the removal of chlorinated solvents from GW remains a diverse and constant field of research [13]. Different kinds of methods have been applied to eliminate organic pollutants from contaminated GW [14]. Within advanced chemical oxidation treatments, one of the most promising treatments is persulfate (PS) activated using different catalysts [15]. PS is a strong oxidant that is commonly used in soil treatments due to its low cost and low soil interaction [16]. For example, PS has been successful in degrading some emerging compounds like triclosan and other pharmaceuticals [17]. However, PS alone lacks the capability to effectively eliminate recalcitrant organic contaminants and requires activation [18]. The activation of PS is achieved through direct electron transfer or free radical reactions, where electron transfer reactions are relatively slow and selective. PS in combination with different activators (i.e., transition metals, temperature, UV) can degrade a wide variety of organic pollutants (i.e., pharmaceuticals [17], industrial compounds [19], pesticides [18]). Nevertheless, the effectiveness of its pollutant removal is contingent upon the nature of the contaminants, the methodologies employed for its activation, and the porous media to be treated [15]. One of these activators is the ferrate ion, which has drawn increasing attention for water treatment. This transition metal is, furthermore, also a strong oxidant that has been shown to be effective in removing organic pollutants such as PFASs from water [20], even without an activator. Potassium ferrate (Fe(VI)) is the best-known ferrate derivative, due to its stability and easy preparation. Nonetheless, no literature research has studied the effectiveness of PS activated by ferrate ion in removing chlorinated solvents until present [21]. Another possible choice is the employment of nano zero-valent iron (nZVI), a strong reductant that has shown good results in degrading a wide variety of halogenated organic compounds [14]. Zero-valent iron (ZVI) can also be used to activate PS [17]. It has been proposed that ZVI, as an iron source, gradually releases ferrous ions, such as ferrous sulfate (Fe(II)), avoiding the scavenging effect at high iron concentrations and enhancing the production of sulphate radicals [19]. The use of ZVI has been widely reported [22–25] for the effective remediation of different contaminants from GW. The main driver of this process is the corrosion of iron, coupled with the dehalogenation of contaminants. The reduction of halogenated compounds by iron drives contaminant degradation, but rapid reactions with oxygen and GW constituents lead to the formation of iron oxides, thickening the shell and reducing electron transfer efficiency in the dehalogenation process [26]. To solve this problem, the sulfidation of nZVI (S-nZVI) particles has been reported to increase longevity and improve reactivity, one of the objectives of this project. The Fe(II) coat formed during sulfidation enhances electron transfer between the iron and the surrounding organics (i.e., chlorinated solvents) and, at the same time, reduces the corrosion process [27]. Despite the reported literature on the combined use of PS and activators, there is a lack of comparative studies conducted under uniform conditions to evaluate their efficacy in removing chlorinated solvents from GW.

As mentioned above, the synergistic effect achieved by combining various reagents has proven to be more effective than employing them individually [23]. However, only a limited set of oxidation agent combinations has been comprehensively evaluated to date, presenting an opportunity for further investigation. As part of the H2020 project PROMISCES (https://www.promisces.eu/, accessed on 25 March 2024), this study aims to assess the occurrence of chlorinated solvents in an industry-impacted GW area in NE Spain. The effectiveness of using PS with different activators (Fe(II), S-nZVI, and Fe(VI))

to remove pollutants from synthetic and real GW, as well as the potential formation of intermediate transformation products, will be evaluated. By exploring a broader range of combinations, this research seeks to identify more efficient and sustainable approaches to GW remediation.

2. Materials and Methods

2.1. Site Description and Sampling

The Besòs River catchment, which supplies water to Barcelona (Spain) and discharges into the NW Mediterranean, is surrounded by many industrial areas. The surveyed area, spanning 15,300 m^2, ceased its industrial operations three years ago, following a fire accident that triggered a spill. GW samples from this area were taken in February 2023. The GW's direction of maximum hydraulic gradient is predominantly from the NE to the SW and its aquifer depth ranges from 5.5 to 6.5 m. This small plot of about one hectare is paved. It has a total of four wells: one GW well (Figure 1) and three monitoring wells (MW-2, MW-6, and MW-14). The area's lithology consists mainly of silt with different proportions of sand and clay, depending on depth. Between 7 and 8 m depths, a very permeable layer of gravel with silty sand is present.
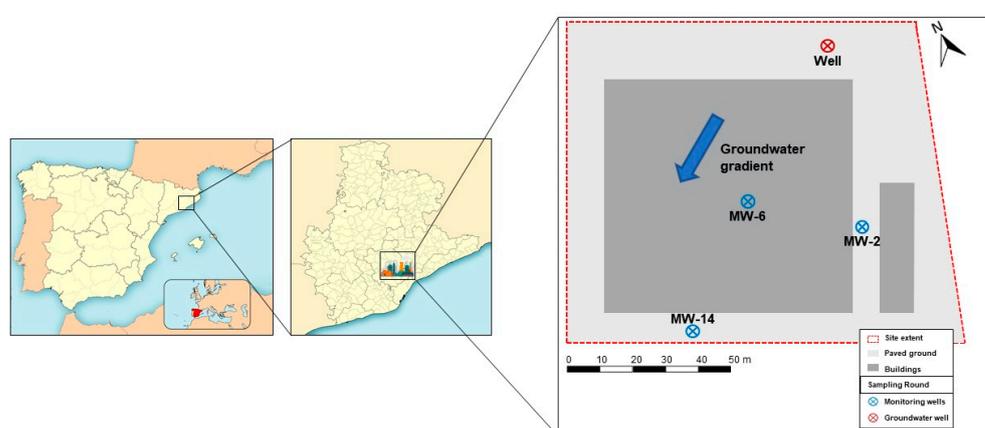

Figure 1. Layout showing the groundwater (GW) sampling points (three monitoring wells (MW) and one groundwater well) and water flow direction.

Different clean containers were used depending on the subsequent analyses. Samples analysed for metals, cations, and anions were collected in 250 mL HDPE bottles. Samples analysed for TOC were collected in 50 mL Falcon tubes. GW for the analyses of chlorinated solvents was sampled in duplicate in 40 mL glass vials on February 2022.

As a quality control measurement, one transport blank and one field blank were performed for each site. The first consisted of reagent water that was carried throughout sampling and handling to check contamination from external sources. The second consisted of ultrapure water that passed through all the sampling equipment to determine possible contamination during the sampling process.

2.2. Chemicals and Reagents

DCE, TCE, PCE, and vinyl chloride standards, PS and sodium chloride, were purchased from Sigma-Aldrich (St. Louis, MO, USA). Fe(VI) (Envifer) and S-nZVI (Nanofer 25DS) from NANO IRON, s.r.o. (Židlochovice, Czech Republic). Fe(II) and salts (Ca^{2+}, Mg^{2+}, Cl$^-$, NO$_3{}^-$, HCO$_3{}^-$) for the synthetic water were provided by Scharlab (Barcelona, Spain). VOC Mix, 2000 µg/mL in methanol, was obtained from Dr. Ehrenstorfer (GmbH, Augsburg, Germany). Methanol and water (HPLC-MS grade) were obtained from Merck (KGaA, Darmstadt, Germany). Total organic carbon (TOC) was tested using a Schimadzu TOC 5050A. All standards were of high purity (95% or higher). Solid-phase microextraction (SPME) fibers were obtained from Supelco (Bellefonte, PA, USA).

2.3. Physico-Chemical Characterization of Besòs Groundwater

GW level and physico-chemical parameters (pH, conductivity, and dissolved oxygen (DO)) were measured in situ with a portable multimeter equipped with specific probes (Xylem Analytics Germany Sales GmbH & Co., KG, Am Achalaich, Germany) and a specific sensor in the case of redox potential (Eh) (Hamilton Company, Reno, NV, USA). The total suspended solids (TSSs) were determined after the filtration of 200 mL of water through a membrane filter (0.45 μm) and weighing the retained solids after drying at 105 °C. TOC, sulfide, and sulfate contents were determined with a TOC analyser (Shimadzu TOC 5050A). Cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) and anions (Br^-, Cl^-, PO_4^{3-}, NO_3^- and SO_4^{3-}) were analysed by ionic chromatography (Dionex Thermo Scientific Aquion and Dionex 2100 CC, respectively). The bicarbonate content was estimated from Ca^{2+} and Mg^{2+} concentrations. GW metals' (Cd, Co, Pb, Zn, Fe, Ni, V, Cu, Ba, Mn, and As) content was determined using an Agilent Inductively Coupled Plasma-Mass Spectrometry 7500 cx (ICP-MS, Agilent Technologies, Inc., Santa Clara, CA, USA) after acid digestion.

2.4. Experimental Design

The experimental design followed the scheme described in Table 1. The first agitated batch experiments consisted of assessing eight different novel oxidation treatments (oxidants and activators on their own, PS, Fe(II), S-nZVI, and Fe(VI), and mixtures of PS + Fe(II), PS + S-nZVI, PS + Fe(VI) + PS, and Fe(VI) + S-nZVI) at different incubation times (1, 2.5 and 5 h) and at low (PS, Fe(II), Fe(VI) at 1 mM and S-nZVI at 1 g/L) and high (PS, Fe(II), Fe(VI) at 10 mM and S-nZVI at 10 g/L) concentrations for the evaluation of the in situ removal, at 20 °C, of a single chlorinated compound (initial concentration 100 μg/L). The concentration of the oxidant agent was selected based on the literature [17,19,24], which indicates a notable enhancement in the degradation of various persistent organic pollutants and emerging contaminants within the concentration range of 1 to 20 mM. The spiked chlorinated solvent was TCE. This choice was made based on the concentrations found on the site: TCE was the compound with highest concentration in Besòs GW (7.81 μg/L) (see Section 3.1. and Table S1 for further details). The matrix for the first set of experiments consisted of synthetic GW, based on the physico-chemical parameters collected and presented in Table 2 and Table S2, with 1.2 mM Ca^{2+}, 0.85 mM Mg^{2+}, 3.23 mM Cl^-, 0.25 mM NO_3^- and 0.17 mM HCO_3^- with <1 mg/L of TOC and no presence of TSSs, a pH of 7.4 and electrical conductivity of 500 μs/cm in order to simulate the features of Besòs GW.

The second batch of experiments was performed in similar conditions, but with a combination of spiked chlorinated solvents (DCE, TCE, and PCE). Each compound was added at a concentration of 10 μg/L to the batch reactors to closely mimic their real occurrence in Besòs GW. The synthetic matrix in this case contained 2.2 mM Na^+, 1.2 mM Ca^{2+}, 0.82 mM Mg^{2+}, 3.3 mM Cl^-, 1.1 mM SO_4^{2-}, 0.25 mM NO_3^-, and 0.18 mM HCO_3^-, while its pH was 6.8 and electrical conductivity was 1350 μs/cm, with <1 mg/L of TOC.

The last two batches of experiments (Batch 3 and 4) were aimed at testing real Besòs GW in triplicate, spiked with 10 μg/L at different incubation times (0–5 h and 0–24 h, respectively). The real GW's characterization is shown in Table 2 and Table S2. Furthermore, vinyl chloride was also analysed in order to determine the degradations of the chosen chlorinated solvents by this compound.

Control assays were conducted simultaneously for all batches, involving GW spiked or unspiked with chlorinated solvents, but without the addition of the oxidation agents.

Table 1. Tested batch experiments and their experimental features. Trichloroethylene (TCE), cis-1,2-dichloroethylene (DCE), tetrachloroethylene (PCE), persulfate (PS), ferrous sulfate (Fe(II)), potassium ferrate (Fe(VI)), and sulfidated nano-zero valent iron (S-nZVI). * Spiked concentration of each chlorinated solvent.

Batch Experiment	Spiked Comp.	Spiked Conc. *	Water Matrix	Incubation Time	Experiment Reagent	Rationale for the Reagent
1	TCE	100 µg/L	Synthetic GW	1, 2.5 and 5 h	PS	Strong oxidant
					Fe(II)	Catalyst
					PS + Fe(II)	Strong oxidant and catalyst
					S-nZVI	Weak oxidant and catalyst
					PS + S-nZVI	Weak and strong oxidant and catalyst
					Fe(VI)	Strong oxidant and indirect catalyst
					PS + Fe(VI)	Two strong oxidants and indirect catalyst
					PS + Fe(VI) + S-nZVI	Weak and two strong oxidants and two catalysts
2	DCE, TCE and PCE	10 µg/L	Synthetic GW	1, 2.5 and 5 h	PS + S-nZVI	Weak and strong oxidant and catalyst
					PS + Fe(VI) + S-nZVI	Weak and two strong oxidants and two catalysts
3	DCE, TCE and PCE	10 µg/L	Real GW	0 and 5 h	PS + S-nZVI	Weak and strong oxidant and catalyst
4	DCE, TCE and PCE	10 µg/L	Real GW	0, 9 and 24 h	PS + S-nZVI	Weak and strong oxidant and catalyst

2.5. Analytical Methodology for the Monitoring of Volatile Organic Compounds in Groundwater

GW samples were analysed using a Purge-and-Trap (PT) technique coupled with gas chromatography-mass spectrometry (GC-MS). The PT manually dispensed 10 mL of the water sample or standard solution. The samples were then purged with helium for 11 min at a flow rate of 40 mL/min and trapped in an adsorbent. After desorption at 250 °C for 4 min, the VOCs were transferred directly into a Trace GC coupled to an MS equipped with a CP-Select 624 CB capillary column (60 m × 250 µm × 1.4 µm). The column temperature was gradually increased from 40 to 210 °C. The injector was operated in split mode and helium was used as the carrier gas. The MS was operated in full-scan acquisition mode in the m/z 35–380 Da range. Quantification was performed via an internal calibration method using fluorobenzene, 4-bromofluorobenzene, and 1,2-dichloroethane-d4 as internal standards and nine-point calibration curves. The 59 VOCs determined in the GW samples are listed in Table S1, along with their limits of detection and quantification.

2.6. Analytical Methodology—Quantification of Chlorinated Solvents' Removal

The analysis of DCE, TCE, and PCE in the water samples from the first three experimental batches was conducted as described. Water samples were collected in 20 mL amber vials to a volume of 3 mL, along with NaCl (250 mg), for headspace SPME analysis using a TriPlus 500 headspace sampler. The solutions were agitated for 20 min at 40 °C. The optimum sampling conditions were as follows: incubation time, 5 min; incubation temperature, 40 °C; extraction time, 15 min; extraction temperature, 40 °C; stirring speed, 700 rpm; desorption time, 10 min; desorption temperature, 260 °C.

The microextractions were performed using a manual solid-phase microextraction fibre assembly fitted with an 85 µm carboxen/polydimethylsiloxane (85-CAR/PDMS) fibre and a fibre coated with a 7 µm thickness film of PDMS (7 µm PDMS) for the first, second, and third experiments' samples, respectively. When new, both fibres were conditioned for 30 min in a GC injector port at 300 °C before analysis.

A Trace GC Ultra gas chromatograph, coupled to a Nitrogen Phosphorus Detector and Electron Capture Detector Trace (Thermo Fisher Scientific, Waltham, MA, USA), was used for analytical separation and detection. The chromatographic column was a 60 m × 0.25 mm × 1.4 µm DB-624 column (Phenomenex, Torrance, CA, USA). The carrier gas was helium at a constant flow of 1.0 mL/min; and the inlet temperature was 260 °C. The oven temperature gradually increased from 40 to 280 °C. The splitless time was 0.8 min and the detector temperature was 300 °C. The limits of detection and quantification are detailed in Table S1.

The identification and quantification of the chlorinated solvents and vinyl chloride in the water samples from Batch 4 were performed using a PT-GC-MS instrument, as described in Section 2.5.

2.7. Environmental and Human Health Risk Assessments

An environmental risk assessment was also calculated using equations outlined elsewhere [28]. Briefly, the environmental risk quotient (EQ) is based on the ratio of the actual monitored concentration of pollutants (µg/L) to the predicted no-effect concentration (PNEC, µg/L) of the molecules detected. Based on widely accepted environmental risk assessment standards, ecological risk is categorized into three tiers: $EQ < 0.1$ signifies the least risk; $0.1 \leq EQ < 1$ indicates a moderate risk level; and $EQ \geq 1$ indicates a high-risk scenario. In order to obtain trustworthy and standardized PNECs of freshwater, the NORMAN ecotoxicology database (see https://www.norman-network.com/nds/, accessed on 15 November 2023) collates PNEC values for $\geq$40,000 substances that are based on experimental data, and quantitative structure activity relationships have predicted PNECs for four taxonomic groups: protists (*Tetrahymena*), vertebrates (fish), aquatic plants (algae), and invertebrates (*Daphnia*). To derive PNEC values for individual substances, the lowest no-observed-effect concentration across the four taxa is divided by an assessment factor of 1000 [29].

A human health risk assessment was computed utilizing the equations for non-cancer and cancer risks detailed by the Agency for Toxic Substances and Disease Registry (https://www.atsdr.cdc.gov/, accessed on 20 November 2023) and the literature [30]. The non-cancer hazard quotient (NCQ) was calculated to evaluate the potential for non-cancer health hazards to occur due to oral exposure to a contaminant. It is typically derived by dividing the chronic daily average intake (D, mg/kg/day) by the corresponding non-cancer health guideline reference dose (RfD, mg/kg/day). After obtaining the NCQ, it is compared to the threshold. NCQ values below 1 suggest a lower concern regarding non-cancerous hazards. However, an NCQ exceeding 1 indicates a surpassing of the non-cancer health guidelines. Furthermore, to calculate the cancer risk quotient (CQ), the daily exposure dose (D, mg/kg/day) has to be divided by the cancer slope factor (CSF, mg/kg/day). After the CQ is obtained, it is assessed as to whether it exceeds 1.0×10^{-6}; if it falls below this value, it is considered to be under control as a cancer risk.

2.8. Statistical Analysis

Our experimental results were statistically evaluated using GraphPad software version 9.2.322 (LLC, St. Diego, CA, USA). In the first experiment (Batch 1), which involved the initial screening of various oxidation combinations, the oxidizing agent concentration and incubation time factors were compared. Similarly, for the second experiment (Batch 2), a comparison was made between treatments for each compound since no statistical differences were obtained between incubation times.

In the context of the third and the fourth experiments (Batches 3 and 4), a comparison was made between spiked and unspiked real GW samples and incubation times, respectively, for each compound, since the oxidation assays were performed in triplicate.

Every statistical comparison mentioned above was conducted using a non-parametrical and paired Friedman test, corrected using multiple comparison (False Discovery Rate, FDR), and calculated with 95% confidence ($p < 0.05$).

3. Results and Discussion

3.1. Groundwater Characterization

The groundwater (GW)'s physico-chemical characterization showed great variability between wells (Table 2). For example, the pH ranged from 5.21 to 7.49 and the conductivity ranged from 0.42 to 57.60 mS/cm. In all cases, the results indicate that, while the well water showed no industrial impact, in monitoring well (MW) 6 the impact was the greatest, as can be seen from the increase in the conductivity, total suspended solids (TSSs), and decrease in pH of its water. Following the GW gradient, MW-14 had a reduction in conductivity and TSSs and a slight increase in pH, due to its distance from the main industrial hotspot. Additionally, the chemical analysis of MW-6 and MW-14 samples presented an increase in all monitored ions, (i.e., Cl^- and Ca^{2+}) and metals (i.e., Fe, Ni, and Cu) (Tables S2 and S3). This is very relevant since these ions can be involved in the catalysis of the proposed advanced oxidation processes suggested in this study. All this suggests that the buildings indicated in Figure 1 are the main source of this pollution, which follows the direction of GW flow.

Table 2. Besòs GW's in situ parameters. Dissolved oxygen (DO), redox potential (Eh), total organic carbon (TOC), and total suspended solid (TSS).

	Depth	Temperature	pH	Conductivity	DO	Eh	TOC	TSS
	m	°C		mS/cm	mg/L	mV	mg/L	mg/L
Well	6.21	16.8	7.40	0.42	2.38	65.9	<2	15
MW-2	7.19	16.3	7.49	1.44	0.82	−68.5	3	979
MW-6	7.33	17.3	5.21	57.60	1.33	69.2	-	2336
MW-14	7.42	19.1	5.52	11.68	5.32	158.7	-	103

The study of volatile organic compounds (VOCs), including the chlorinated solvents in various wells, indicates that 13 out of the 59 studied chemicals were quantifiable in at least one monitored sample (Table 3 and Table S1). The two monitoring wells that showed the greatest concentration of VOCs (MW-6 and MW-14) were those in which the highest conductivity and concentration of ions were identified. The most abundant chlorinated solvents that were detected in both MW-6 and MW-14 were trichloroethylene (TCE), with a concentration of 2.86 and 7.81 μg/L, respectively, and tetrachloroethylene (perchloroethylene, PCE), with concentration levels of 0.28 and 6.33 μg/L, respectively. Consistent with these results, other publications [30,31] reported VOC occurrences and, specifically, elevated concentrations of TCE and PCE in GW. Other compounds occurred in relevant concentrations were toluene (1.96 and 0.20 μg/L, respectively) and cis-1,2-dichloroethylene (DCE) (0.45 and 0.84 μg/L, respectively). O-xylene and chloromethane were also quantified in at least MW-6, at 1.48 and 1.35 μg/L, respectively. The presence of these VOCs suggests that the contamination may have originated from one or multiple point sources near MW-6, which is where these physico-chemical factors exhibit their highest values and more VOCs were detected. However, the highest concentrations of DCE, TCE, and PCE were detected in MW-14. This can be explained by their high mobility (Table S5), allowing them to disperse over large spatial areas, in accordance with the literature [32]. Moreover, this observation could signify a shift in the industrial spill of solvents or an enhanced remediation of chlorinated solvents in the spill area, possibly due to the higher presence of organic matter and TSSs. In relation to the concentration ratio between TCE and PCE, a review of the literature [9] indicates that PCE has a high potential for dichlorination, leading to the production of more TCE, in concordance with our results. It is noteworthy that industrial activities ceased in the area three years ago, eliminating the expectation of further inputs of chlorinated solvents from this specific industry. Nevertheless, it is crucial to highlight the possibility of potential diffuse industrial pollution sources in the surrounding area contributing to ongoing contamination. Additionally, since these sorts of

contaminants have been classified as persistent, mobile, and toxic (PMT) compounds, they may persist in GW at concentrations higher than those recommended by the European Parliament for tap water. While the limit has been set at 10 µg/L for the sum of TCE and PCE, the aggregated concentration of these two chlorinated solvents in the Besòs GW was measured as 14.1 µg/L [12]. Therefore, it is best to first assess different oxidation agents in bench-scale experiments and then employ the most effective ones for the in situ remediation of the contaminated area.

Table 3. Concentration of the quantified volatile organic compounds (VOCs) identified in at least one of the four sampling points of the Besòs GW near an industrial area. VOCs that are not shown were below the limit of quantification (see Table S1).

Compound	Well	MW-2	MW-6	MW-14
Benzene	<LOD	<LOD	0.66	<LOD
Chloromethane	<LOD	<LOD	1.35	<LOD
Cis-1.2-dichloroethylene	<LOD	<LOD	0.45	0.84
Ethylbenzene	<LOD	<LOD	0.87	<LOD
M-xylene/p-xylene	<LOD	<LOD	0.67	<LOD
Naphthalene	<LOD	<LOD	0.26	<LOD
O-xylene	<LOD	<LOD	1.48	<LOD
Tetrachloroethylene	<LOD	<LOD	0.28	6.33
Toluene	<LOD	<LOD	1.96	0.20
Trichloroethylene	<LOD	<LOD	2.86	7.81
1,2,4-trimethylbenzene	<LOD	<LOD	0.60	<LOD
1,2-dichlorobenzene	<LOD	0.28	<LOD	<LOD
1,3,5-trimethylbenzene	<LOD	<LOD	0.31	<LOD

3.2. Remediation of Chlorinated Solvents in Synthetic Groundwater

Based on the Besòs GW's characterization, TCE was selected for the first batch of remediation experiments described in Table 1. TCE was selected due to its high detected concentration (Table 3 and Table S1) and the fact that this compound is an excellent indicator of the chlorinated solvent pollution in GW [7]. Observing Figure 2, the whole set of samples from the first experiment (Batch 1) was split into the different studied factors (oxidizing agent's concentration, incubation time, and treatment). TCE removal efficiencies were generally affected by oxidant concentration, with zero oxidizing agent concentration obtaining the lowest TCE eliminations. The removal observed in the 0 mM reactors may be attributed to TCE's volatilization within the reactors, with a range spanning from 1 to 25%, as previously reported elsewhere [33]. Higher oxidant concentrations (10 mM) resulted in higher removal efficiencies. This agrees with previous studies indicating that chloronitrobenzene reduction was enhanced significantly, from 11 to 90%, with an increase in zero valent iron (ZVI) dosage from 1 to 10 g in a treatment that combined it with persulfate (PS) [24]. Moreover, TCE removal increased with longer incubation periods, reaching its highest elimination scores at 5 h, but no statistical differences were observed. The results obtained agreed with the predicted effectiveness of most studied treatments according to our literature review (Table S6).
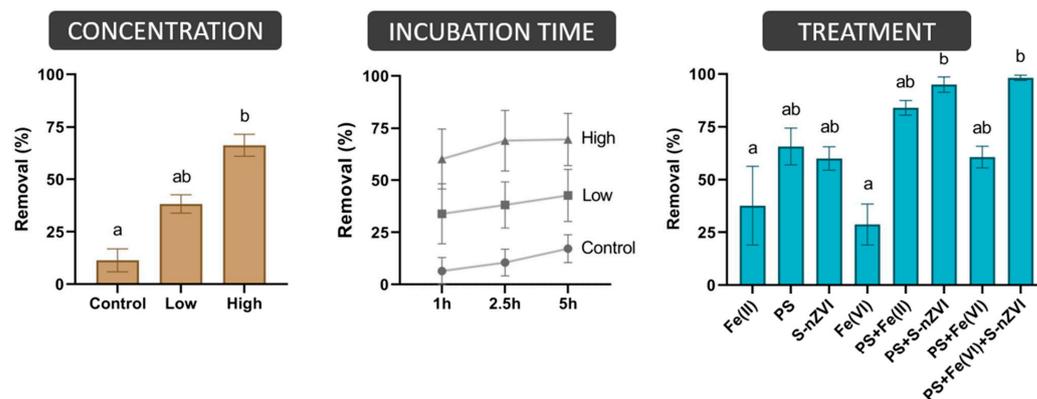
Figure 2. Comparison of eight novel treatment methods for the removal of TCE spiked to 100 µg/L in synthetic GW (Batch 1). Various concentrations of PS, Fe(II), and Fe(VI) (0, 1, and 10 mM) and S-nZVI (0, 1, and 10 g/L) were tested (Control, Low, and High, respectively) at different incubation times (1, 2.5, and 5 h). Significant differences between samples, identified by different lower-case letters, were determined by a Friedman test with FDR correction for concentrations and treatments ($p < 0.05$) due to paired and non-parametric samples.

For the treatment comparison, as the incubation times did not show statistical differences, treatments were evaluated based on the three different incubation periods and the highest concentrations of oxidant agents (10 mM and 10 g/L). The two negative controls were assessed separately using ferrous sulfate (Fe(II)) as a catalyst and PS as an oxidant. These compounds were individually presumed to produce low removal. Fe(II) obtained TCE removal rates between 12 and 48% and PS produced eliminations of 45–73%, confirming prior studies in which it is reported that isolated PS and Fe(II) could attenuate around 30% of TCE's concentration [24,34]. Focusing on the suitability of treatments, sulfidated nano-zero valent iron (S-nZVI) and potassium ferrate (Fe(VI)), separately, which are compounds that act like a weak oxidant and catalyst (S-nZVI) and strong oxidant and indirect catalyst (Fe(VI)), reported the lowest TCE eliminations (45–65 and 22–40%, respectively) verifying the importance of combining a stronger oxidant and catalyst, respectively [24,34]. The combination of PS + Fe(VI) obtained similar attenuation efficiencies (26–30 and 56–66% for 1 and 10 mM of oxidant, respectively). When examining the mixtures of PS + Fe(II) and PS + S-nZVI, it is noteworthy that, despite both treatments utilizing the same oxidation agent, the presence of S-nZVI had a significant impact on TCE removal rates, in agreement with the results obtained elsewhere [34]. Hence, the two combinations of chemical reagents that generated the highest removals and had statistically significant differences from the others were PS + S-nZVI and PS + Fe(VI) + S-nZVI at 10 mM reagent concentrations (92–99% removal). Based on the already-stated results, these two treatments were selected for the next experiment.

In the second experiment (Batch 2), the synthetic GW was spiked with three chlorinated solvents (DCE, TCE, and PCE) at 10 µg/L for each compound, and the two best oxidant combinations (PS + S-nZVI and Fe(VI) + PS + S-nZVI) were applied at 10 mM. Figure 3 shows that the removal efficiencies were greater (59–90%) when using the PS + S-nZVI treatment at the two longest incubation times, compared to the treatment that combined Fe(VI) + PS + S-nZVI (48–74%). However, our statistical analysis revealed significant differences only in the removal of DCE between the two treatments. The removal of chlorinated solvents was compound-dependent. The attenuation of DCE (89%) and TCE (87%) was greater than that of PCE (59%). Our results agree with the experiments [8,9] that observed that, in the remediation of contaminated GW under flow-through conditions by S-nZVI and Fe(VI) treatments, higher efficiencies were achieved when employing S-nZVI rather than Fe(VI) under similar conditions. Because of the acidic media, Fe(VI) was more strongly retained in the soil column than S-nZVI particles. Moreover, the removal efficiencies achieved in this batch for TCE were lower than those observed in the previous

assay using the same combinations of oxidation agents (Figures 2 and 3). This can be explained by the fact that the TCE concentration was reduced from 100 to 10 µg/L, but also by the addition of DCE and PCE to the reactor. Additionally, it is pertinent to note that, owing to the reported dichlorination of PCE primarily into TCE [9] and DCE [6,14], the removal of TCE may have decreased. However, it is reported that those TCE by-products normally account for less than 5% of the total degradation products [25].
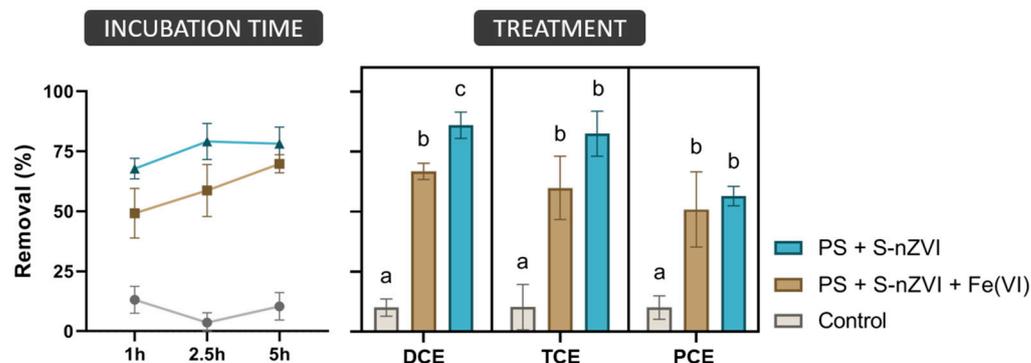

Figure 3. Removal efficiencies of chlorinated solvents (DCE, TCE, and PCE) in GW exposed for different incubation times (0, 1, 2.5, and 5 h) and the best preselected oxidation treatments, at 10 mM, with each compound spiked at 10 µg/L (Batch 2). Significant differences between treatments within each compound, identified by different lower-case letters, were determined by a Friedman test with FDR correction for treatments ($p < 0.05$) due to paired and non-parametric samples.

3.3. Remediation of Chlorinated Solvents in Real Groundwater

Since the combination of PS + S-nZVI was identified as the most suitable treatment for chlorinated solvents' attenuation in synthetic GW, it was tested on real Besòs GW at both 0 and 5 h of incubation time, with the addition of the three selected chlorinated solvents at 10 µg/L (see Table S4 for further information). As shown in Figure 4, the PS + S-nZVI treatment combined with spiked GW removed a portion of the chlorinated solvents after 5 h (50–99%). However, the removal was still compound-dependent, as while the TCE elimination reached 99%, DCE and PCE achieved values of 50 and 58%, respectively. TCE and PCE's removals were greater and similar, respectively, than the previous experiment with synthetic GW (87 and 59%), but a lower DCE removal occurred (50%) in comparison with the 89% achieved previously. This removal decrease in comparison with the previous experiments may be produced by the matrix effect. Since real GW contained more total organic carbon (TOC) than the synthetic GW (3 mg/L vs. <1 mg/L, respectively), the removal efficiency of the treatment may be decreased, as reported elsewhere [8]. Therefore, higher incubation times were required for the real GW matrix.

Additionally, 5 h reactions with unspiked GW demonstrated the removal of chlorinated solvents at low concentrations. As shown in Figure 4, TCE and PCE's removals were around 73–94%. In the case of the unspiked GW samples, as DCE was not detected, no elimination was reported for this compound. Hence, this study has shown that a PS + S-nZVI treatment efficiently removes TCE and PCE statistically similarly.
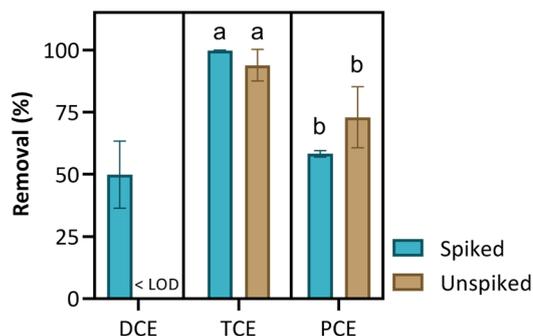
Figure 4. Removal of chlorinated solvents (DCE, TCE, and PCE) by a PS + S-nZVI treatment after a 5 h incubation time in spiked (10 μg/L each compound) and unspiked real Besòs GW and 10 mM of oxidant (Batch 3). Significant differences between the spiked and unspiked reactions' removals within each compound, identified by different lower-case letters, were determined by a Friedman test with FDR correction for treatments ($p < 0.05$) due to paired and non-parametric samples. Since DCE was not detected in unspiked samples (0 nor 5 h), the statistical comparison had enough samples to be compared.

3.4. Effect of Incubation Time on the Remediation of Chlorinated Solvents

Figure 5 reveals that, with longer incubation times (9 and 24 h), there is a consistent trend of increasing chlorinated solvent removal, with the rates reaching 69% for DCE and 92% for PCE after 24 h. Meanwhile, for TCE, a 99% elimination was already reached at 9 h without statistical differences. The results showed an increase in the removal of DCE and PCE with the PS + S-nZVI remediation treatment between 9 (38 and 85%) and 24 h (up to 69 and 92%). Furthermore, this removal was greater than the one previously observed at 5 h. These results lead us to think that incubation times longer than 24 h (i.e., two days, five days, a week) may result in the complete removal of chlorinated solvents when using this combination of oxidation agents in real GW. Furthermore, samples with zero incubation time achieved removals between 11 and 25%. Additionally, vinyl chloride, a highly toxic compound generated from TCE's oxidation [6,7], was also analysed to ensure that none of the chlorinated solvents studied had transformed into vinyl chloride. However, vinyl chloride was not detected in any of the analysed samples. Furthermore, the possibility of additional degradation products resulting from the application of these oxidation agents in the removal of the investigated chlorinated solvents cannot be ignored. Research studies have identified other intermediate products, such as formic, glyoxylic, dichloroacetic, and oxalic acids, which may be involved in the degradation pathway of TCE [35,36].
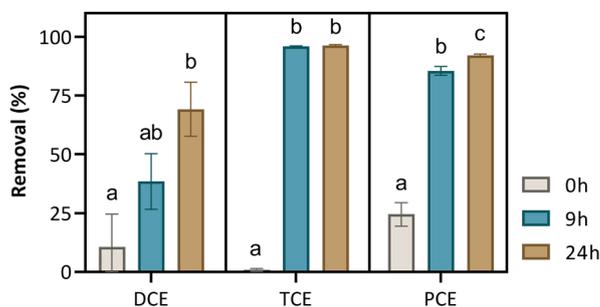

Figure 5. Removal of chlorinated solvents by PS + S-nZVI treatment at 0, 9, and 24 h of incubation in real Besòs GW spiked with 10 μg/L of each of the selected compounds (DCE, TCE, and PCE) and 10 mM of oxidant (Batch 4). Significant differences between different incubation times within each compound, identified by different lower-case letters, were determined by a Friedman test with FDR correction for the treatments of each compound ($p < 0.05$) due to paired and non-parametric samples.

3.5. Environmental and Human Health Risk Assessments

Table 4 shows the environmental risk assessment for the selected chlorinated solvents in unspiked GW (0 and 5 h) samples treated with PS + S-nZVI based on the lowest values in the experimental data, quantitative structure activity relationships, and predicted no-effect concentration (PNEC) values for freshwater and four taxonomic groups: protists (*Tetrahymena*), vertebrates (fish), aquatic plants (algae), and invertebrates (*Daphnia*) (Table S7) [29]. The results show that although no risk was identified when studying both compounds individually (environmental risk quotient (EQ) of 0.5–0.6), the accumulated risk was greater than 1, indicating that a risk was present. Aligned with these findings, a significant EQ for TCE and PCE was calculated due to the high concentrations detected in GW [29]. Thanks to the PS + S-nZVI treatment, however, this risk was reduced to less than 0.2. Regarding the human health risk due to this GW's consumption as tap water, the sum of both concentrations (11.1 µg/L) was greater than the recommended concentration according to European legislation (10 µg/L for the sum of TCE and PCE in tap water) [12]. Nevertheless, Table 4 and Table S4 indicate that the experimental concentration detected in unspiked GW 0 h samples eluded the non-cancer hazard quotient (NCQ) and cancer risk quotient (CQ) quotients for human health based on the Agency for Toxic Substances and Disease Registry, obtaining a HQ of around 0.1 and a CR of 3.4×10^{-9}. These low values agree with other studies performed on the use of GW as drinking water in California, EEUU. In contrast, other publications [30] show higher risks due to elevated GW occurrences of these chlorinated solvents (2–21 µg/L, PCE; 0.98–231 µg/L, TCE; 1–82.4, µg/L DCE; 4.25–651 µg/L, vinyl chloride) in Taiwan. Even though the human health risk assessment calculated for the sum of both concentrations was below the risk levels mentioned above, the PS + S-nZVI treatment helped to reduce the probability of the NCQ (0.01 for C5h 0.12 vs. 0.007 for TCE and 0.01 vs. 0.003 for PCE) and the CQ (2.5×10^{-10} for C5h 3.3×10^{-9} vs. 2.0×10^{-10} for TCE and 1.7×10^{-10} vs. 4.6×10^{-11} E-11 for PCE) even further (see Tables 4 and S4). The results suggest that the proposed remediation approach is effective in significantly reducing both ecological and human health risks. Therefore, it could be applied to produce drinking water. However, despite the risks posed by the monitored contaminants, an additional concern arises from the co-occurrence of unknown compounds (i.e., PFASs) potentially exacerbating this risk [37].

Table 4. Human health and environmental risk assessment calculations conducted for chlorinated solvents and their combined sum in unspiked Besòs GW treated with PS + S-nZVI, at 0 and 5 h. The risk levels are categorized as follows: non-cancer hazard quotient (NCQ) > 1 indicates high concern; cancer-risk quotient (CQ) > 1.0E-06 indicates high concern; and environmental risk quotient (EQ) < 0.1 indicates the least risk, as EQ values between 0.1 and 1 suggest moderate risk, while EQ ≥ 1 represents a high-risk scenario. * According to the Agency for Toxic Substances and Disease Registry, there is inadequate information to assess the carcinogenic potential of DCE.

	Non-Cancer Hazard Quotient (NCQ)		Cancer Risk Quotient (CQ)		Environmental Risk Quotient (EQ)	
	0 h	5 h	0 h	5 h	0 h	5 h
PCE	$1.2 \times 10^{-2} \pm 1.7 \times 10^{-3}$	$3.1 \times 10^{-3} \pm 1.4 \times 10^{-3}$	$1.7 \times 10^{-10} \pm 2.5 \times 10^{-11}$	$4.6 \times 10^{-11} \pm 2.1 \times 10^{-11}$	$5.9 \times 10^{-1} \pm 8.7 \times 10^{-2}$	$1.6 \times 10^{-1} \pm 7.3 \times 10^{-2}$
TCE	$1.2 \times 10^{-1} \pm 2.45 \times 10^{-2}$	$7.4 \times 10^{-3} \pm 7.7 \times 10^{-3}$	$3.2 \times 10^{-9} \pm 6.6 \times 10^{-10}$	$2.0 \times 10^{-10} \pm 2.1 \times 10^{-10}$	$5.2 \times 10^{-1} \pm 1.0 \times 10^{-1}$	$3.2 \times 10^{-2} \pm 3.3 \times 10^{-2}$
DCE	$5.87 \times 10^{-4} \pm 0.0$	$5.87 \times 10^{-4} \pm 0.0$	*	*	$1.5 \times 10^{-2} \pm 0.0$	$1.5 \times 10^{-2} \pm 0.0$
Σ	$1.3 \times 10^{-1} \pm 5.8 \times 10^{-2}$	$1.1 \times 10^{-2} \pm 3.4 \times 10^{-3}$	$3.4 \times 10^{-9} \pm 1.6 \times 10^{-9}$	$2.5 \times 10^{-10} \pm 9.5 \times 10^{-11}$	$1.1 \times 10^{0} \pm 5.6 \times 10^{-2}$	$2.1 \times 10^{-1} \pm 3.5 \times 10^{-2}$

3.6. Comparison with Current Available Remediation Solutions and Their Limitations

The main remediation processes and technologies commonly used for the in situ treatment of chlorinated solvent plumes include biodegradation, phytoremediation, thermal removal, air injection, chemical oxidation/reduction, and sorption [38]. Comparatively, advanced oxidation processes offer a much faster remediation of chlorinated-solvent-contaminated GW, typically taking less than 24 h, whereas bioremediation can extend over a variable timeframe ranging from 1 to 17 months [39]. Similarly, phytoremediation requires plant growth to reach the pollution plume. In comparison to sorption and thermal

processes, oxidation can result in better performance due to the former technologies' need for the continuous addition of sorption material or high energy consumption. Nevertheless, above all, the development during the last few years of nanomaterials for water remediation, such as the S-nZVI used in this study, have resulted in an improvement in the effectiveness of in situ oxidation treatments [40]. The comparison of this approach with ex situ treatments such as reverse osmosis or electrolysis is clear, as in situ treatments have lower energy requirements and therefore lower costs. However, further studies on the actual application of this combination of oxidant agents in attenuating chlorinated solvents in real GW are needed to assess its economic benefits accurately.

Therefore, although this study has been validated using real GW, it is crucial to recognize that this experimentation was conducted at the bench scale. Consequently, additional validation is imperative through in situ assays, which need to be executed within real hydrogeological systems. Scaling up the bench studies poses challenges and may impact the treatments' effectiveness. Finally, another noteworthy aspect that requires careful consideration involves the synergistic utilization of oxidation agents in conjunction with sorption materials like biochar or carbon nanotubes [41]. Empirical evidence suggests that this combined approach may significantly enhance the attenuation of pollutants in GW [42].

4. Conclusions

Our study found that the persulfate and sulfidated nano-zero valent iron combination treatment, combined with high concentrations of oxidizing agent (10 mM) and longer incubation times (5 h), yielded the best results in synthetic groundwater. This approach achieved removal rates of 89% for cis-1,2-dichloroethylene, 87% for trichloroethylene, and 59% for tetrachloroethylene. However, when tested with real groundwater containing 10 μg/L of each of the selected compounds, its performance decreased significantly (to 50, 99, and 58%, respectively). This suggests the need for longer incubation times for the effective treatment of real groundwater. The application of this combined approach with real, unspiked groundwater showed removal rates of 94% for trichloroethylene and 73% for tetrachloroethylene over a 5 h period, demonstrating its effectiveness in mitigating the presence of these contaminants. In a 24 h spiked experiment, removal rates of 69, 99, and 92% were achieved for cis-1,2-dichloroethylene, trichloroethylene, and tetrachloroethylene, respectively, without generating transformation products like vinyl chloride. These results indicate that longer incubation times, beyond 24 h, may be necessary for complete chlorinated solvent removal when using this oxidation agent mixture on real groundwater. Moreover, the treatment of actual groundwater samples revealed a significant decrease in environmental and human health risks. Further field-scale studies are required to assess its practical effectiveness in in situ pollutant remediation.

(HQ), cancer risk (CR)) and environmental (risk quotient (RQ)) risk assessment parameters obtained necessary for calculations. * According to the Agency for Toxic Substances and Disease Registry, there is inadequate information to assess the carcinogenic potential of cis-1,2-dichloroethylene (DCE). References [8,22,26,30,33–35,43] are cited in the Supplementary Materials file.

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