Abatement of Dichloromethane using Persulfate Activated by Alkali: a kinetic study

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Abstract

The alkaline activation of persulfate (PS) has been tested in this study as *in situ* oxidation technology for the abatement of dichloromethane (DCM), a chlorinated volatile organic pollutant commonly found in groundwater due to its wide use as solvent in the chemical industry during the last decades. The addition of an alkali (NaOH) as persulfate activator generates hydroxyl and superoxide radicals, achieving the total degradation of the pollutant (X_{DCM} = 99%, 96h, C_{DCM} = 1.2 mmol L^{-1}, C_{PS} = 42 mmol L^{-1}, C_{NAOH} = 169 mmol L^{-1}). From the results obtained in the presence of a hydroxyl radical-scavenger (methanol, C_{MeOH} = 313 mmol L^{-1}), it has been concluded that only hydroxyl radicals are responsible of DCM abatement. Trichloroethylene was identified as intermediate compound and formic acid and chloride as degradation products. The conversion of DCM increased as the initial concentration of the pollutant decreased (from 1.2 mmol L^{-1} to 0.1 mmol L^{-1}), whereas an increase in the oxidant concentration (from 8 to 168 mmol L^{-1}) led to an increase in the degradation rate of the pollutant. Finally, the molar ratio NaOH:PS (in the range 1 to 4) did not affect the degradation of the pollutant when a pH high enough (>12) was maintained. A kinetic model, able to predict adequately the experimental DCM concentration profiles as a function of the concentration of DCM, PS and NaOH, has been developed. The kinetic model discriminated was zero order, first order and hyperbolic order for NaOH, PS and DCM concentration, respectively.

Key Words: dichloromethane, persulfate, alkaline activation, chlorinated solvents, hydroxyl radical, kinetic model

Introduction

Chlorinated volatile organic compounds (Cl-VOCs) are chemicals extensively used as solvents, degreasing agents, dry cleaning and a variety of commercial products such as pesticides, pharmaceuticals, adhesives, refrigerants, etc. (Huang et al., 2014). Thus, Cl-VOCs are ubiquitous contaminants commonly found in contaminated soils, air and any kind of aquatic mediums such as groundwater, rivers and lakes (Pecoraino et al., 2008, Huang et al., 2014). These pollutants are characterized by their high volatility and strong recalcitrance to degradation (Huang et al., 2014, Lapeyrouse et al., 2019, Iordache et al., 2017, Moran et al., 2007).

Dichloromethane (DCM), also known as methylene chloride, is a colorless and liquid Cl-VOC commonly used as solvent for metal degreasing and paint removal, as finishing solvent in electronics manufacturing, as a degreasing agent for citrus fruit and removal of caffeine from coffee (Ravi et al., 2010) during the last decades. Due to the spills from storage tanks, DCM is among the most frequent Non Aqueous Phase Liquids (NAPLs) found in groundwater in the investigated sites (Siegrist et al., 2011) with a concentration greater than the Maximum Contaminant Levels (MCLs) (Moran et al., 2007).

Acute inhalation exposure to high levels of DCM can affect the central nervous systems (Ravi et al., 2010). According to the Environmental Protection Agency, DCM has been classified in the B2 group as a probable human carcinogen (WHO, 1996) and it has been associated with the risk of spontaneous abortions. The use of DCM in the food industry has been restricted (WHO, 1993) and DCM is listed among the Substance Priority List by the Agency for Toxic Substances and Disease Registry in 2017 (ATSDR, 2017). Therefore, remediation technologies are required for the decontamination of the DCM-polluted sites.

Among the remediation techniques for DCM elimination in groundwater, recently reviewed by Shestakova et al. (2013), some physical process, such as air stripping (Verma and Tyagi, 2012), adsorption (Iakovleva and Sillanpää, 2013) and pervaporation (García et al., 2009) were effective in the separation of DCM from water (efficiencies of about 99%, 90% and 80% were achieved with these treatments, respectively) but further treatments were required for the destruction of the pollutant. Other processes as photodegradation over TiO_2 (Calza et al., 1997), photo-Fenton (Rodríguez et al., 2005), electrocatalysis over Cu-impregnated carbon fiber electrode (Sonoyama et al., 1999), acoustic cavitation (Destaillats et al., 2001) and radiolysis (Mak et al., 1997) could be efficient but not feasible for an *in situ* treatment of the groundwater. On the contrary, *In situ Chemical Oxidation* (ISCO), that involves the injection of an oxidant in the subsurface becomes a suitable technique to abate the organic pollutants present in the groundwater plumes or adsorbed in the soil (Watts and Teel, 2006; Krembs et al., 2010; Baciocchi, 2013; Siegrist et al., 2014). Among the oxidants employed, the use of persulfate (PS) for the abatement of a wide variety of organic pollutants both in soil and groundwater, has been recently proved to be an efficient technology (Tsitonaki et al., 2010; Pardo et al., 2015; Peluffo et al., 2015; Wacławek et al., 2017; Santos et al., 2018). PS shows higher stability in soil and groundwater than hydrogen peroxide, and consequently, it can be transported greater distances in the subsoil (Wacławek et al., 2017). Moreover, this oxidant presents lower affinity for the natural organic substances of the soil than H_2O_2 (Matzek and Carter, 2016), has a moderate cost and results in the production of benign byproducts (Rodriguez et al., 2012; Sra et al., 2014; Devi et al., 2016). Besides, an additional advantage of PS over H_2O_2 is that PS can be applied to a wider range of pHs. PS can be activated to generate free radicals able to react with the organic pollutants at higher rates than the PS anion. The main activation ways of PS are

i) the application of heat or UV light (Eq. 1), the use of iron-based materials (also valid for other transition element ions as Co^{2+}, Ni^{2+}, Cu^{2+}, Ru^{3+}, Ag^{+}, etc.) (Eq. 2), and the addition of an alkali (Eqs. 3 and 4).

$$S_2O_8^{2-} \xrightarrow{heat,\ UV} 2\,SO_4^{\cdot -} \qquad \text{(Eq. 1)}$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot -} \qquad \text{(Eq. 2)}$$

$$2\,S_2O_8^{2-} + 2\,H_2O \xrightarrow{OH^-} 3\,SO_4^{2-} + SO_4^{\cdot -} + O_2^{\cdot -} + 4\,H^+ \qquad \text{(Eq. 3)}$$

$$SO_4^{\cdot -} + OH^- \rightarrow SO_4^{2-} + {}^{\cdot}OH \qquad \text{(Eq. 4)}$$

The radical species generated during the activation of PS are sulfate, hydroxyl and superoxide radicals, depending on the pH and the type of activator used (Eqs. 1-4). These radical species can attack the organic matter following an oxidative (in the presence of sulfate and hydroxyl radicals) or a reductive (in the presence of superoxide radical) mechanism. Therefore, choosing the proper activator and the operating conditions, activated PS is a versatile system able to eliminate a wide type of organic contaminants.

DCM, in the presence of other VOCs, has been treated by thermally activated PS with limited success at mild temperature (X_{DCM}=19% at 72 h, 30ºC and 40 ºC) (Huang et al., 2005) probably due to the refractoriness of DCM towards sulfate radicals. The activation of PS by reduced transition metals (as Fe^{2+}) often requires the addition of a chelating agent to keep the iron in solution when the soil has a neutral pH. The chelating agent can compete with the pollutant causing the non-productive loss of the oxidant (Pardo et al., 2015).

Therefore, the alkaline activation of persulfate (Eqs. 3 and 4), process in which hydroxyl radicals are the predominant species (Furman et al., 2010; Furman et al., 2011), can be proposed to the treatment of DCM in groundwater. From the best of our knowledge, this treatment had not been studied before and it will be the aim of the present study. The degradation mechanism of DCM will be investigated and a kinetic model, considering the effect of the main operating variables on DCM degradation (the initial pollutant concentration, the concentration of PS and the molar ratio NaOH:PS) will be proposed and validated.

1. Materials and Methods

2.1. Reagents

The abatement of dichloromethane (DCM, CH_2Cl_2) with sodium persulfate ($Na_2S_2O_8$, PS) activated by the presence of an alkali (NaOH, in this case) has been studied. Solutions of DCM (Panreac) in milli-Q water at different concentrations were prepared to study the abatement of this pollutant. Sodium persulfate was purchased by Sigma-Aldrich and sodium hydroxide, by Riedel-de Haën. Methanol (CH_3OH, LabScan) was used as hydroxyl radical-scavenger to determine the degradation mechanism of DCM at the studied operating conditions.

Sodium sulfate (Na_2SO_4, Sigma-Aldrich) was used for the preparation of the reaction samples before their analysis by gas-chromatography, and methylcyclohexane (C_7H_{14}, Sigma-Aldrich) was used as internal standard compound (ISTD) for DCM quantification. Potassium iodide (KI, Fisher Chemical), sodium hydrogen carbonate ($NaHCO_3$, Panreac), sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$, Sigma-Aldrich) and acetic acid ($C_2H_4O_2$, Sigma-Aldrich) were used for PS quantification. Sodium hydrogen carbonate, sodium carbonate anhydrous (Na_2CO_3, Panreac), acetone (C_3H_6O, Sigma-Aldrich), oxalic acid ($C_2H_2O_4$, Riedel-de Haën) and sulfuric acid (H_2SO_4, Fisher Chemical) were used for ion chromatography (IC) analyses. Sodium chloride (NaCl, Sigma-Aldrich) was used for chloride calibration. All the reagents used in the present work were of analytical grade and were used without further purification. The solutions were prepared with ultrapure laboratory grade water obtained from a deionizing system.

2.2. Oxidation Runs

Oxidation runs were carried out batch-wise placing the reactors in an orbital shaker (100 rpm, Unitronic Orbital by Selecta) at constant temperature (20ºC). The reaction mixture was prepared by adding the needed volumes of stock aqueous solutions of the pollutant (DCM, 6 mmol L^{-1}), the oxidant (PS, 420 mmol L^{-1}), the activator (NaOH, 2500 mmol L^{-1}), a radical-scavenger (methanol, pure (when applicable)), and Milli-Q water. Aliquots of the prepared solution were immediately taken and placed in individual 2 mL-glass reactors without head-space and Teflon caps (gas chromatography vials), in order to minimize the loss of the pollutant by volatilization. Each reactor represented one experimental time of the overall reaction. For a given reaction time, the corresponding reactor was sacrificed and the remaining concentration of DCM and PS, as well as the concentration of chlorides released to the liquid phase and the degradation by-products, were immediately measured.

Table 1 summarizes the experiments carried out, including the initial concentration of DCM, NaOH and PS, and the presence, or not, of a radical-scavenger. Some preliminary experiments to evaluate the possible volatilization of DCM at the operating conditions tested, the stability of PS and the oxidation of DCM by PS without NaOH activation were also performed (R1-R6). All the experiments were carried out by duplicate and the standard deviation obtained was lower than 10% in all cases.

It should be noted that the carried-out experiments have been performed with a large excess of PS and NaOH to simulate the experimental conditions that would be applied in a future *in situ*-treatment, with the aim of ensuring that high radius of influence of PS transportation in groundwater is reached.

Table 1. Operating conditions of the DCM oxidation runs

Run	Objective	DCM (mmol L^{-1})	NaOH (mmol L^{-1})	PS (mmol L^{-1})	NaOH:PS (mmol:mmol)	Scavenger (mmol L^{-1})
R1	Preliminary experiments	1.5	0	0	-	-
R2		1.5	169	0	-	-
R3		1.5	0	42	-	-
R4		0	0	42	-	-
R5		0	169	42	4	-
R6		1.5	169	42	4	-
R6	DCM degradation mechanism	1.5	169	42	4	-
R7		1.5	169	42	4	MeOH (313)
R8		1.5	650	168	4	-
R9		1.5	650	168	4	MeOH (313)
R10	DCM initial concentration	0.15	169	42	4	-
R11		0.38	169	42	4	-
R12		0.76	169	42	4	-
R6		1.5	169	42	4	-
R13	PS initial concentration	1.5	34	8	4	-
R6		1.5	169	42	4	-
R8		1.5	650	168	4	
R14	NaOH:PS ratio	1.5	34	42	1	-
R15		1.5	85	42	2	-
R6		1.5	169	42	4	-

2.3 Analytical methods

The concentration of DCM was determined by headspace with gas chromatography coupled with a mass spectrometry detector (GC/MS) using a CTC CombyPAL (GC sampler 80) with a new method developed for this purpose. The preparation of the sample prior to GC/MS analysis consisted on the addition of 1 mL of the aqueous reaction sample to a 20 mL-GC cap-sealed vial containing 0.1 mL of the ISTD and 8.9 mL of a Na_2SO_4-saturated aqueous solution. Na_2SO_4 was used to enhance the extraction of the organic compounds of the sample to the vapor phase. The headspace-GC analysis started placing the 20 mL vials in a thermostated oven at 80 ºC under agitation (250 rpm) during 720 s. After the incubation time, the vapor phase generated was extracted using a tight syringe of 2.5 mL heated at 85ºC to avoid the condensation of analytes. After that, the sample was injected in the GC at 250°C using a split ratio of 1:10, with helium as a carrier gas. The pressure was maintained at 50.7 kPa with a flow of 2 mL min^{-1} thought the column. The temperature of the detector was set at 250 °C. A HP-5MS column (30 m x 0.25 mm Øi x 0.25 μm) was used as a stationary phase. The GC column was maintained at constant temperature (45 °C) for 10 min and a post run of 250 ºC during 5 min was thereafter applied. The retention time of DCM at these conditions was 2.64 min. An example of GC-chromatogram can be seen in Fig S.M. 1 (Supplementary Material). The reaction samples were analyzed by duplicated.

The chlorine balance was determined from the chlorides released to the liquid phase, which were quantified by IC (Metrohm 761 Compact IC) with anionic chemical suppression, using a conductivity detector. Before the analysis, the samples were diluted with milli-Q water. The used mobile phase was an aqueous solution of 3.2 mM of Na_2CO_3 and 1 mM of $NaHCO_3$ (0.7 mL min^{-1}) and a Metrosep A SUPP5 5-250 column (25 cm length, 4 mm diameter) was used as a stationary phase. The sample injection system (250 µL) included an online filtering device (0.45 µm).

The concentration of PS in solution was determined by iodometric titration with sodium thiosulfate, using a potentiometric titration analyzer supplied by Metrohm (Ti amo 2.3). The pH evolution of the reaction medium was measured using a Basic 20-CRISON pH electrode.

3. Results and discussion

3.1 Preliminary experiments

3.1.1 DCM degradation

The evolution of the normalized concentration of DCM under different experimental conditions is shown in Fig. 1. As can be seen, the concentration of DCM remained invariable in aqueous solution during reaction time (96 h) at neutral pH (R1) and pH > 13 (in the presence of NaOH, R2). Thus, the volatilization of DCM (boiling point ≈ 40 ºC, 760 mmHg) at the operating conditions tested (20 ºC, 100 rpm, vials without headspace) was discarded. Moreover, the alkaline hydrolysis of the pollutant, observed for other chlorinated pollutants, such as hexachlorocyclohexanes (Santos et al., 2018), chloroform (Hine, 1950), polychlorinated biphenyls, trinitrotoluene and dinitrotoluene (Waisner et al., 2008), was also discarded.

When PS (42 mmol L^{-1}) was added to the pollutant solution (run R3), a slight decrease of DCM concentration with reaction time was observed (the conversion of DCM, X_{DCM} was 23% at 48 h reaction time, and the concentration of chlorides released to the reaction medium, negligible (0.196 mg L^{-1})). Without activation, the persulfate anion ($S_2O_8^{2-}$) can react with some organic compounds (Block et al., 2004; Wacławek et al., 2017), but the degree of removal achieved is usually low and very long reaction times are required due to the relatively low oxidation potential of this anion (E^0 = 2.01 V) (Matzek and Carter, 2016). In the presence of the alkali, NaOH (R6), PS was activated generating different radical species (Eqs. 3 and 4). In alkaline conditions, PS generates in a first step sulfate, $\mathrm{SO_4^{\cdot-}}$ (E^0 = 2.5-3.1 V (Ike et al., 2018; Zhu et al., 2018)) and superoxide radicals, $\mathrm{O_2^{\cdot-}}$ (E^0 = -0.33 V), and hydroxyl radicals, $\mathrm{{}^{\cdot}OH}$, (E^0 = 2.80 V) in a second step. At these conditions, the presence of sulfate radicals can be neglected, the hydroxyl radical being the predominant radical specie (Furman et al., 2010).

As can be seen in Fig. 1, the generation of radicals in the reaction media highly increased the degradation of the pollutant (X_{DCM} = 99% at 96 h reaction time, R6). Thus, the effect of the alkaline activation of PS on the degradation of DCM can be clearly assessed by comparing the results obtained in the experiments in the absence (R3) and the presence (R6) of the activator (NaOH).

The pH of the solution after 96 h of reaction time in R6 remained above 13, which indicates that the activator:oxidant molar ratio selected (NaOH:PS=4:1) was more than enough to guarantee strong alkaline conditions.

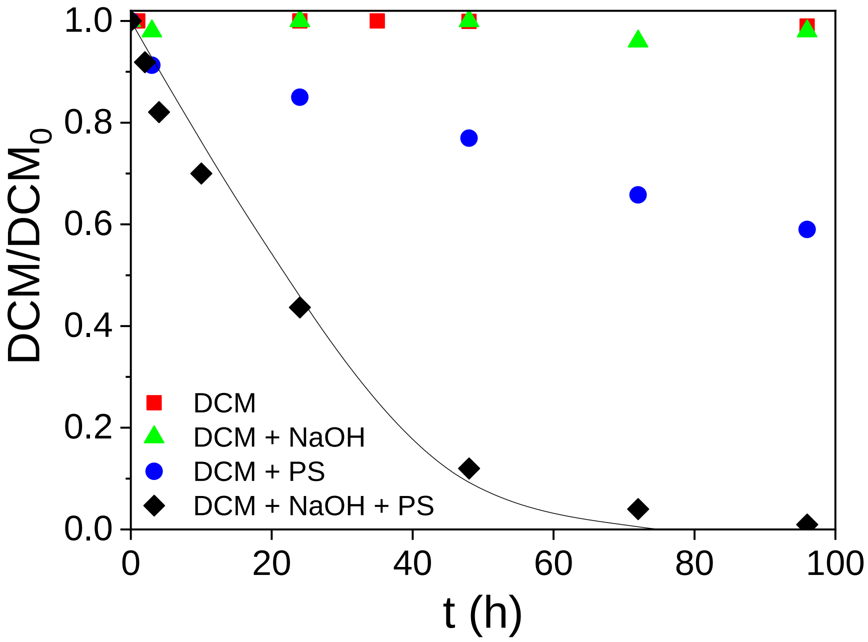

Figure 1. Normalized concentration of DCM (1.5 mmol L^{-1}) when this pollutant is dissolved in water and in the presence of NaOH (169 mmol L^{-1}), PS (42 mmol L^{-1}) and PS-NaOH (42 and 169 mmol L^{-1}, respectively, NaOH:PS = 4:1). Experimental data (symbols) and predicted values (lines, when applicable) calculated from Eq. 19.

3.1.2 Oxidation consumption

PS was completely stable in aqueous solution during the time period studied both at neutral (R4) and alkaline conditions (R5) (S.M. 2), indicating that the unproductive consumption of the oxidant in the presence of NaOH (under the operating conditions selected, 20 ºC) was negligible, which represents an important advantage for an *in situ* application of this technology. These results agree with the PS stability study performed by Lominchar et al. (2018a) in aqueous and slurry soil-water systems (a sandy clay loam). In that study, it was found that the addition of NaOH increased the decomposition rate of PS but it remained in the reaction medium for more than 40 days at the operating conditions selected (Lominchar et al., 2018a).

In the presence of DCM (R6), the consumption of PS during reaction time was also very low (a conversion of PS < 2% was achieved at 96 h reaction time, S.M. 2). According to the stoichiometry for DCM mineralization (Eq. 5), the concentration of PS (42 mmol L^{-1}) is in excess in relation to the pollutant one (molar ratio DCM:PS = 1:28, which represents 5 times the stoichiometric amount of PS for DCM mineralization), although within the typical pollutant:PS molar ratio range found in the bibliography, and considered suitable for *in situ* applications (Matzek and Carter, 2016). The concentration ranges of oxidant and activator used here are also in agreement with those reported in the application of alkaline activated persulfate at field scale, for the remediation of soils polluted with Total Petroleoum Hydrocarbons (TPHs) (Smith, 2016), TPHs, Benzene, toluene, ethylbenzene, xylenes (BTEXs) and chlorinated ethenes (Wilson at al. 2013) or chlorobenzenes and hexachlorocyclohexanes (Project LIFE DISCOVERED, 2017).

$$CH_2Cl_2 + 4\,{}^{\cdot}OH \rightarrow CO_2 + 2\,H_2O + 2\,HCl \qquad \text{(Eq. 5)}$$

It should be noted that 8 moles the PS should be required for the oxidation of 1 mol of DCM (2 moles of PS are needed for the generation of 1 mol of $^{\cdot}\mathrm{OH}$ according to Eqs. 3 and 4).

3.2 DCM degradation mechanism

Although three types of radical species are involved in the alkaline activation of persulfate (the sulfate radical, the hydroxyl radical, and the superoxide radical, Eqs. 1-4), when working at pHs higher than 11 (as is the current case), the generation of hydroxyl radicals (Eq. 4) is very favored and therefore, the contribution of sulfate radical can be neglected, as previously stated (Liang and Su, 2009; Furman et al., 2011). Thereby, the degradation of DCM can be mainly attributed to the action of hydroxyl radicals or superoxide radicals by an oxidation or reductive mechanism, respectively.

To confirm which type of radical species was the responsible of DCM degradation, a known hydroxyl radical-scavenger, methanol, MeOH (Teel et al., 2001; Devi et al., 2009), was added to the reaction media. A concentration of 313 mmol L^{-1} of MeOH, which implies a great excess of hydroxyl radical-scavenger *vs.* the pollutant (molar ratio MeOH:DCM ≈ 200) was chosen to carry out these tests. Therefore, the hydroxyl radicals generated from PS activation will be rapidly consumed by this solvent, giving rise to formic acid and protons (Eq. 6). The study was performed at two different concentrations of PS: 42 mmol L^{-1} (R7) and 168 mmol L^{-1} (R9), maintaining the molar ratio NaOH:PS = 4:1, and the results thus obtained were compared with the corresponding ones in the absence of this solvent (R6 and R8, respectively) (Fig. 2).

$$CH_3OH + 4\ {\cdot}OH + OH^- \rightarrow HCO_2^- + 4\,H_2O \qquad \text{(Eq. 6)}$$

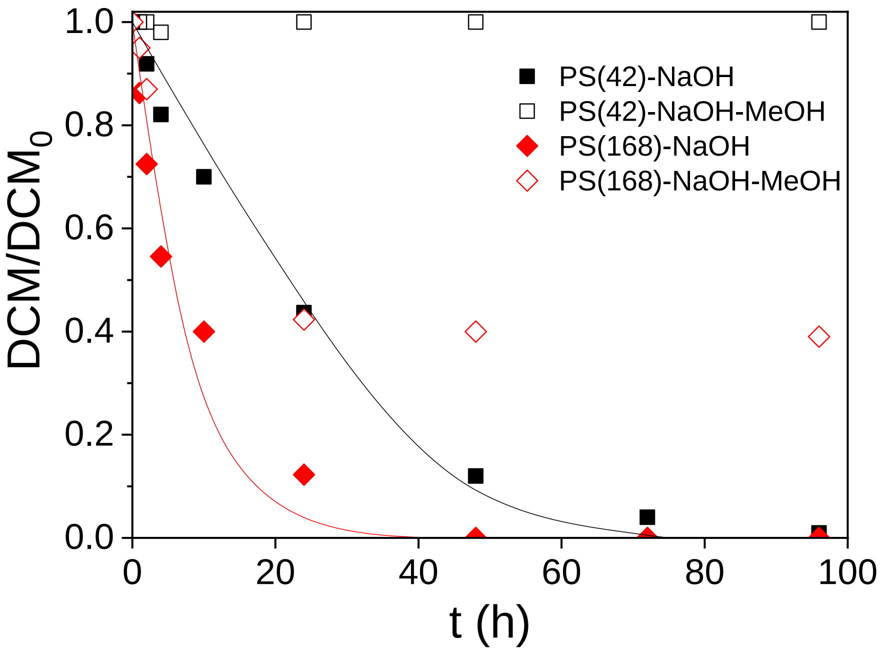

Figure 2. Oxidation of DCM (1.5 mmol L^{-1}) by the alkaline activation of PS in the absence and presence of MeOH at two different concentration of PS, maintaining the ratio NaOH:PS = 4:1. The numbers in parentheses indicate the concentration, in mmol L^{-1}, of PS. Experimental data (symbols) and predicted values (lines) calculated from Eq. 19.

As can be seen comparing the results obtained in R6 (DCM+PS+NaOH) and R7 (DCM+PS+NaOH+MeOH), the presence of MeOH highly slowed down the degradation of the pollutant. The conversion of DCM at 96 h reaction time when MeOH was added to the system was less than 2%, while 100% of DCM conversion was achieved in the absence of this compound. As previously indicated, MeOH rapidly consumed the hydroxyl radicals generated under alkaline conditions (Eq. 6). In this way, there were no available hydroxyl radicals to oxidize the contaminant, and the conversion of DCM at these conditions was negligible.

When a concentration of PS four times higher was used (R9, PS = 168 mmol L^{-1}), keeping the pollutant and methanol concentrations constant, it has been corroborated that the presence of methanol was also negative (DCM conversion decreased from 100% to 73% at 48 h when 313 mmol L^{-1} of MeOH was added), but its effect was less noticeable. The amount of hydroxyl radicals generated in this case (PS = 168 mmol L^{-1}) was greater and, although a part of them were scavenged by methanol, there were still hydroxyl radicals available for the oxidation of the pollutant.

The effect of adding a hydroxyl radical-scavenger can be also noted in the chlorides released to the liquid phase (Fig. 3). In the presence of this reductant, the chlorides concentration was highly decreased. This fact has been evidenced when working at the two different oxidant doses.

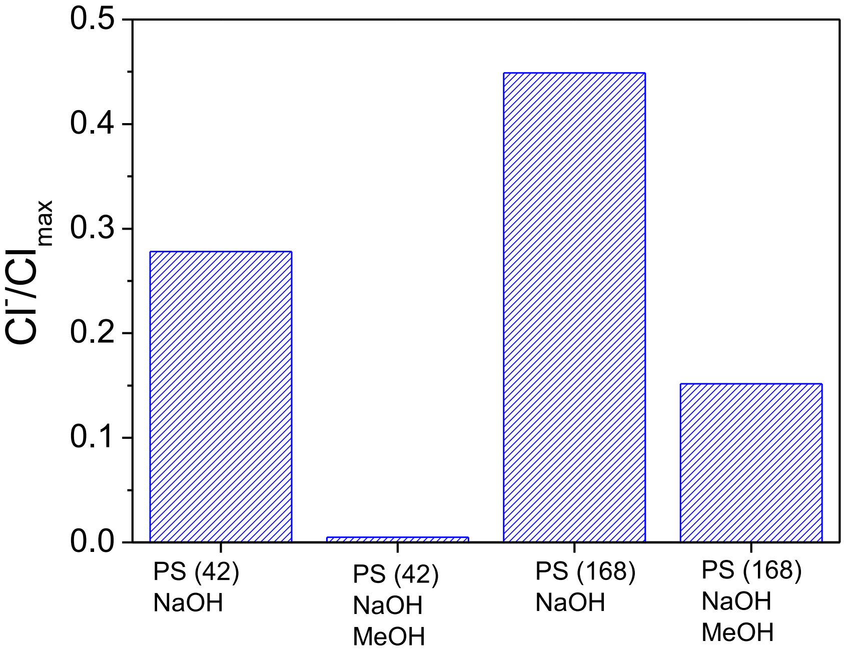

Figure 3. Fraction of chlorine identified as chlorides from DCM degradation (1.5 mmol L^{-1}) by the alkaline activation of PS in the absence and presence of a hydroxyl radical-scavenger (MeOH) at two different concentrations of PS, maintaining the ratio NaOH:PS = 4:1, at 48 h reaction time. The numbers in parentheses indicate the concentration, in mmol L^{-1}, of PS.

As could be expected, the consumption of PS highly increased when MeOH was added to the reaction medium. The conversion of this oxidant was above 50% at 48 h reaction time in the presence of 313 mmol L^{-1} MeOH (R9) *vs.* 1% in the absence of the hydroxyl radical-scavenger (R8, Fig S.M. 2). Consequently, the concentration of formic acid in solution (final product of methanol oxidation, Eq. 6) also increased (data not shown).

From all these data it can be concluded that DCM is degraded by hydroxyl radicals following an oxidative mechanism, which agrees with the results obtained by Calza et al. (1997), who studied the photocatalytic degradation of several chlorinated methanes in the presence of electron and hole-scavengers.

Notably, if superoxide radical participated in DCM degradation, the presence of MeOH in the reaction medium would have increased the degradation rate of the pollutant, since this solvent i) enhances the stability and reactivity of the superoxide radical and ii) increases its generation rate. These findings were recently achieved by Dominguez et al. (2019) in the degradation of carbon tetrachloride using PS activated by NaOH and enhanced by the addition of MeOH. In that case, as MeOH and the pollutant did not compete for the same radical species (hydroxyl radicals for MeOH and superoxide radicals for carbon tetrachloride), the addition of MeOH resulted in a great improvement in the degradation of the pollutant (Dominguez et al., 2019).

3.3 Systematic study of the main operating variables

The effect of the main operating variables influencing the oxidation of DCM in the alkaline activation of PS was explored.

3.3.1 Influence of the initial pollutant concentration on DCM degradation

The evolution of the normalized concentration of DCM *vs.* reaction time working at initial pollutant concentrations of 0.15, 0.38, 0.76 and 1.5 mmol L^{-1} (R10-R12 and R6, respectively), and maintaining unchanged the other operating conditions (PS concentration and NaOH:PS molar ratio), is depicted in Fig. 4. As can be seen, DCM was faster converted as the initial concentration of the pollutant decreased. From these results, a reaction order below one can be inferred for the initial pollutant concentration. This behavior has been frequently found in the bibliography for different pollutants and oxidation treatments, such as activated PS, photo-oxidation, etc. (Mak et al., 1997 ; De et al., 1999 ; Modirshahla and Behnajady, 2006; Salari et al., 2009, Lin et al., 2011).

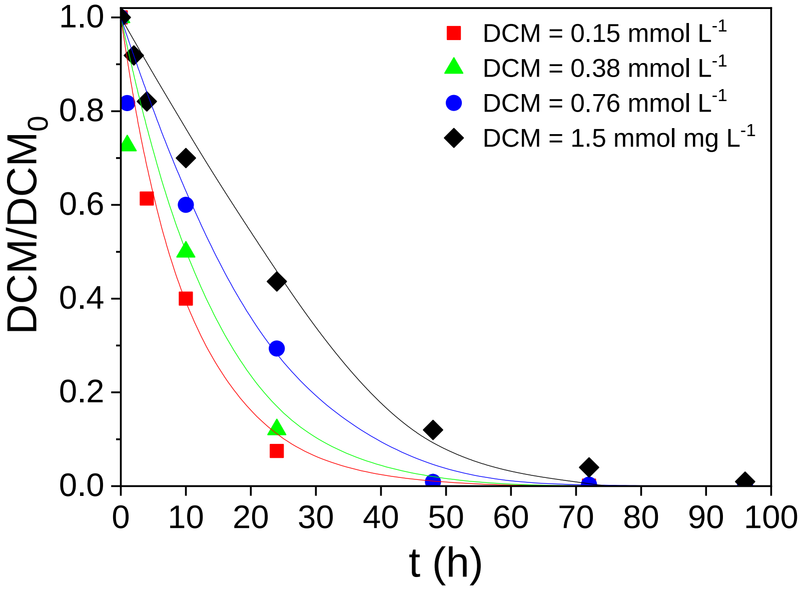

Figure 4. Oxidation of DCM at different initial pollutant concentrations by the alkaline activation of PS (PS = 42 mmol L^{-1}, NaOH:PS = 4:1). Experimental data (symbols) and predicted values (lines) calculated from Eq. 19.

3.3.2 Influence of PS concentration on DCM degradation

The evolution of the normalized concentration of DCM during reaction time at three initial concentrations of PS (8, 42 and 168 mmol L^{-1}, R13, R6 and R8) is represented in Fig. 5. In this study, the ratio NaOH:PS and the initial concentration of DCM were maintained constant (NaOH:PS = 4:1, DCM = 1.5 mmol L^{-1}). As can be seen, the degradation rate of DCM clearly increased when the initial concentration of the oxidant increased, which has been already noticed in most of the works found in the bibliography dealing with the oxidation of different pollutants by PS (Romero et al., 2010; Zhao et al., 2014; Ji et al., 2015; Santos et al., 2018). In the PS concentration range studied in the present work (C_{PS} = 8 - 168 mmol L^{-1}), the degradation rate of DCM (data not shown) increases linearly with PS concentration and thus, the recombination reactions between radical species can be ruled out. The positively proportional relationship between contaminants degradation rates and PS concentration has been reported in previous studies (Nie et al., 2014; Fan et al., 2015; Feng et al., 2017). In these cases, the concentration of generated radicals was proportional to the concentration of PS. The higher the PS concentration the higher the production of hydroxyl radicals. The complete elimination of DCM was achieved at 48 h reaction time when working with a concentration of PS of 168 mmol L^{-1}, whereas only 12% of pollutant conversion was obtained with the lowest oxidation concentration tested (PS = 8 mmol L^{-1}) at the same reaction time.

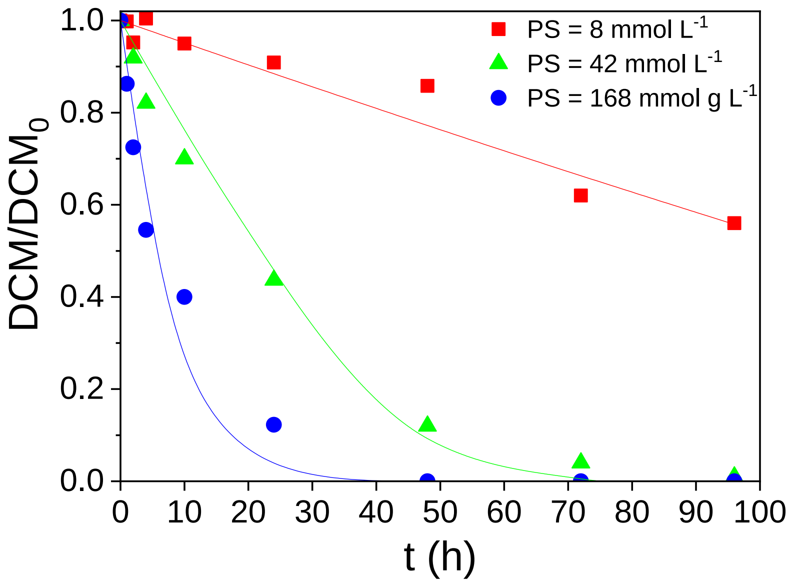

Figure 5. Normalized concentration of DCM at different initial PS concentrations (DCM = 1.5 mmol L^{-1}, NaOH:PS = 4:1). Experimental data (symbols) and predicted values (lines) calculated from Eq. 19.

3.3.3 Influence of the NaOH:PS molar ratio on DCM degradation

The alkaline activation of PS requires high pH values. Considering i) the acidic pH generated by the dissolution of PS in aqueous medium (Eq. 7), ii) the progressive consumption of the activator during the reaction (NaOH acts as a reagent (Eqs. 3 and 4)) and iii) the buffering capacity of the soils, enough NaOH should be added to guarantee strongly alkaline conditions. It has been reported in the literature that to maintain an adequate pH in the long-term and efficiently oxidize the recalcitrant chlorinated compounds, the molar ratio NaOH:PS needs to be ≥ 0.4 (Block et al., 2004), although ratios higher than 1 are commonly used to ensure that pH keeps at values above 12. Thus, the activator:PS ratios usually found in the literature are within the range 1:1 to 8:1, being the ratios 2:1 and 4:1 frequently applied (Liang and Guo, 2012; Lominchar et al., 2018b, 2018c, Santos et al., 2018). The evolution of the normalized concentration of DCM (1.5 mmol L^{-1}) when working with an initial concentration of PS = 42 mmol L^{-1} and different NaOH:PS molar ratios (between 1 and 4, R14, R15 and R6) is represented in Fig 6.

$$S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + \frac{1}{2}O_2 \qquad \text{(Eq. 7)}$$

The degradation of DCM was not affected by the molar ratio NaOH:PS, suggesting that the oxidation of the pollutant follows zero-order kinetics respect to NaOH concentration, at least in the experimental range studied (NaOH:PS molar ratio from 1 to 4 and pH ≥ 13). This behavior was previously noticed by the authors in the abatement of other chlorinated compounds, such as hexachlorocyclohexanes, chlorobenzenes and carbon tetrachloride (Santos et al., 2018, Dominguez et al., 2019).

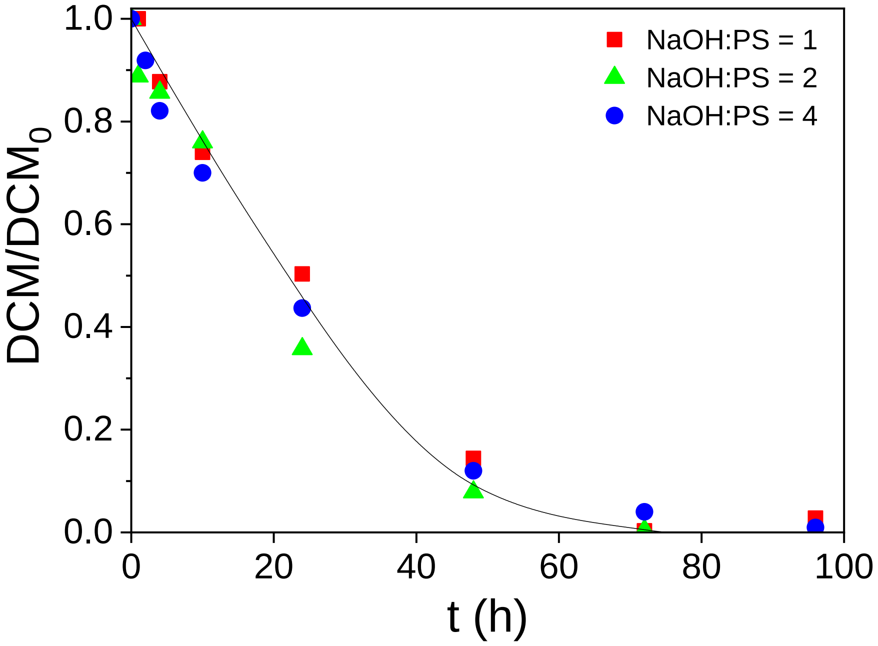

Figure 6. Normalized concentration of DCM at different NaOH:PS molar ratios (DCM = 1.5 mmol L^{-1}, PS = 42 mmol L^{-1}). Experimental data (symbols) and predicted values (line) calculated from Eq. 19.

3.3.4 Dechlorination degree and DCM degradation intermediates

The dechlorination degree, expressed as the relative amount of chlorides measured in the liquid medium normalized by the total chlorine content of the initial amount of DCM treated, increased as the pollutant concentration decreased. As an example, the results obtained in R6, are shown in Figure S.M. 3 of the supplementary material. As can be seen in this figure, the concentration of chloride measured is lower than that expected for the DCM reacted. This could mean that other chlorinated compounds, organic or inorganic, have been generated. It should be also noted that the quantification of chlorides in the reaction samples by IC analysis can be underestimated due to the high concentration of PS and NaOH, which cause interferences in the measurements.

Some unstable chlorinated organic compounds formed in the oxidation of DCM by other treatments, such as $CH(OH)Cl_2$ and $CH_2(OH)Cl$ (Calza et al., 1997, Rodríguez et al., 2005), were not detected by GC/MS analysis. Therefore, if these compounds were generated, they were quickly transformed. In this study, formic acid was detected as organic oxidation byproduct of DCM (4.8 mg L^{-1}) at the end of the treatment and traces of trichloroethylene (C_2HCl_3) as intermediate reaction times (24 and 48 h), disappearing at the end of the experiments ($t \geq 72$ h). Therefore, the mismatch in the chlorine balance could be due to further reactions of the generated chloride (Eq. 5) to other inorganic species.

The presence of other inorganic chlorinated species, such as chlorite, chlorate and perchlorate (ClO_2^-, ClO_3^- and ClO_4^-) was discarded by IC measurements. The reaction of chlorides with hydroxyl and sulfate radicals and further recombination to chlorine gas (Cl_2) has been previously reported in the literature (Wacławek et al., 2017), where the following reactions have been proposed:

$$SO_4^{\cdot -} + Cl^- \rightarrow Cl^{\cdot} + SO_4^{2-} \qquad \text{(Eq. 8)}$$

$$Cl^{\cdot} + Cl^- \rightarrow Cl_2^{\cdot -} \qquad \text{(Eq. 9)}$$

$$Cl_2^{\cdot -} + Cl_2^{\cdot -} \rightarrow 2Cl^- + Cl_2 \qquad \text{(Eq. 10)}$$

$$Cl^- + {}^{\cdot}OH \rightarrow ClOH^{\cdot -} \qquad \text{(Eq. 11)}$$

Although the oxidation of chlorides by hydroxyl radicals (Eq. 11) is faster than its oxidation by sulfate radicals (Eq. 8) (rate constant from 3.0 to 4.3 x 10^9 and from 1.3 to 6.6 x 10^8, respectively (Wacławek et al., 2017)), is an acid-catalyzed reaction (only becomes important at pH < 3) and therefore, it can be considered negligible at the alkaline conditions used in the present work, with pHs always above 12.

On the other hand, if chlorine gas is produced, it can undergo disproportionation at alkaline conditions, producing chloride and hypochlorite anions:

$$2\,OH^- + Cl_2 \rightarrow ClO^- + Cl^- + H_2O \tag{Eq. 12}$$

Unfortunately, hypochlorite (ClO^-) and chlorine gas, species that could contribute to explain the mismatch in the chlorine balance, could not be measured with the available analysis techniques.

On the other hand, the differences between the chloride measured and that corresponding to the initial pollutant were found to be function of the initial concentration of DCM, as can be seen in Fig 7a. The corresponding conversion values of DCM at 48 h reaction time have been also indicated in this figure. As can be seen, the higher the initial DCM concentration, the lower concentration of chloride. This fact could indicate a higher reaction order for chloride disappearance than for DCM removal. The influence of PS concentration on chloride formation at 48 h is shown in Fig 7b. An increase in the initial concentration of PS led to an increase in the percentage of chlorine identified as chlorides.

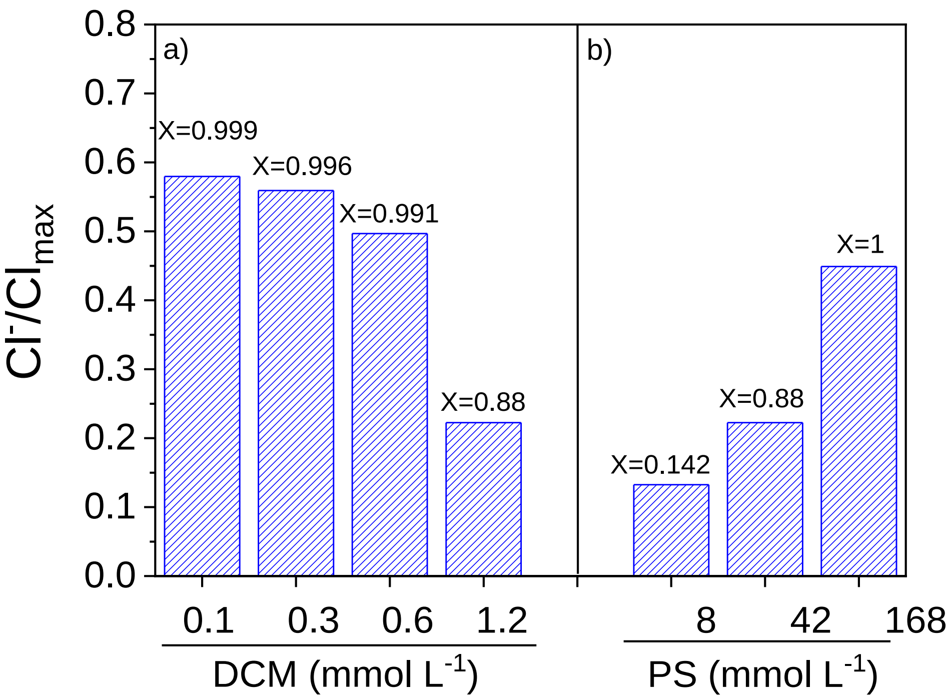

Figure 7. Chlorine balance from DCM degradation by the alkaline activation of PS at different initial concentrations of DCM (PS = 42 mmol L^{-1} (a) and PS (DCM = 1.5 mmol L^{-1}) (b) at 48 h reaction time, maintaining the molar ratio NaOH:PS = 4:1.

The formation of chlorine and hypochlorite and their effects on the chemistry of the subsurface is a topic that should be deeply studied. However, it should be taken into account that, when in situ treatments are applied, chlorine gas, if generated, does not release into the atmosphere since the remediation is carried out injecting the oxidant and activators in the subsurface. Moreover, at alkaline conditions the chlorine gas produced is very unstable and undergo disproportionation according to Eq 12.

3.4. Kinetic model for DCM oxidation by persulfate activated by NaOH

The mass balance of DCM degradation by PS activated by alkali in a batch reactor can be described as follows:

$$\frac{-dC_{DCM}}{dt} = -R_{DCM} \therefore 1 - X_{DCM} = -\frac{1}{C_{DCM_o}} \int_o^t R_{DCM} dt \qquad \text{(Eq. 13)}$$

Where C_{DCM} and C_{DCMo} are the DCM concentration at a reaction time = t and 0, respectively, X_{DCM} is the conversion of DCM at a reaction time = t, and $-R_{DCM}$ is the disappearance rate of DCM.

As a first approach, a potential kinetic model (Eq. 14) has been tested to describe the reaction rate of DCM disappearance:

$$-R_{DCM} = k \cdot C_{DCM}^{a} \cdot C_{PS}^{b} \cdot C_{NaOH}^{c} \qquad \text{(Eq. 14)}$$

being k, the kinetic constant, C_{DCM}, C_{PS} and C_{NaOH}, the concentration of dichloromethane, persulfate and NaOH, respectively and a, b and c, the partial order with respect to the different reagents.

Firstly, the experimental data obtained in the experiments carried out with different initial pollutant concentrations and the same PS and NaOH doses (runs R10-12 and R6) have been analyzed. As previously indicated, PS and NaOH have been used in great excess and, therefore, the concentration of these species with reaction time can be considered constant. Following this hypothesis, Eq. 14 can be simplified into Eq. 15:

$$-R_{DCM} = k' \cdot C_{DCM}^{a} \qquad \text{with} \quad k' = k \cdot \mathrm{C}_{\mathrm{PS}}^{\mathrm{b}} \cdot \mathrm{C}_{\mathrm{NaOH}}^{\mathrm{c}} \qquad \text{(Eq. 15)}$$

The values of *k'* and *a* have been obtained by fitting the fractional remaining concentration of DCM (1-X_{DCM}) obtained in the aforementioned runs (R10 to R12 and R6) to Eq. (13), using non-linear regression (Marquardt algorithm) coupled with Euler integration. The values obtained are *k'* = 0.0528±0.016, a = 0.842±0.254, weighted residual sum of squares = 0.554 and percentage of variation explained = 87.17%.

The partial order with respect to DCM is below one, which agrees with the results previously shown in Fig. 4, where it could be seen that as the initial concentration of DCM increased, the conversion of the pollutant decreased.

Secondly, the following hyperbolic kinetic model (Eq. 16) has been proposed to better explain the influence of DCM concentration:

$$-R_{DCM} = k' \cdot \frac{C_{DCM}^{n1}}{(1+k_2 C_{DCM})^{n2}} \qquad \text{with} \quad k' = k \cdot \mathrm{C}_{\mathrm{PS}}^{\mathrm{b}} \cdot \mathrm{C}_{\mathrm{NaOH}}^{\mathrm{c}} \qquad \text{(Eq. 16)}$$

Again, data of fractional remaining concentration of DCM ($1\text{-}X_{DCM}$) obtained in the runs R10 to R12 and R6 have been fitted to Eq. (13), The values obtained for n_1 and n_2 were closed to the unity and therefore, *k'* and k_2 have been recalculated by fixing $n_1 = n_2 = 1$, obtaining the following parameters: $k' = 0.131 \pm 0.023\ h^{-1}$, $k_2 = 3.049 \pm 1.41\ L\ mmol^{-1}$, weighted residual sum of squares = 0.426 and percentage of variation explained = 93%.

Therefore, it is considered that the hyperbolic model tested explain adequately the influence of DCM concentration on the reaction rate. As previously stated, the decrease in the pollutant conversion with time when the initial concentration of the pollutant increases has been often found in the literature (Mak et al., 1997; De et al., 1999, Modirshahla and Behnajady, 2006; Salari et al., 2009; Lin et al., 2011).

Once the hyperbolic model has been chosen, the influence of NaOH concentration has been modelled. In this case, the results obtained in runs R6, R14 and R15 (carried out at the same initial concentration of DCM and PS) have been fitted to Eq. 16, using the following kinetic expression (Eq. 17):

$$-R_{DCM} = k'' \cdot C_{NaOH}^{c} \frac{C_{DCM}}{(1+k_2\, C_{DCM})} \qquad k'' = k \cdot C_{\mathrm{PS}}^{\mathrm{b}}\,, \;\; k_2 = 3.049\, L\, mmol^{-1} \quad \text{(Eq. 17)}$$

The calculated value for the partial order *c* was -0.1, meaning that the influence of NaOH concentration in the experimental range studied is almost negligible, which agrees with the results shown in Fig. 6 and those also found in the literature at these conditions (NaOH:PS molar ratio from 1 to 4 and pH ≥ 13, Santos et al., 2018, Dominguez et al., 2019). Therefore, the partial order with respect to NaOH concentration, *c*, has been set to 0. The value of k'' resulted to be = 0.12±0.016 h^{-1} and the percentage of variation explained = 95.2%.

Finally, the partial order with respect to PS concentration, *b*, has been determined by fitting the results obtained in the runs carried out at the same initial DCM and NaOH concentrations (runs R6, R8 and R13):

$$-R_{DCM} = k \cdot C_{NaOH}^{0} C_{PS}^{b} \frac{C_{DCM}}{(1+3.049\ C_{DCM})} \qquad \text{(Eq. 18)}$$

The value obtained for this parameter was 0.94±0.19, and the percentage of variation explained = 95%. Therefore, the partial order with respect to PS concentration can be fixed as the unity.

Once the values of the partial kinetic orders for pollutant, NaOH and oxidant concentrations have been discriminated ($n_1 = n_2 = b = 1$, $c = 0$), and taking into account the value obtained for k_2, the value of the kinetic constant, *k*, has been calculated by fitting simultaneously the experimental results obtained in runs R6 and R10-15 to Eq. 19, resulting a value of $k = 0.00329 \pm 0.00034\ \mathrm{L\ mmol^{-1} h^{-1}}$. The rate of disappearance of DCM can then be expressed by the following kinetic equation:

$$-R_{DCM}\left(\frac{mmol}{L.h}\right) = 0.00329\ \cdot C_{NaOH}^{0} C_{PS} \frac{C_{DCM}}{(1+3.049\ C_{DCM})} \qquad \text{(Eq. 19)}$$

C_{NaOH}, C_{PS} and C_{DCM} expressed in mmol L^{-1}, with weighted residual sum of squares = 0.66 and percentage of variation explained = 93%.

The simulated values of the remaining DCM fraction (DCM/DCM_0) with reaction time are showed with lines in Figs. 1, 2, 4, 5 and 6. Predicted values have been obtained by substituting the kinetic parameters obtained from Eq. 19 in Eq .13 at the operation conditions used in R6, R10-15. As can be seen, a good agreement was found between experimental and predicted values. The comparison of the model prediction and the experimental data (parity plot) is shown in Fig. 8.

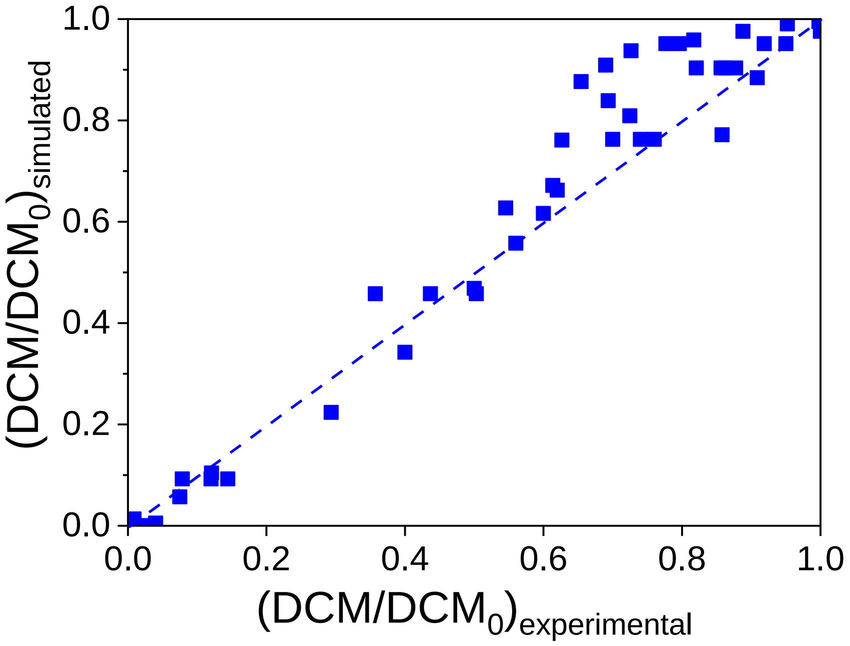

Figure 8. Parity plot of experimental and simulated values from Eq. 19 for DCM normalized concentration at the different operation conditions tested in the alkaline activation of PS.

4. Conclusions

The chemical oxidation of DCM using persulfate activated by alkali has demonstrated to be a feasible alternative for the *in situ* treatment of groundwaters contaminated with this pollutant, although further research to study the final destination of chlorine is required. DCM is efficiently degraded with a very low consumption of PS and activator (NaOH), assuring that the oxidant could be transported in the subsurface far distances from the injection point. The addition of MeOH (a hydroxyl radical-scavenger) to the reaction medium allowed to discriminate the mechanism of degradation of this pollutant. In the presence of this compound, the removal of DCM was negligible. MeOH rapidly reacted with the hydroxyl radicals generated, competing with the pollutant. Thus, it has been concluded that, among the pull of radical species generated by this activation method (mainly superoxide and hydroxyl radicals) DCM is oxidized by hydroxyl radicals. Trichloroethylene was detected in trace amounts and the only degradation products identified were formic acid and chloride. The study of the main operating conditions revealed that the degradation rate of DCM improved increasing the oxidant concentration (from 8 to 168 mmol L^{-1}) and reducing the concentration of the pollutant (from 1.5 mmol L^{-1} to 0.5 mmol L^{-1}), whereas the alkali:PS ratio (from 1 to 4) had no influence in the operating conditions interval studied. A kinetic model has been developed and validated from the experimental results, including as variables, the concentration of the pollutant and the oxidant. This model is able to predict the concentration of DCM in a relatively wide range of operation conditions (C_{DCM} = 0.01 – 1.5 mM. C_{PS} = 8 – 168 mM, C_{NaOH} = 34 – 650 mM).

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REFERENCES

ATSDR (2017). Agency for Toxic Substances and Disease Registry). Priority List of Hazardous Substances.

Baciocchi, R. (2013). Principles, developments and design criteria of in situ chemical oxidation. Water, Air, Soil Pollut., 224(12), 1717.

Block, P.A., Brown, R.A., Robinson, D. (2004). Novel activation technologies for sodium persulfate in situ chemical oxidation. In Proceedings of the Fourth International Conference on the remediation of chlorinated and recalcitrant compounds (24-27). Columbus, OH: Battelle Press.

Calza, P., Minero, C., Pelizzetti, E. (1997). Photocatalytic transformations of chlorinated methanes in the presence of electron and hole scavengers. J. Chem. Soc. Faraday Trans. 93, 3765.

De, A.K., Chaudhuri, B., Bhattacharjee, S., Dutta, B.K. (1999). Estimation of· OH radical reaction rate constants for phenol and chlorinated phenols using UV/H2O2 photo-oxidation. J. Hazard. Mat., 64(1), 91-104.

Destaillats, H., Lesko, T.M., Knowlton, M., Wallace, H., Hoffmann, M.R. (2001). Scale-up of sonochemical reactors for water treatment. Ind. Eng. Chem. Res. 40(18), 3855.

Devi L.G., Kumar S.G., Reddy K.M., Munikrishnappa C. (2009). Photo degradation of Methyl Orange an azo dye by Advanced Fenton Process using zero valent metallic iron: Influence of various reaction parameters and its degradation mechanism. J. Hazard. Mater.; 164:459-67.

Devi P., Das U., Dalai A.K. (2016). In-situ chemical oxidation: principle and applications of peroxide and persulfate treatments in wastewater systems. Sci. Total Environ.; 571:643.

Dominguez C.M., Rodriguez V., Montero E., Romero A., Santos A. (2019). Methanol-enhanced degradation of carbon tetrachloride by alkaline activation of persulfate: kinetic model. Sci. Total Environ. 666, 631.

Fan, Y., Ji, Y., Kong, D., Lu, J., Zhou, Q. (2015). Kinetic and mechanistic investigations of the degradation of sulfamethazine in heat-activated persulfate oxidation process. Journal of hazardous materials, 300, 39-47.

Feng, Y., Song, Q., Lv, W., Liu, G. (2017). Degradation of ketoprofen by sulfate radical-based advanced oxidation processes: Kinetics, mechanisms, and effects of natural water matrices. Chemosphere, 189, 643-651.

Furman O.S., Teel A.L., Ahmad M., Merker M.C., Watts R.J. (2011). Effect of basicity on persulfate reactivity. J Environ. Eng.; 137:241.

Furman, O.S., Teel, A.L., Watts, R.J. (2010). Mechanism of base activation of persulfate. Environ. Sci. Technol., 44(16), 6423.

García, V., Pongrácz, E., Muurinen, E., Keiski, R.L. (2009). Pervaporation of dichloromethane from multicomponent aqueous systems containing n-butanol and sodium chloride. J. Membr. Sci., 326(1), 92.

Hine, J. (1950). Carbon Dichloride as an Intermediate in the Basic Hydrolysis of Chloroform. A Mechanism for Substitution Reactions at a Saturated Carbon Atom1. J. Am. Chem. Soc., 72(6), 2438.

Huang B., Lei C., Wei C., Zeng G. (2014). Chlorinated volatile organic compounds (Cl-VOCs) in environment—sources, potential human health impacts, and current remediation technologies. Environ Int; 71:118.

Huang, K.C., Zhao, Z., Hoag, G.E., Dahmani, A., Block, P.A. (2005). Degradation of volatile organic compounds with thermally activated persulfate oxidation. Chemosphere, 61(4), 551.

Iakovleva, E., Sillanpää, M. (2013). The use of low-cost adsorbents for wastewater purification in mining industries. Environ. Sci. Pollut. Res., 20(11), 7878.

Ike, I. A., Linden, K. G., Orbell, J. D., Duke, M. (2018). Critical review of the science and sustainability of persulphate advanced oxidation processes. Chem. Eng. J., 338, 651-669.

Iordache, M., Iordache, I., Popescu, L. R., Marinoiu, A. (2017). Removal of organic compounds from water by sonochemical processes. Progress of Cryogenics & Isotopes Separation, 20(1).

Ji Y., Dong C., Kong D., Lu J., Zhou Q. (2015). Heat-activated persulfate oxidation of atrazine: Implications for remediation of groundwater contaminated by herbicides. Chem. Eng. J.; 263:45.

Krembs, F.J., Siegrist, R.L., Crimi, M.L., Furrer, R.F., Petri, B.G. (2010). ISCO for groundwater remediation: analysis of field applications and performance. Ground Water Monit. Rem., 30(4), 42.

Lapeyrouse, N., Liu, M., Zou, S., Booth, G., Yestrebsky, C. L. (2019). Remediation of Chlorinated Alkanes by Vitamin B12 and Zero-Valent Iron. J Chem, 2019.

Liang C, Guo Y. (2012). Remediation of diesel-contaminated soils using persulfate under alkaline condition. Water, Air, Soil Pollut., 223:4605-14.

Liang C., Su H.W. (2009). Identification of sulfate and hydroxyl radicals in thermally activated persulfate. Ind. Eng. Chem. Res., 48:5558.

Lin, Y.T., Liang, C., Chen, J.H. (2011). Feasibility study of ultraviolet activated persulfate oxidation of phenol. Chemosphere, 82(8), 1168.

Lominchar M.A., Rodríguez S., Lorenzo D., Santos N., Romero A., Santos A. (2018b). Phenol abatement using persulfate activated by nZVI, H2O2 and NaOH and development of a kinetic model for alkaline activation. Environ. Technol.; 39:35-43.

Lominchar, M.A., Lorenzo, D., Romero, A., Santos, A. (2018a). Remediation of soil contaminated by PAHs and TPH using alkaline activated persulfate enhanced by surfactant addition at flow conditions. J. Chem.Technol. Biotechnol., 93(5), 1270.

Lominchar, M.A., Santos, A., de Miguel, E., Romero, A. (2018c). Remediation of aged diesel contaminated soil by alkaline activated persulfate. Sci. Total Environ, 622, 41.

Mak, F.T., Zele, S.R., Cooper, W.J., Kurucz, C.N., Waite, T.D., Nickelsen, M.G. (1997). Kinetic modeling of carbon tetrachloride, chloroform and methylene chloride removal from aqueous solution using the electron beam process. Wat. Res., 31(2), 219.

Matzek L.W., Carter K.E. (2016). Activated persulfate for organic chemical degradation: a review. Chemosphere; 151:178-88.

Modirshahla, N., Behnajady, M.A. (2006). Photooxidative degradation of Malachite Green (MG) by UV/H2O2: Influence of operational parameters and kinetic modeling. Dyes and Pigments, 70(1), 54-59.

Moran, M.J., Zogorski, J.S., Squillace, P.J. (2007). Chlorinated solvents in groundwater of the United States. Environ. Sci. Technol., 41(1), 74-81.

Nie, M., Yang, Y., Zhang, Z., Yan, C., Wang, X., Li, H., Dong, W. (2014). Degradation of chloramphenicol by thermally activated persulfate in aqueous solution. Chemical Engineering Journal, 246, 373-382.

Pardo, F., Rosas, J.M., Santos, A., Romero, A. (2015). Remediation of a biodiesel blend-contaminated soil with activated persulfate by different sources of iron. Water, Air, Soil Pollut., 226(2), 17.

Pecoraino, G., Scalici, L., Avellone, G., Ceraulo, L., Favara, R., Candela, E.G., Provenzano, M.C. Scaletta, C. (2008). Distribution of volatile organic compounds in Sicilian groundwaters analysed by head space-solid phase micro extraction coupled with gas chromatography mass spectrometry (SPME/GC/MS). Water Res., 42(14), 3563-3577.

Peluffo, M., Pardo, F., Santos, A., Romero, A. (2015). Use of different kinds of persulfate activation with iron for the remediation of a PAH-contaminated soil. Sci. Total Environment. 563, 649-656.

Project LIFE DISCOVERED, 2017, http://en.lifediscovered.es/resultados.html

Ravi, R., Philip, L., Swaminathan, T. (2010). Comparison of biological reactors (biofilter, biotrickling filter and modified RBC) for treating dichloromethane vapors. J. Chem. Technol. Biotechnol., 85(5), 634.

Rodriguez S., Santos A., Romero A., Vicente F. (2012). Kinetic of oxidation and mineralization of priority and emerging pollutants by activated persulfate. Chem. Eng. J.; 213:225.

Rodríguez, S.M., Gálvez, J.B., Rubio, M.I.M., Ibáñez, P.F., Gernjak, W., Alberola, I.O. (2005). Treatment of chlorinated solvents by TiO2 photocatalysis and photo-Fenton: influence of operating conditions in a solar pilot plant. Chemosphere, 58(4), 391.

Romero A., Santos A., Vicente F., González C. (2010). Diuron abatement using activated persulphate: effect of pH, Fe (II) and oxidant dosage. Chem. Eng. J.; 162:257.

Salari, D., Niaei, A., Aber, S., Rasoulifard, M.H. (2009). The photooxidative destruction of C.I. basic yellow 2 using UV/S2O2 8 process in a rectangular continuous photoreactor. J. Hazard. Mater. 166, 61.

Santos, A., Fernandez, J., Rodriguez, S., Dominguez, C.M., Lominchar, M.A., Lorenzo, D., Romero, A. (2018). Abatement of chlorinated compounds in groundwater contaminated by HCH wastes using ISCO with alkali activated persulfate. Sci. Total Environ., 615, 1070-1077.

Shestakova, M., Sillanpää, M. (2013). Removal of dichloromethane from ground and wastewater: a review. Chemosphere, 93(7), 1258.

Siegrist, R. L., Crimi, M., Thomson, N.R., Clayton, W. S., Marley, M.C. (2014). In situ chemical oxidation. In Chlorinated Solvent Source Zone Remediation (253-305). Springer, New York, NY.

Siegrist, R.L., Crimi, M., Simpkin, T.J. (2011). In situ chemical oxidation for groundwater remediation. Springer Science & Business Media.

Smith, B.A. 2016. Application of Alkaline Activated Persulfate to Treat Petroleum Hydrocarbon Contamination Beneath the Active Construction of a 32-Story High-Rise Residential Tower.

Sonoyama, N., Sakata, T. (1999). Electrochemical continuous decomposition of chloroform and other volatile chlorinated hydrocarbons in water using a column type metal impregnated carbon fiber electrode. Environ. Sci. Technol. 33, 3438–3442.

Sra K.S., Thomson N.R., Barker J.F. (2014). Stability of activated persulfate in the presence of aquifer solids. Soil and Sediment Contamination: An International Journal; 23:820.

Teel A.L., Warberg C.R., Atkinson D.A., Watts R.J. (2001). Comparison of mineral and soluble iron Fenton's catalysts for the treatment of trichloroethylene. Water Res.; 35:977.

Tsitonaki, A., Petri, B., Crimi, M., Mosbæk, H., Siegrist, R. L., Bjerg, P. L. (2010). In situ chemical oxidation of contaminated soil and groundwater using persulfate: a review. Crit. Rev. Env. Sci. Technol., 40(1), 55.

Verma, M.K., Tyagi, R.K. (2012). Aeration of volatile organic compounds using gas dispersion impellers. J. Mech. Eng. Res., 4(7), 213.

Wacławek, S., Lutze, H.V., Grübel, K., Padil, V.V., Černík, M., Dionysiou, D.D. (2017). Chemistry of persulfates in water and wastewater treatment: A review. Chem. Eng. J., 330, 44.

Waisner, S., Medina, V.F., Morrow, A.B., Nestler, C.C. (2008). Evaluation of chemical treatments for a mixed contaminant soil. J. Environ. Eng., 134(9), 743-749.

Watts, R. J., Teel, A.L. (2006). Treatment of contaminated soils and groundwater using ISCO. Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, 10(1), 2-9.

WHO. (1993). Toxicological Evaluation of Certain Food Additives and Naturally Occurring Toxicants. WHO Food Additive Series, Geneva.

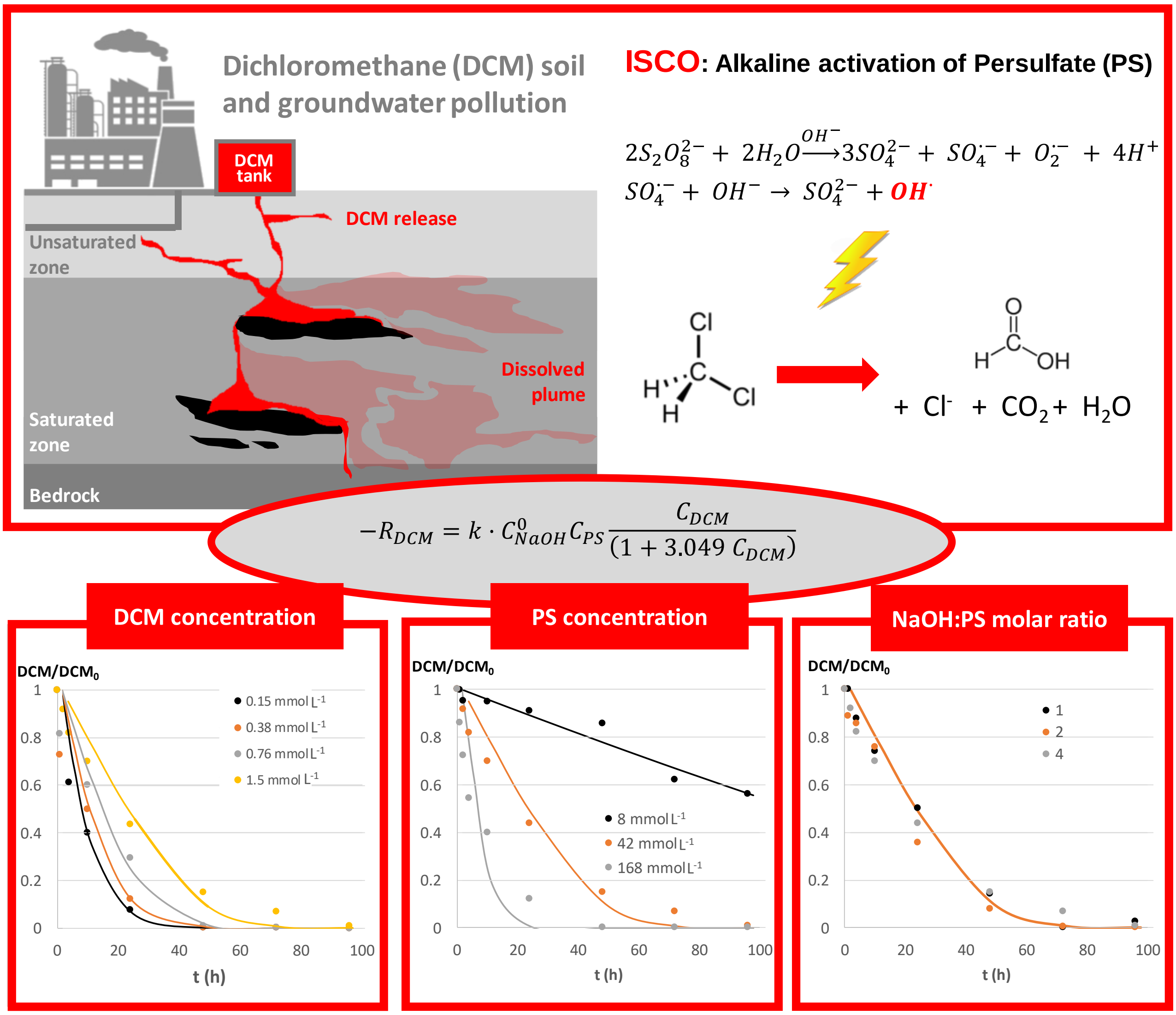
WHO. (1996). Methylene Chloride. Environmental Health Criteria 164, Geneva.

Wilson, S., Farone, W., Leonard, G., Birnstingl, J., Leombruni, A.J.R.B.P.I., San Clemente, CA, USA, 2013. Catalyzed persulfate: advancing in situ chemical oxidation (ISCO) technology.

Zhao L., Hou H., Fujii A., Hosomi M., Li F. (2014). Degradation of 1, 4-dioxane in water with heat-and Fe 2 -activated persulfate oxidation. Environ. Sci. Pollut. Res.; 21:7457.

Zhu C., Zhu F, Dionysiou D.D, Zhou D., Fang G., Gao J. (2018). Contribution of alcohol radicals to contaminant degradation in quenching studies of persulfate activation process. Water Res. 139: 66-73.

Graphical abstract



Supplementary Material

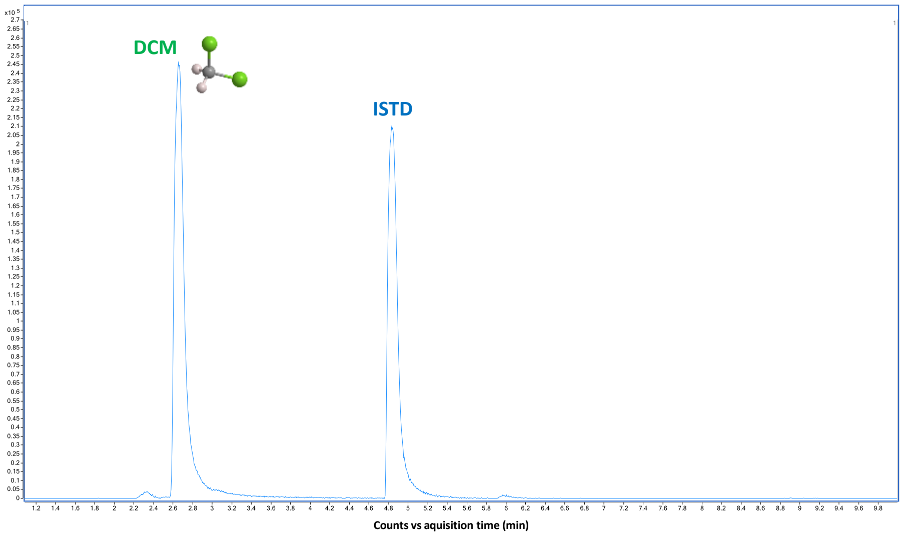


Figure S.M. 1. Chromatogram of DCM by headspace with gas chromatography coupled with a mass spectrometry detector (GC/MS).

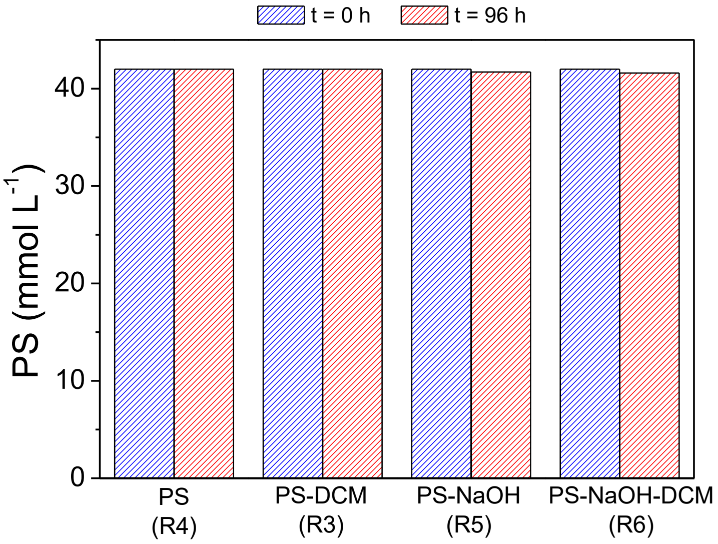


Figure S.M. 2. PS concentration at 0 and 96 h reaction time under different experimental conditions: R4 (PS), R3 (PS-NaOH), R5 (PS-CT) and R6 (PS-NaOH-CT). (C_{PS} = 42 mmol L^{-1}, C_{NaOH} = 169 mmol L^{-1}, C_{DCM} = 1.5 mmol L^{-1}).

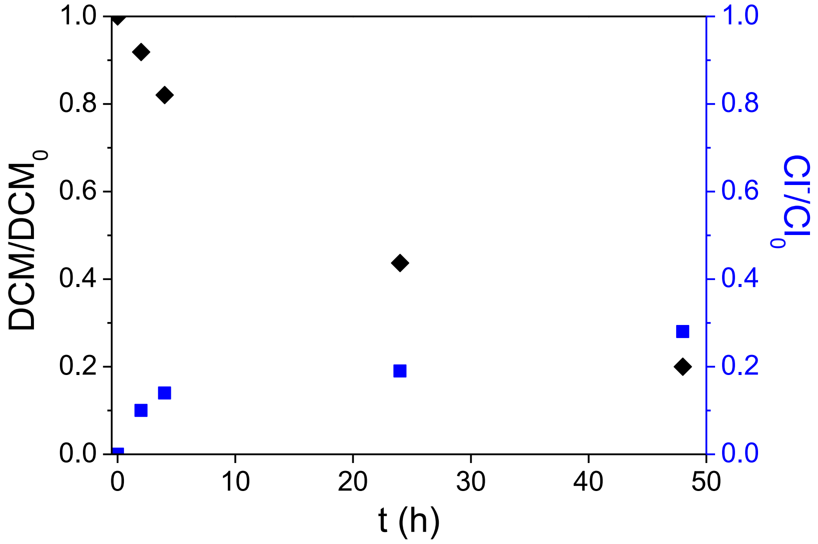


Figure S.M. 3. Normalized concentration of DCM (1.5 mmol L^{-1}) and chlorides released to the liquid phase (normalized by the initial concentration of chlorine) during the oxidation of DCM by PS (42 mmol L^{-1}) activated with alkali (169 mmol L^{-1}).