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Submitted to *Science of The Total Environment*

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Abstract

Oil hydrocarbons are widespread pollutants in sub-surface sediments with serious threats to terrestrial and aquatic environment. However, very limited data is available about remediation of historically contaminated sediments. This study reports the use of magnetite-catalyzed chemical oxidation (H_2O_2 and $Na_2S_2O_8$) to degrade oil hydrocarbons in aged contaminated sediments. For this purpose, oil contaminated sediments were sampled from three different locations in France including two harbors and one petroleum industrial channel. These sediments were characterized by different hydrocarbon index (HI) values (3.7 – 9.0 g kg^{-1}), total organic carbon contents (1.9% – 8.4%) and textures (sand, slit loam and silt). Chemical oxidation was performed in batch system for one week at circumneutral pH by: H_2O_2 alone, H_2O_2/Fe(II), H_2O_2/magnetite, $Na_2S_2O_8$ alone, $Na_2S_2O_8$/Fe(II), and $Na_2S_2O_8$/magnetite. Results obtained by GC-FID indicated substantial hydrocarbon degradation (40 – 70%) by H_2O_2/magnetite and $Na_2S_2O_8$/magnetite. However, oxidants alone or with soluble Fe(II) caused small degradation (< 5%). In the presence of H_2O_2/magnetite, degradation of extractable organic matter and that of HI were highly correlated. However, no such correlation was observed for $Na_2S_2O_8$/magnetite which resulted in higher removal of HI indicating its selective oxidation behavior. Treatment efficiency was negatively influenced by organic carbon and carbonate contents. For being the first study to report chemical oxidation of oil hydrocarbons in real contaminated sediments, it may have practical implications to design a remediation strategy for target contaminants.

Keywords: Oil hydrocarbons; Harbor sediments; Remediation; Fenton-like; Persulfate; Magnetite

1. Introduction

Oil hydrocarbons are widespread pollutants in sub-surface sediments which pose serious threats to terrestrial and aquatic environment. Therefore, development of novel and effective remediation techniques for oil-contaminated sediments is of considerable environmental interest (Lim et al., 2016). Various remediation techniques have been developed including biological (Chaîneau et al., 2003; Benyahia et al., 2005), chemical (Usman et al., 2012a; 2013; Chen et al., 2016) and combined approaches (Silva-Castro et al., 2013; Souza et al., 2014; Agarwal and Liu, 2015; Xu et al., 2016a). Bioremediation is the most commonly used technique to remediate oil contaminated matrices (soils, sediments and water) primarily because of its cost-effective and environment friendly nature (Lim et al., 2016). Majority of molecules in crude oil spills and refined products are biodegradable and thus can largely be removed by bioremediation (Prince, 1993). However, bioremediation often leaves non-biodegradable residues due to incomplete mineralization and thus cannot meet the stringent environmental cleanup standards reported by environmental regulations (Płaza et al., 2005). Contamination level had reached a plateau for long time in soil subjected to bioremediation for two years (Lu et al., 2010). Bioremediation or natural attenuation of n-alkanes present in oil lead to their degradation whereby leaving unresolved complex mixture (UCM) composed of iso- and cyclo-alkanes, which is totally refractory to microbial attack (Chaillan et al., 2006; Farrington and Quinn, 2015). However, chemical oxidation has shown strong efficiency to remove oil hydrocarbons where different oxidants are used to degrade organic pollutants. Recent studies employing chemical oxidation for the remediation of oil hydrocarbons are summarized in Table 1. Among chemical oxidation-based treatments, Fenton and persulfate oxidation are showing great remediation potential to remove oil hydrocarbons. Both oxidants require ferrous iron Fe(II) to produce stronger radicals through following reactions:

$$Fe(II) + H_2O_2 \quad \rightarrow \quad Fe(III) + HO^{-} + HO^{\bullet} \qquad (1)$$

$$S_2O_8^{2-} + Fe(II) \rightarrow SO_4^{\bullet-} + SO_4^{2-} + Fe(III) \quad (2)$$

Activation by soluble Fe(II) requires an acidic pH (~ 3) to avoid its precipitation which is harmful for soil quality and microbial population (Laurent et al., 2012). This initial acidification can be avoided by using chelating agents or iron minerals to perform chemical oxidation at circumneutral pH (Usman et al., 2016b). Iron oxides especially mixed-valent Fe(II)-Fe(III) minerals like magnetite [$Fe(II)Fe(III)_2O_4$] and green rust were found more effective to catalyze chemical oxidation as compared to the ferric minerals or soluble Fe(II) at circumneutral pH due to the presence of structural Fe(II) (Usman et al., 2018). Previous batch (Usman et al., 2012a) and column experiments (Usman et al., 2013) showed that magnetite-catalyzed chemical oxidation (Fenton-like and persulfate) is highly efficient to remove oil hydrocarbons (90% degradation) in crude oil as well its refractory product after biodegradation (UCM). However, these findings were based on artificially contaminated sand where oil hydrocarbons were spiked on sand after extraction from contaminated sediments. To date, no study has been published on use of chemical oxidation to remediate real oil-contaminated sediments. It should be noted that chemical oxidation resulted in significant removal (80%) of polycyclic aromatic hydrocarbons (PAHs) when extracted from aged contaminated soils and spiked in sand. However, these treatments were ineffective (<5% degradation) in aged contaminated soils (without any extraction) which has been attributed to the contaminant unavailability (Usman et al., 2012b; 2012c; 2016a; Biache et al., 2015). In the present study, we aim to evaluate the efficiency of hydrogen peroxide (H_2O_2) and persulfate ($Na_2S_2O_8$) catalyzed by magnetite to remove oil hydrocarbons in aged contaminated sediments. Remediation of three kinds of sediments sampled from different locations in France were investigated. These sediments were subjected to magnetite-catalyzed chemical oxidation at circumneutral pH under different conditions (H_2O_2 or $Na_2S_2O_8$ with or without Fe(II) or magnetite as catalyst). Organic analyses were performed by using Gas

Chromatography - flame ionization detector (GC-FID). The performance of chemical oxidation treatment in correlation with the availability of oil hydrocarbons in aged contaminated sediments was discussed.

Oxidant	Catalyst type	Target pollutant and its initial concentration	Medium	Experimental conditions	Extent / rate of pollutant degradation	Ref.
H_2O_2	Magnetite (Commercial) Screened through 0.3 mm sieve.	Petroleum hydrocarbons 1 g Kg^{-1}	Spiked sand/ Batch	pH = 3, magnetite = 5 wt%, H_2O_2 = 15 wt%	50% hydrocarbon removal after 8 days	(Kong et al., 1998)
H_2O_2	Soluble Fe(II)	Diesel 10-12 g Kg^{-1}	Spiked sand and peat soil/ Batch	pH = 3, H_2O_2:Fe(II) molar ratio = 10:1 liquid/solid = 1 and 20 mL g^{-1} for sand and peat	>80% removal of hydrocarbons after 72 h in sand	(Goi et al., 2006)
H_2O_2	Basic oxygen furnace slag	Fuel oil or diesel TPH = 10 g kg^{-1}	Spiked sand and sandy loam/ Batch	pH = 6.7, H_2O_2 = 15% Slag = 100 g kg^{-1}	TPH removal of 96% and 76% in diesel and fuel oil tests after 40 h	(Tsai and Kao, 2009)
H_2O_2	Soluble Fe(II) in the presence or absence of natural soil Fe minerals (hematite mainly)	Diesel 5 g Kg^{-1}	Spiked loam soil/ Batch	pH = 2.5 – 3, Fe(II) = 12 mM H_2O_2 = 0.045 g g^{-1} soil	28% of diesel was degraded with soil minerals (without Fe(II)) while degradation reached 48% in the presence of soluble Fe(II) after 84 h	(Villa et al., 2010)
H_2O_2	Soluble Fe(III) with EDTA	Petroleum hydrocarbons Dichloromethane-extractable organics 14.8 g Kg^{-1}	Soil samples collected from areas adjacent to oil wells/ Batch	pH = 7, H_2O_2 = 2.45 mol Kg^{-1} soil, H_2O_2:Fe(III) molar ratio = 200:1.	>80% removal of hydrocarbons	(Lu et al., 2010)
$Na_2S_2O_8$	Soluble Fe(II)	Diesel 5 g Kg^{-1}	Spiked sand and soil/ Batch	pH = 3, Oxidant:Fe molar ratio = 100:1	38% removal but inclusion of metal oxides improved the oxidation efficiency	(Do et al., 2010)
$Na_2S_2O_8$	Soluble Fe(II)	Diesel TPH = 3.5 g Kg^{-1}	Soil from an oil refining plant/Batch	Oxidant = 20% Oxidant:Fe = 1:0.01	Total removal 40% after 60 days, Reaction rate constant = 1.47×10^{-2} day^{-1}	(Yen et al., 2011)
H_2O_2 or $Na_2S_2O_8$	Soluble Fe(II) Or Magnetite (lab synthesized)	Petroleum hydrocarbons 4 g Kg^{-1} of crude and weathered oil	Spiked sand/ Batch	pH = 6.7, 20 – 25 °C, magnetite = 10% w/w, oxidant:Fe molar ratio = 10:1 (H_2O_2) and 1:1	80-90% of hydrocarbon removal by both oxidants in the presence of magnetite after one week. <10 % of	(Usman et al., 2012a)

	30 nm; 103 m^2 g^{-1}			($Na_2S_2O_8$)	pollutant removal with soluble Fe(II) as catalyst	
H_2O_2 or $Na_2S_2O_8$	Magnetite (lab synthesized) 30 nm; 103 m^2 g^{-1}	Petroleum hydrocarbons 4 g Kg^{-1} of weathered oil	Spiked sand/ Saturated column	pH = 6.7, 20 – 25 °C, magnetite = 10% w/w, oxidant:Fe molar ratio = 10:1 (H_2O_2) and 1:1 ($Na_2S_2O_8$)	60-70% of hydrocarbon removal by both oxidants	(Usman et al., 2013)
H_2O_2	Soluble Fe(III) with or without chelating agent	Biodiesel blend (20 % biodiesel, 80 % diesel) TPH = 1 g Kg^{-1}	Spiked sandy clay loam/ Batch	pH = < 3 (without chelating agent) and 4.5 – 6 (with chelating agent) Fe (III) = 20 mM, Citrate = 50 mM, H_2O_2 = 4000 mM	75% of TPH removal in the absence of chelating agent while 37% of TPH removal in its presence after 300 h	(Pardo et al., 2014)
H_2O_2	Magnetite and ZVI	Diesel TPH = 5 g Kg^{-1}	Spiked soil/ Batch	pH = 6.7–7.4 Catalyst = 4.27 wt% H_2O_2 = 2.17 mol L^{-1}	TPH removal was 57% (magnetite) and 67% (ZVI)	(Jamialahmadi et al., 2015)
H_2O_2	Soluble Fe(II) with chelating agent	Crude oil TPH = 15.2 and 27.7 g Kg^{-1}	Soils collected from two oil wells / Batch	pH = 7.5, Fe(II) = 5.8 mM, H_2O_2 = 1100 mM Citric acid = 17.9 g L^{-1}	40-50% of TPH removal	(Xu et al., 2016b)
H_2O_2	Soluble Fe(II) with chelating agent	Crude oil contamination TPH = 23.4 g Kg^{-1}	Soil collected from an oil well/ Batch	pH = 6.5 – 7, Fe(II) = 2.9 mM, H_2O_2 = 900 mM	>20% removal of hydrocarbons in 10 days	(Xu et al., 2017)
$Na_2S_2O_8$	NaOH	Diesel TPH = 4.9 g Kg^{-1}	Soil collected from train maintenance facility/Batch	pH = ≥ 12, 20 °C, $Na_2S_2O_8$ = 420 mM, NaOH:$Na_2S_2O_8$ = 4, Liquid/solid = 2 mL g^{-1}	98% removal of TPH after 56 days.	(Lominchar et al., 2018)

Table 1: Summary of studies using chemical oxidation to remove oil hydrocarbons in contaminated soils.

2. Experimental section

2.1. Chemical reagents and materials

Following reagents were used: $FeSO_4.7H_2O$ with purity greater than 98% obtained from VWR, sodium persulfate ($Na_2S_2O_8$) and hydrogen peroxide 35% (H_2O_2) of Acros Organics. Dichloromethane and chloroform, both purchased from VWR were used as received. Deionized water was produced with a Milli–Q system from Millipore.

Magnetite used in the present study was synthesized and characterized in the context of previous study (Usman et al., 2012a). This magnetite is characterized as nano-magnetite (particle size range of 30 – 50 nm) with BET surface area of 103 ± 2 m^2 g^{-1}, PZC of 7.9 and Fe(II)/Fe(III) ratio of 0.46.

2.2. Sediment samples

This study concerned three contaminated sediments from two different harbors, and one petroleum industrial channel. The locations of these three sites are shown in the Figure 1 and are detailed below: LGH Sediments were sampled in February 2007 by dredging in Le Guilvinec harbor (north-western of France), TMH Sediments were dredged in Toulon military harbor (southern France) in April 2008, PIC sediments were sampled in 2011 in a petroleum industrial channel located in the south of France. These samples were freeze-dried, sieved at 2 mm, placed in glass bottles, and stored at 5 °C before analysis and/or treatment. Properties of the tested sediments are reported in Table 2.

These three locations are affected by petroleum by-product contamination for several decades and polluted sediments have already undergone natural biological alteration.

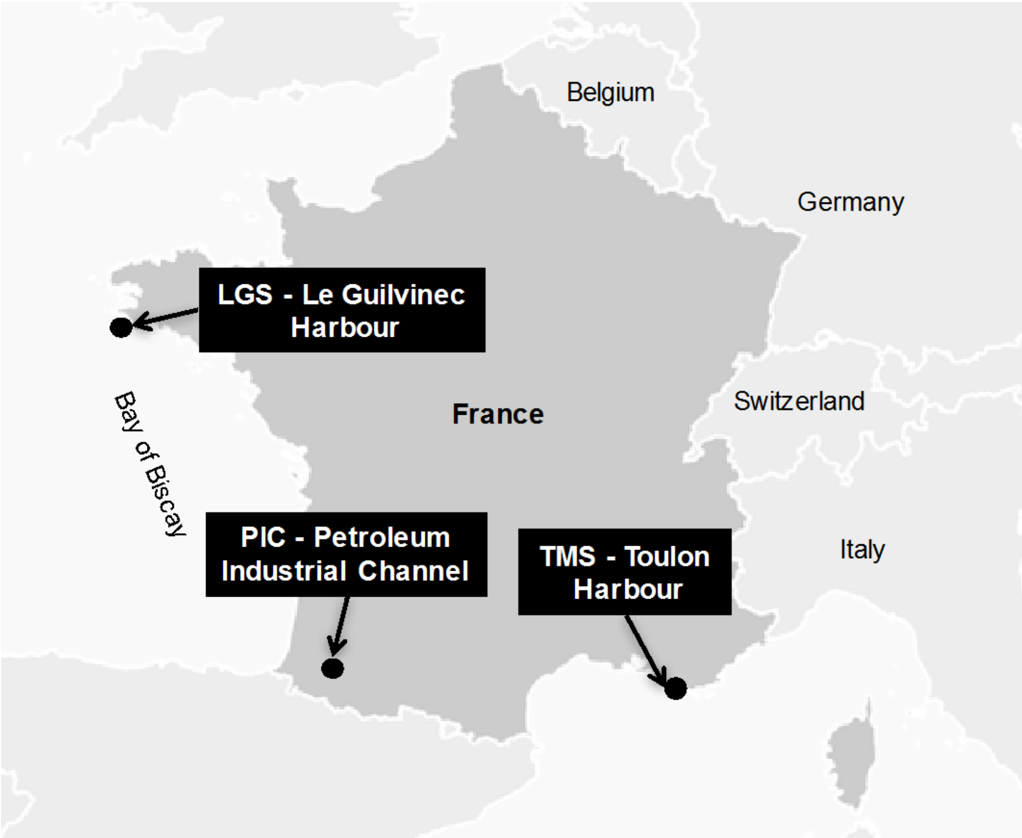

Figure 1: Location of tested sediments in France

2.3. Oxidation procedures

Following experiments were performed to evaluate the chemical oxidation of contaminated sediments: H_2O_2 alone, H_2O_2/Fe(II), H_2O_2/magnetite, $Na_2S_2O_8$ alone, $Na_2S_2O_8$/Fe(II), and $Na_2S_2O_8$/magnetite. Experiments were performed in batch slurry without pH adjustment (circumneutral), room temperature (20 – 25 °C), in the absence of light (by aluminum foil coverings). Oxidant dose was adjusted according to the oxidant:Fe molar ratio equal to 20:1 (H_2O_2) and 2:1 ($Na_2S_2O_8$) in slurry on the basis of our previous studies (Usman et al., 2012a; 2012b). Because the parasite reactions including nonproductive oxidant demand and hydroxyl radical scavenging are more important for H_2O_2 (Liang et al., 2004; Xue et al., 2009b; Usman et al., 2012a; 2012b), we used higher dose of H_2O_2 than persulfate. Blank experiments were performed by using magnetite alone without any oxidant but no pollutant degradation was observed (data not shown). Magnetite was added in concerned sediments to achieve 10% w/w as final contents (0.1 g of magnetite for 1 g of sediment). Equivalent molar amount of Fe was used to compare the efficiency of both catalysts (soluble Fe(II) and magnetite) to activate the tested oxidants. Standard procedure is detailed in our previous study by Usman et al. (2012a). Sediments (2 g) were stirred for 15 minutes with suitable amount of water to have a final volume of 20 mL after oxidant addition. Photocatalytic degradation was avoided by using aluminum foil coverings. Theses slurries were reacted for one week under vigorous magnetic-stirring. Reaction was then stopped by freezing these batches. After two days, water was removed by freeze drying these samples.

One week time point was chosen based on previous studies where no further degradation was observed after one week (Usman et al., 2012a; 2012b) while oxidants were fully consumed after this period as confirmed by iodometric titration (Rybnikova et al., 2016). All experiments were performed in duplicates and results are expressed as a mean value of the 2 experiments and standard deviation of the duplicates was less than 5%.

2.4. Extraction and analysis

Quantification of extractable organic matter (EOM): Freeze-dried sediments were extracted with chloroform at 60 °C for 45 min as detailed previously (Usman et al., 2016a). This was performed in a glass vessel which was connected to a water-cooled reflux condenser to let reflux the evaporated solvent. Temperature of extraction medium was homogenized by magnetic stirring. After extraction, the vessel was allowed to cool at room temperature before opening it. The supernatant was filtered through a pre-washed glass microfiber filter (d = 45 mm, porosity = 0.7 mm; Whatman). Volume of organic extract was reduced to 20 mL under N_2 and 5 mL of this solution was transferred in a pre-weighed vial. The amount of extractable organic matter (EOM) was determined by weighing the vial after evaporation of the solvent. This method resulted in complete recovery of EOM in previous studies (Usman et al., 2012a; 2012c).

Hydrocarbon Index (HI) quantification: The HI was measured according to the ISO 16703:2004 procedure using a GC-FID 7890 Agilent technologies. Briefly, a standard mixture (ASTM D5307) is used to define the integration limits of the chromatogram area. These limits correspond to the *n*-decane ($C_{10}H_{22}$) and *n*-tetracontane ($C_{40}H_{82}$) retention time. An ISO 11046 standardized oil is used as standard solution (external calibration). Seven solutions of different concentrations (0.5, 1, 2, 4, 6, 8 and 10 mg mL^{-1}) are prepared from this standardized oil solution and injected into the chromatograph in order to obtain calibration curves. The integration of the area under each chromatogram is corrected by the background noise (by integrating the area chromatogram obtained with a sample of pure dichloromethane that serves as a control).

3. Results and discussion

3.1. Characterization of sampled sediments

The main properties of tested sediments are reported in Table 2. These sediments were characterized by different mineral fractions including sand (LGH, 98% sand), silt loam (TMH, 35% sand, 57% silt), and silt (PIC, 9% sand, 81% silt, 10% clay) with different pH values: 8.60 (LGH), 8.28 (TMH) and 7.67 (PIC). Total organic carbon (TOC) contents were in order of 1.85%, 4.96% and 8.39% in LGS, TMH and PIC sediments, respectively. Observed order of TOC contents could be correlated to increasing silt contents and decreasing sand contents as reported by Augustin and Cihacek (2016). Indeed, total silt was positively correlated ($P \leq 0.01$) to the TOC while sand was negatively correlated ($P \leq 0.10$) to it. An order similar to TOC was observed for HI values: LGH (3.7 g kg^{-1}) < TMH (5.5 g kg^{-1}) < PIC (9.0 g kg^{-1}). These sediments contained higher $CaCO_3$ amounts of 18.63% (LGH), 28.43 (TMH) and 23.1 (PIC). Higher content of Cu, Pb and Zn were also detected in these sediments (Table 2).

The molecular distributions of initial sediments (Figure 2) are dominated by UCM which comprise a mixture of iso- and cyclo-alkanes (Tolosa et al., 2004) and cannot be resolved by classical chromatographic column. The main identified products correspond to pentacyclic triterpanes. Such signatures are typical of biodegraded and weathered oil containing compounds which are resistant to biodegradation (Tolosa et al., 2004; Farrington and Quinn, 2015). Sampled areas were under natural attenuation for years which eliminated the easily biodegradable *n*-alkanes leaving UCM as the sole contamination in three sediments. GC-FID chromatograms (Fig. 2) provide a visual representation of efficiency of chemical oxidation to degrade UCM as observed previously in spiked sand (Usman et al., 2012a).

	LGH	**TMH**	**PIC**
Origin of sediments	Le Guilvinec harbor	Toulon military harbor	Petroleum industrial channel
Granulometric fraction	0-1 mm	0-1 mm	0-2 mm
Clay (<2 μm) (g kg^{-1})		75	100
Fine silt (2–20 μm) (g kg^{-1})	15*	376	440
Coarse silt (20–50 μm) (g kg^{-1})		196	370
Fine sand (50–200 μm) (g kg^{-1})	215	266	90
Coarse sand (200–2000 μm) (g kg^{-1})	772	87	0
pH (water)	8.60	8.28	7.67
Total $CaCO_3$ (%)	18.63	28.43	23.1
TOC (%)	1.85	4.96	8.39
HI (g kg^{-1})	3.7	5.5	9.0
Total element contents			
Fe (g kg^{-1})	15.39	30.00	110.29
P (g kg^{-1})	2.12	0.56	9.4
K (g kg^{-1})	5.87	7.69	1
Mg (g kg^{-1})	7.22	14.36	8.9
Ca (g kg^{-1})	67.15	109.77	144.9
Na (g kg^{-1})	2.37	17.08	5.3
As (mg kg^{-1})	N.D.	125.95	46.9
Cd (mg kg^{-1})	N.D.	N.D.	1.9
Cr (mg kg^{-1})	82.36	71.08	135
Cu (mg kg^{-1})	659.65	1498.76	83.7
Hg (mg kg^{-1})	N.D.	59.31	0.5
Ni (mg kg^{-1})	26.13	29.27	43.4
Pb (mg kg^{-1})	364.94	597.52	66.7
Zn (mg kg^{-1})	588.28	1760.74	802

Table 2: Salient characteristics of tested sediments
* represents the sum of clay, fine silt and coarse silt.

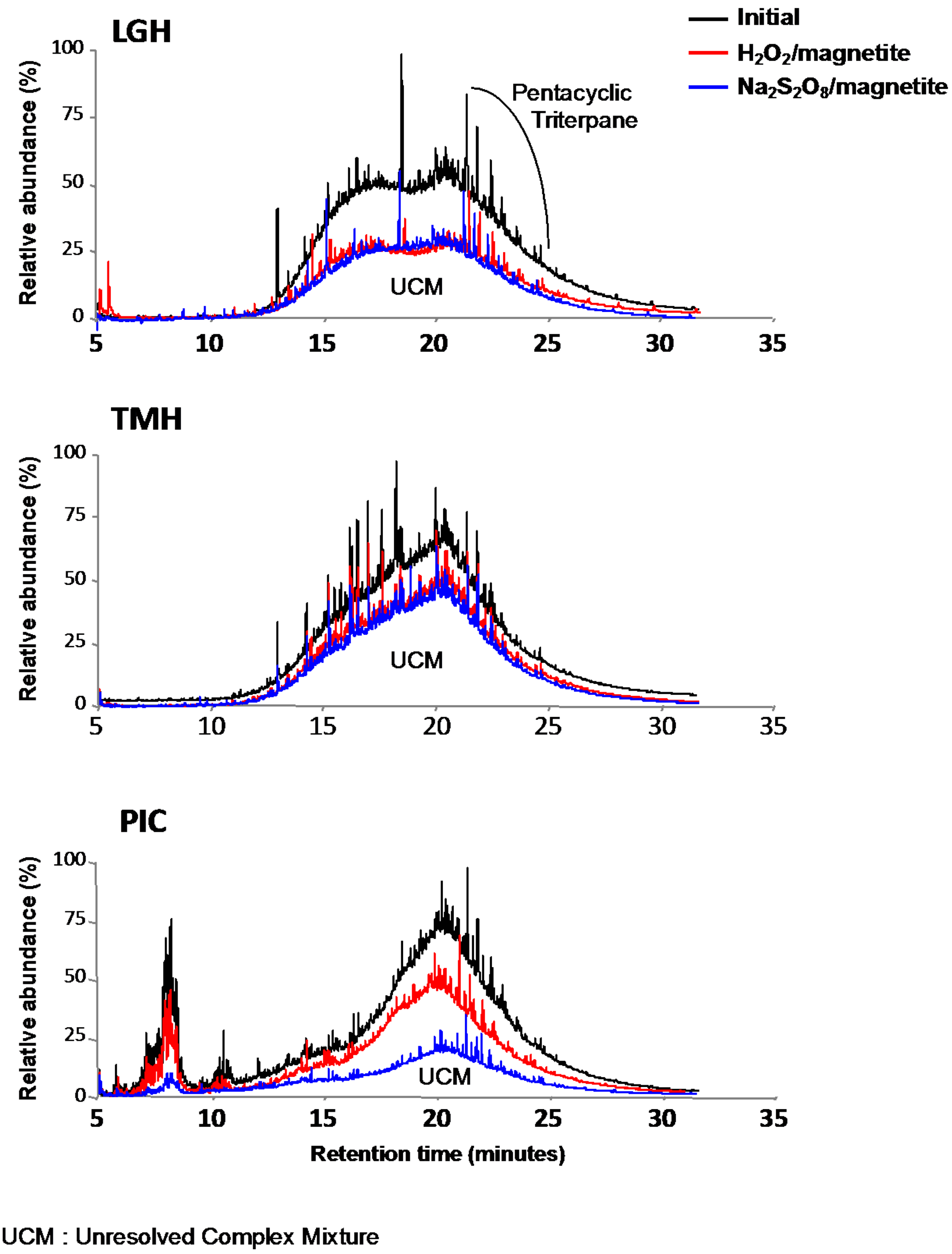

Figure 2: GC-FID spectra of tested sediments before (initial) and after chemical oxidation by H_2O_2/magnetite and $Na_2S_2O_8$/magnetite. Tested sediments were obtained from Le Guilvinec harbor (LGH), Toulon military harbor (TMH) and petroleum industrial channel (PIC). Each organic extract was analyzed by GC-FID using the same procedure (same initial amount of soil before treatment, same amount of solvent for the extraction of sediment after treatment and same volume injected in the GC-FID).

3.2 Chemical oxidation of contaminated sediments

Contaminated sediments were subjected to chemical oxidation in batch experiments. Efficiency of various oxidation treatments was tested at circumneutral pH including H_2O_2 alone, H_2O_2/Fe(II), H_2O_2/magnetite, $Na_2S_2O_8$ alone, $Na_2S_2O_8$/Fe(II), and $Na_2S_2O_8$/magnetite. Evolution of extractable organic matter (EOM) was obtained by measuring the weight of organic extract before and after chemical oxidation (Figure 3).

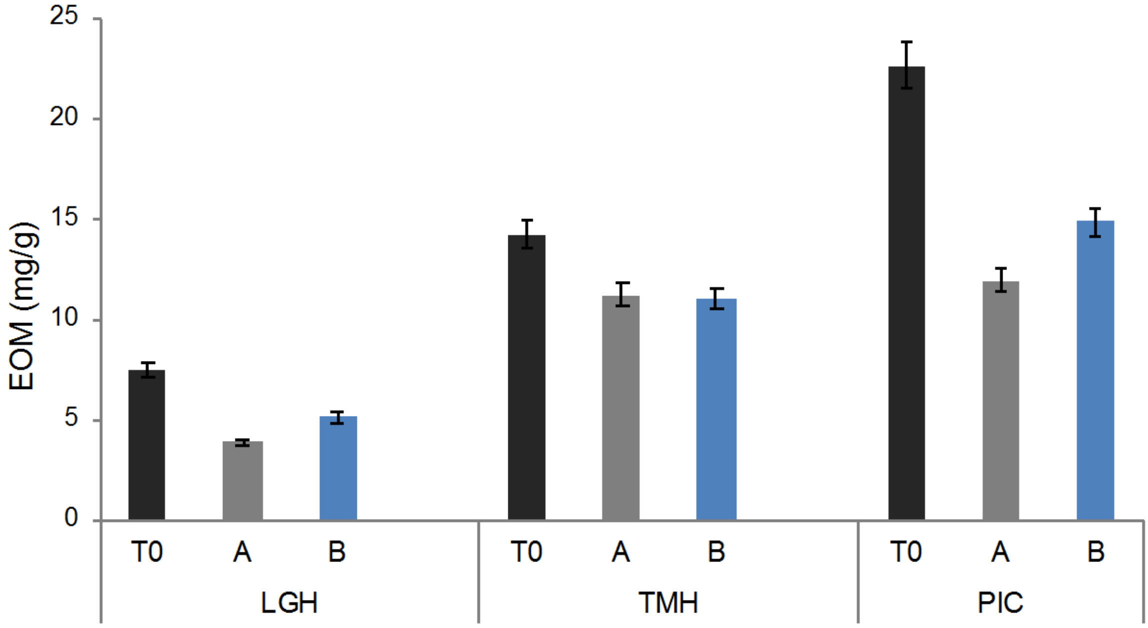

Figure 3: Extractable organic matter (EOM) before (T0) and after chemical oxidation by H_2O_2/magnetite (A) and $Na_2S_2O_8$/magnetite (B) in contaminated sediments obtained from Le Guilvinec harbor (LGH), Toulon military harbor (TMH) and petroleum industrial channel (PIC). Experimental conditions were sediment = 2 g, volume of solution = 20 mL, oxidant doses were used according to the oxidant:Fe molar ratio equal to 20:1 (H_2O_2) and 2:1 ($Na_2S_2O_8$) with 10% w/w magnetite.

Obtained results (Figure 3) indicated a significant decrease in EOM (25 – 50%) when magnetite was used as a catalyst. In TMH, EOM removal extent was lowest (~25% by both oxidants) that might be correlated to its higher carbonate contents (28.43% in TMH sediments as compare to the 18.63% and 23.1% in LGH and PIC sediments, respectively). Carbonates were shown to have scavenging effects for radicals and thus resulting in decreased oxidation efficiency (Liang et al., 2006; Grebel et al., 2010). Loss of EOM was 50% and 32% in LGH sediments and 48% and 35% in PIC sediment by H_2O_2/magnetite and $Na_2S_2O_8$/magnetite, respectively. However, use of both oxidants alone or with soluble Fe(II) resulted in lower removal of EOM (< 5 %, data not shown) that can be associated to the inability of Fe(II) to catalyze chemical oxidation at circumneutral pH (Xue et al., 2009b; Usman et al., 2012a). Soluble Fe(II) precipitates at circumneutral pH which obstructed its catalytic ability. Reaction pH is very important factor controlling the remediation efficiency. Owing to its strong stability, magnetite was found effective at a wide range of pH (Usman et al., 2016b).

Hydrocarbon index (HI) measured by GC-FID is presented in Figure 4. Use of magnetite-catalyzed chemical oxidation resulted in approximately 30 – 70% removal of oil hydrocarbons in tested sediments. On the other hand, negligible degradation (< 5%) was observed when both oxidants were applied alone or with soluble Fe(II) (data not shown). Xu et al. (2017) also reported a comparable oxidation efficiency by H_2O_2 in the presence or absence of Fe(II) at circumneutral pH (6.5 – 7) in loamy soil highlighting the inability of Fe(II) to act as a catalyst. They observed that use of H_2O_2 (225, 450 and 900 mM) with soluble Fe(II) (2.9 mM) resulted in total petroleum hydrocarbon removal of 2, 15, and 25%, respectively whereas a comparable oxidation efficiency was noted by H_2O_2 without Fe(II) of 1, 17, and 22%, respectively (Xu et al., 2017). It should, however, be noted that total concentration of native Fe(II) in their soil was 4.8 g kg^{-1} which could explain the reported oxidation efficiency without any added Fe(II) by Xu et al (2017). Native Fe in contaminated soils has been found to catalyze Fenton-like oxidation with no Fe addition for the removal of PAHs in contaminated soils with 57.5 g kg^{-1} endogenous Fe oxides (amorphous + crystalline) (Watts et al., 2002). Similary, Flotron et al. (2005) reported an equivalent PAH degradation by H_2O_2/soluble Fe(II) and H_2O_2 in contaminated sludge (pH 8.8) and sediments (pH 4.4) bearing 94 and 30 g kg^{-1} as total native Fe, respectively. Owing to the presence of native Fe (16.4 g kg^{-1}), 52% of PAHs were degraded by H_2O_2 (0.4 g g^{-1} soil) under saturated conditions without any Fe(II) addition (Palmroth et al., 2006). Role of endogenous Fe (18.2 g kg^{-1}) was also highlighted by Pardo et al. (2016) when they observed similar degradation of PAHs by Fenton oxidation (882 mM H_2O_2 without pH adjustment) by adding 1 mM Fe(III) or without external addition of Fe. However, Usman et al. (2012b; 2012c) reported that native iron (25 g kg^{-1} Fe_2O_3) was unable to catalyze H_2O_2 and $Na_2S_2O_8$ to remediate PAH contaminated soils at circumneutral pH. Similarly, Ahmad et al. (2010) observed that native iron oxides (8.8 g kg^{-1} amorphous + crystalline) in soil did not promote measureable activation of $Na_2S_2O_8$ in natural soils. They suggested that quantities of native iron oxides are not sufficient to catalyze persulfate oxidation in soils. However, even at varying concentrations of native iron (15 – 110 g kg^{-1}) in tested sediments, it was found ineffective in promoting the oxidation reaction for harbor sediments. Thus, catalytic role of native Fe oxides is variable depending on many factors including their nature, total content and availability of Fe oxides.

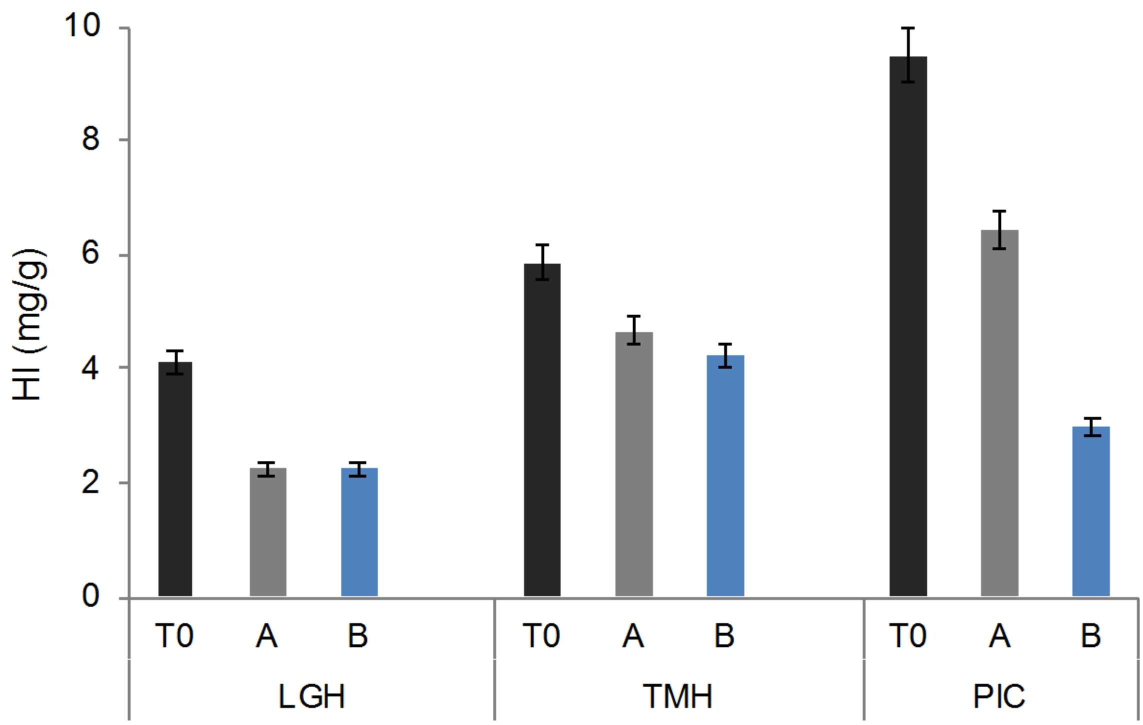

Figure 4: Hydrocarbon index (HI) before (T0) and after chemical oxidation by H_2O_2/magnetite (A) and $Na_2S_2O_8$/magnetite (B) in contaminated sediments obtained from Le Guilvinec harbor (LGH), Toulon military harbor (TMH) and petroleum industrial channel (PIC). Experimental conditions were sediment = 2 g, volume of solution = 20 mL, oxidant doses were used according to the oxidant:Fe molar ratio equal to 20:1 (H_2O_2) and 2:1 ($Na_2S_2O_8$) with 10% w/w magnetite.

A good correlation was observed between hydrocarbon index and extractable organic matter for H_2O_2/magnetite highlighting the non-specific nature of chemical oxidation to degrade the non-target compounds. However, $Na_2S_2O_8$/magnetite resulted in lower removal of EOM while higher loss of HI especially in the PIC sediments. It should be noted that HI quantifies only low molecular weight compounds (less than 40 carbons), whereas EOM quantifies low as well as high molecular weight compounds. This observed difference in degradation of EOM and HI by $Na_2S_2O_8$/magnetite could be caused by selective behavior of persulfate oxidation as observed previously where it showed less efficiency towards high molecular weight PAHs while Fenton oxidation was equally efficient for all PAHs (Usman et al., 2012b; 2012c). Similarly, when crude oil rich in *n*-alkanes with pristane and phytane spiked on sand was subjected to magnetite-catalyzed chemical oxidation (Usman et al., 2012a), H_2O_2/magnetite showed non-selective oxidation with equal efficiency towards all *n*-alkanes (C_{21} – C_{36}). On the other hand, $Na_2S_2O_8$/magnetite was less reactive towards high molecular weight *n*-alkanes (C_{31} – C_{36}). However, it is difficult to point out such selectivity in studied sediments because they are contaminated with UCM whereby individual components of this complex mixture are difficult to resolve (Farrington and Quinn, 2015). Observed difference in term of degradation of EOM and HI for persulfate for PIC sediments could also be correlated to the lower affinity of $Na_2S_2O_8$ towards natural organic compounds leading to higher removal of target pollutants (Lim et al., 2016). Very recently, non-productive consumption of $Na_2S_2O_8$ was lower than 10% after 56 days of reaction in non-polluted soil (despite 6.5% $CaCO_3$) highlighting the low reactivity of oxidant with different soil components (Lominchar et al., 2018). Rather, persulfate was also found to be activated at basic pH by organic compounds similar to those present in soil organic matter (Ahmad et al., 2010). Similarly, the impact of soil matrix was less pronounced on the efficiency of persulfate oxidation to remove PAHs from historically contaminated soil as compared to the Fenton oxidation system (Usman et al., 2012b; 2012c).

3.3 Magnetite-catalyzed chemical oxidation *vs.* common oxidation systems

As mentioned above, the available literature severely lacks investigations on the chemical oxidation of oil hydrocarbons in real contaminated sediments (Table 1) and thus a fair comparison of present findings with the literature is not straightforward. Previous studies were either performed on artificially contaminated sand/soil or soil obtained from contaminated site (Table 1) and present study is the first report of using magnetite-catalyzed chemical oxidation in real sediments.

Most of the remediation studies to degrade oil hydrocarbons employing H_2O_2 and $Na_2S_2O_8$ were performed at acidic pH ($\leq$ 3) by Fe-catalyzed chemical oxidation (Kong et al., 1998; Goi et al., 2006; Do et al., 2010; Villa et al., 2010; Pardo et al., 2014) (Table 1). Due to detrimental effects of this initial acidification, efforts were made to perform chemical oxidation of oil hydrocarbons at circumneutral pH by using catalytic ability of basic oxygen furnace slag (Tsai and Kao, 2009), soluble Fe(III) or Fe(II) with chelating agents (CAs) like EDTA or trisodium citrate or citric acid (Lu et al., 2010; Pardo et al., 2014; Xu et al., 2016b; Xu et al., 2017), magnetite (Usman et al., 2012a; 2013; Jamialahmadi et al., 2015) and zero-valent Fe (Jamialahmadi et al., 2015). Very high pH (>12) also resulted in strong activation of $Na_2S_2O_8$ for the removal of diesel. Use of chelating agents resulted in effective removal of oil hydrocarbons (Table 1). However, these CAs being organic in nature will act as oxidant scavenger by competing with the target pollutants (Pardo et al., 2014; Usman, 2016). For example, Pardo et al. (2014) applied Fenton oxidation to treat biodiesel contaminated soil with or without trisodium citrate as CA (for details of experimental conditions, see Table 1). Obtained oil hydrocarbon removal reached 75% in the absence of CA (at pH <3). Use of CA allowed them to perform chemical oxidation at higher pH (5-6) but degradation efficiency decreased to 37% which was associated to the consumption of oxidant by CA at higher pH. Use of CA can also be pH sensitive as reported by Lu et al. (2010). H_2O_2 catalyzed by Fe(III) in the presence of a CA (EDTA) was more efficient to degrade petroleum hydrocarbons at pH 7 while oxidation efficiency decreased at pH 6 which was associated to quick degradation of EDTA leading to the precipitation of Fe(III). However as reported in literature, magnetite has shown strong stability and catalytic capacity over a wide range of pH and thus, it offers control over drawbacks associated to initial acidification or CAs. Moreover owing to its ferromagnetic nature, it can be easily recovered after reaction by magnetic separation and can be used for further oxidation cycles without any significant decline in catalytic ability (Xue et al., 2009a; Jia et al., 2018). Other reusability studies indicated a decline in oxidation efficiency of 20% after 8 oxidation cycles for the removal of phenol in aqueous solutions (Zhang et al., 2009). However, reusability and/or fate of magnetite has rarely been investigated in soils or sediments.

Regarding efficiency of magnetite-catalyzed chemical oxidation in present study, degradation of hydrocarbons varied between 40 – 70% when tested sediments were subjected to chemical oxidation at circumneutral pH with oxidant:Fe molar ratio equal to 20:1 (H_2O_2) and 2:1 ($Na_2S_2O_8$) with 10% w/w magnetite. This would be economically relevant by avoiding initial acidification and/or use of chelating agents.

It is worth noting that efficiency of chemical oxidation is strongly limited by the availability of polycyclic aromatic hydrocarbons (PAHs) in aged contaminated soils and sediments (Flotron et al., 2005; Choi et al., 2014; Usman et al., 2016b). As a matter of fact,

H_2O_2/magnetite or $Na_2S_2O_8$/magnetite did not cause any PAH degradation unless tested soils were subjected to chemical (Usman et al., 2012c) or thermal pretreatment (Biache et al., 2015; Usman et al., 2016a). However, no such pollutant unavailability was observed for oil hydrocarbons in tested sediments. It might be correlated to difference between the nature of both matrices (soils vs. sediments), history of contamination and type of pollutants (aliphatic vs. aromatic) (Flotron et al., 2005; Trellu et al., 2017; Lominchar et al., 2018). The specific deposition, the preservation in water can probably explain the difference in term of availability between soils and sediments. Moreover, in our case, the contamination originated from petroleum source (a liquid) compared to coal-tar (source of PAHs) which becomes solid with aging while losing the low molecular compounds which leads to enrichment of heavy compounds in coal-tar particles (Trellu et al., 2017). Coal-tar can be observed in historically contaminated soil as a small ball-like aggregate with low specific area as compared to the petroleum pollution which exists as a thin film on minerals in sediments (Trellu et al., 2017).

In addition to the *in-situ* application, magnetite-catalyzed chemical oxidation could offer a quick and cost-effective alternative to conventional remediation strategies (landfilling, stabilization etc.) for dredged sediments (Akcil et al., 2015) ensuring safe reuse of dredged sediments.

4. Conclusion

This is the premier study reporting the use of magnetite-catalyzed chemical oxidation to remove biorefractory oil residues (remaining of natural attenuation) in different historically contaminated sediments. Magnetite showed strong efficiency to catalyze chemical oxidation at circumneutral pH. Oxidation efficiency was, however, limited by the nature and properties of sediments. No issue related to pollutant availability was observed as was the case for PAH aged contaminated soils which might be correlated to the difference of contaminant type (aliphatic hydrocarbons and PAHs) and mediums (soils and sediments). Due to the strong efficiency of magnetite to degrade biorefractory oil residues without any initial acidification (circumneutral pH), this study may have strong implications to design an innovative stand-alone technology for *in-situ* and ex-situ remediation of contaminated sediments.

Acknowledgments:

Authors thank the GISFI (French Scientific Interest Group - Industrial Wasteland, www.gisfi.univ-lorraine.fr).

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