Remediation of oil-drilling cuttings by ozonation in semibatch bubble column reactors

K F Christodoulis1,2, M A Theodoropoulou1,3 and C D Tsakiroglou1,4

1 Foundation for Research and Technology Hellas, Institute of Chemical Engineering Sciences, Stadiou str, Platani, 26504 Patras, Greece
2 University of Patras, Department of Physics, 26504 Patras, Greece
3 Hellenic Open University, 26335 Patras, Greece
4 Corresponding author e-mail: ctsakir@iceht.forth.gr

Abstract. The remediation of oil-drilling cuttings (ODC), containing a high percentage of total organic carbon (TOC), total petroleum hydrocarbons (TPH) and moisture, is a challenge. Ozonation is an advanced oxidation method able to destruct a broad variety of organic substances from water and soil. Oil-drilling cuttings are pre-treated inside a sonication bath with three solutions of artificial seawater containing 0.0, 0.2, and 0.5% w/w sodium dodecyl sulphate (SDS) which acts as surfactant and favours the solubilisation of hydrocarbons from the solid to the liquid phase. Afterwards, each pre-treated ODC is diluted at a ratio 1:5 with the corresponding type of seawater, and ozonation of the suspension occurs in a bubble column reactor made of poly methyl methacrylate (PMMA). The transient changes of the TOC content in ODC during the various stages of its treatment are measured with the Walkley-Black titration method. It seems that a percentage ~12-25% of TOC dissolves and is transferred from ODC to seawater, while the treatment of ODC suspended in seawater with ozone leads to the complete removal of the TOC after 2 hrs.

1. Introduction
Oil-based drilling cuttings (ODC) are the major wastes generated during the process of oil/gas exploration and extraction [1], and the oil content, even after the pre-processing of cuttings, may reach up to 5-10% by weight. The on-site burial or landfill disposal of drill cuttings is inadequate to meet current and future stringent environmental regulations. Due to the high content of salty water, the ODC resemble a soil that is contaminated heavily by non-aqueous phase liquid (NAPL), and is saturated fully with water.

Common methods used for the management of ODC are: (i) surfactant-enhanced washing [2], (ii) thermal [3] and microwave treatment [4], (iii) supercritical fluid extraction [5], (iv) solidification and stabilization [6], (v) phytoremediation [7], and (vi) bioremediation [8]. Heavy hydrocarbons which are present in ODC have low solubility in water so that the biodegradation becomes inefficient. Among the advanced oxidation methods used for soil remediation, ozonation seems well-promising as a method for the fast removal of hydrocarbons from contaminated soils and ODC. Ozone is a strong oxidant (E° = +2.07 V) and also strong electrophile [9]. The oxidation of organic compounds proceeds by reacting either directly with molecular O3 [10], or indirectly with free hydroxyl radicals [11]. An alternative to direct ozonation might be its combination with surfactant-enhanced dissolution. In this
manner, a significant fraction of hydrocarbons might dissolve and be transferred to the aqueous phase, where its direct oxidation by dissolved ozone looks more tractable. Regarding the surfactant-enhanced dissolution of oil, the best TPH removal (up to 75%) was achieved when ODC was treated with surfactant-containing seawater [12]. The pre-washing of cuttings with aqueous phase of variable pH did not improve the degradation of hydrocarbons [13].

The aim of the present work is to investigate the performance of ODC remediation by combining its pre-treatment with surfactants with its post treatment with ozonation. The ODC pre-treatment is done by mixing it with artificial seawater, at weight ratio 1:5, inside an ultra-sound bath, with and without the addition of the anionic surfactant SDS. Then, semi-batch experiments are conducted where the ozone-rich gas outflowing from an ozone generator is injected through a column reactor pre-occupied with the pre-treated mixture of ODC and seawater. To evaluate the performance of the process, the transient changes of the total organic carbon in dry ODC are measured by collecting samples from the column and using the Walkley-Black titration method [14].

2. Methods and Materials

2.1. Chemicals

A tightly sealed container of 50 L filled with homogenized and fully water-saturated ODC, originating from off-shore wells of North Greece, was delivered to FORTH/ICE-HT by Polyeco Waste Management (Thessaloniki Division) to be used as a reservoir of samples for treatment studies. Tri-distilled water (3DW) and the following chemicals of analytical grade were used for the preparation of solutions used in ODC treatments and application of titration method: magnesium sulphate MgSO₄ (Carlo Erba), calcium chloride CaCl₂ (Merck), potassium chloride KCl (Merck), sodium chloride NaCl (Merck), sodium dodecyl sulphate SDS (Merck), potassium dichromate K₂Cr₂O₇, sulfuric acid H₂SO₄, ammonium iron(II) sulfate hexahydrate Fe(NH₄)₂(SO₄)₂ 6H₂O, Ortho–phosphoric acid H₃PO₄ (Scharlau).

2.2. Preparation of seawater and surfactant solutions

Three types of seawater solutions were prepared: seawater, seawater containing 0.2% SDS, and seawater containing 0.5% SDS. For the preparation of seawater, 12.854 g of MgSO₄, 1.0154 g of CaCl₂, 2.6181 g of KCl and 27.5419 g NaCl were weighed. With the aid of a funnel the materials were placed in a 1000 mL volumetric bottle, which was filled with 3DW. To prepare SDS solution of 0.2% w/w concentration, 1.875 g of SDS was weighed and placed in a volumetric bottle of 500 mL along with seawater until filling the bottle which was then shaken. Respectively for SDS solution of 0.5% w/w concentration 5 g of SDS was weighed and the same procedure was followed.

2.3. ODC pretreatment for the dissolution of organic species

Samples of ODC were treated with the foregoing seawater solutions. Specifically, 25 g of ODC was placed in a flask along with 125 g of each seawater solution. The flasks were placed in an ultrasonic bath (Witeg WUC-D 3.3 40 kHz) and sonicated for 30 min in 30°C.

2.4. Rheology of treated ODC

After the sonication, each suspension was placed in 15 mL centrifuge falcon tubes, centrifuged (MegaFuge™ 16) for 15 min in 11000 rpm, and the supernatant solution was removed. Almost 1.5 g of treated ODC was placed between parallel plates of diameter 40 mm with the gap set at 1 mm, and the rheological properties were measured in a Dynamic Strees Rheometer (SR-200, Rheometric Scientific). Steady stress and dynamic frequency sweep tests were carried out to measure the shear viscosity and the storage and loss moduli at various temperatures (25-45°C) by using the setup of electro-heated plates.
2.5. Ozonation experiments
A schematic diagram of the experimental setup used to conduct ozonation tests on ODC samples is shown in figure 1. A long cylindrical column of PMMA with inner diameter 4 cm and height 50 cm was equipped with inlet / outlet ports and four sampling ports across its side wall (Figure 1). The pre-treated samples were diluted with seawater solution at a weight ratio 1:5, and in each column 75 g of treated ODC was added along with 375 g of seawater. The ozone was produced from bottled oxygen which was fed at a flow rate 0.5 L/min through a gas mass flow controller (SmartTrack 50, SIERRA) to an ozone generator (LAB2B, Suez), after having been purified by a HEPA filter (Sigma) and dried by a silica gel adsorbent (Figure 1). The ozone concentration in gas phase was monitored on-line with an ozone analyzer BMT 965 (BMT Messtechnik Gmbh), connected to the host computer and having an upper detection limit \(\sim 200 \text{ g/Nm}^3\). The ozone-rich gas was humidified by passing through a gas washing bottle (DURAN), and the humid gas was injected in the PMMA column through a spherical diffuser (Figure 1). The inlet and outlet gas pressures across the column were measured by two pressure transmitters (Model P1, Analysis Ltd) and transmitted to a data acquisition system (ADAM 4561 & ADAM 4117, Advantech) connected to the host computer. The gas escaping from the column outlet passed, first, through a sealed glass bottle to separate gas from liquid drops and solid particles, then through a silica gel adsorbent to remove moisture, and finally through an ozone destruction catalytic reactor (OD-O100, Ozonetech) to minimize the O\(_3\) emission to environment (Figure 1). Occasionally, it was possible to monitor the composition of exhaust gases, for a maximum period of 30 min, by using a portable gas analyzer (Optima 7, MRU) equipped with sensors capable of tracking the concentrations of O\(_2\), CO\(_2\), CO, NO\(_x\), VOCs, and transferring the data to host computer with the aid of MRU4win software. For safety reasons, the entire system was placed inside a fume hood. All experiments were conducted over a temperature range 30-35°C. After every 15 min, with the aid of a syringe, 32 g of suspension was collected from a sampling port and centrifuged at 11000 rpm for 15 min. Then, the supernatant solution was removed and the residual ODC was left under a fume hood for 16 h to air dry.

**Figure 1.** Flowsheet of the experimental setup.
2.6. Measurement of the total organic carbon

2.6.1. The Walkley–Black method. For analyzing the total organic carbon in ODC before and during the ozonation tests, the Walkley–Black titration method [14] was used. This method is based on the oxidation, Eq.(1), of organic matter by a mixture of K₂Cr₂O₇ and H₂SO₄, followed by back titration of the excessive dichromate by Fe(NH₄)₂(SO₄)₂·6H₂O, Eq.(2)

\[ 2 \text{Cr}_2\text{O}_7^{2-} + 3 \text{C}^0 + 16 \text{H}^+ \rightarrow 4 \text{Cr}^{3+} + 3 \text{CO}_2 + 8 \text{H}_2\text{O} \] (1)

\[ 6 \text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 16 \text{H}^+ \rightarrow 2 \text{Cr}^{3+} + 6 \text{Fe}^{3+} + 7 \text{H}_2\text{O} \] (2)

2.6.2. Preparation of solutions. First, 103.27 g of K₂Cr₂O₇ was weighed and placed inside a volumetric bottle of 250 mL along with 3DW. The mixture was stirred until total dissolution. Then, the solution of ferrous ammonium sulfate of 0.5N was prepared by dissolving 19.6 g of Fe(NH₄)₂(SO₄)₂·6H₂O with 3DW in a bottle of 100 mL. Then, 0.36 g of diphenyl amine indicator was weighted and placed in a 10 mL volumetric bottle by adding ethanol until reaching the notch of the bottle.

2.6.3. Titration. 0.5 g of the air-dried ODC was weighed, transferred within a 500 mL conical flask and kept on wire gauge. Then 5 mL of 1N K₂Cr₂O₇ and 10 mL of concentrated H₂SO₄ were added in the conical flask and kept aside for 30 min. After that, 50 mL of distilled water and 10 mL of 85% H₃PO₄ were added in the mixture. Then, 2 to 3 drops of 0.5 % diphenylamine indicator were added in the flask. Finally, the sample was titrated by placing Fe(NH₄)₂(SO₄)₂·6H₂O of concentration 0.5 N in a burette and adding it in the solution dropwise. The change of the solution color from violet blue to dark green signified the end of titration. The initial and final indications of the burette were recorded for all titrations, and the same procedure was followed for a blank sample.

The following formula was used to calculate the percentage of total organic carbon (TOC)

\[ \text{TOC} \% = \frac{100}{\text{m}_{\text{ODC}}} \frac{(B-S)}{\text{m}_{\text{FAS}}} \frac{\text{CFAS}}{\text{MWC}} \] (3)

B=volume of ferrous ammonium sulphate (FAS) used to titrate the blank; S=volume of ferrous ammonium sulfate used to titrate the sample; CFAS=Normality of ferrous ammonium sulfate solution =0.5 N; MWC=meq. wt. of carbon=0.003; mODC=weight of ODC (g).

3. Results and Discussion

The composition of ODC, shown in Table 1, was given by Polycoco Waste Management. Evidently, the ODC is characterized by high TOC, TPH and moisture values, and its treatment with an advanced oxidation process, such as ozonation, is a challenge.

| Property                                      | Mean value |
|-----------------------------------------------|------------|
| Moisture                                      | 13.1-23.8  |
| Ash (550°C)                                   | 64-71.4    |
| Total Organic Carbon, TOC (% w/w)             | 5.89       |
| Total Petroleum Hydrocarbons, TPH (mg/kg-dry95000 mass) |            |

3.1. Rheological measurements

The shear viscosity along with the storage, G’, and loss, G” moduli of ODC pre-treated with the three types of seawater are shown in Figure 2. The shear viscosity of ODC follows a shear-thinning behaviour of a power law fluid, and is reduced by one order of magnitude with the presence of SDS at
its maximum concentration (Figure 2a). On the other hand, both the storage and loss moduli decrease with the presence of SDS in seawater (Figure 2b), weakening the viscoelastic behaviour of pre-treated ODC. Therefore, among others, it is evident that the presence of SDS in seawater enhances the “fluid” character and weakens the “solid” character of ODC, facilitating the creation of suspensions and making their treatment more tractable.

Figure 2. (a) Shear viscosity and (b) storage and loss moduli of ODC pre-treated with the three types of seawater.

3.2. Ozonation in bubble column reactor

Ozonation tests were conducted on the bubble column reactor filled with ODC pre-treated and mixed with the three types of synthetic seawater (Figure 3). Due to the removal of a quantity of aqueous phase after each sampling, gradually the total mass of suspension and height of column occupied by it dropped. Accounting for the density of ODC ($\rho_{\text{ODC}}=1.38 \text{ g/cm}^3$), the total mass of seawater and ODC, and sampling mass, it is estimated that the volume of suspension was reduced by $\sim30.5$ cm$^3$ after each sampling. For each test, the pressure drop measured across the column, and the concentration of O$_3$ detected at column inlet are shown in Figure 4a, b. The pressure fluctuations are associated with the generated bubble size distribution. It seems that the presence of SDS stabilizes the bubbles over a narrow size range, resulting in weaker fluctuations (Figure 4a). On the other hand, the concentration of produced ozone ranges between 40 and 60 g/Nm$^3$ (Figure 4b).

Figure 3. A photograph of the experimental apparatus.
3.3. TOC analyses

Figure 5 depicts the results of TOC analyses in various samples measured with the application of the Walkley – Black titration method. It’s worth mentioning that a respectable reduction of the initial TOC (~5.9%) occurred in all cases (~13-28%) at the beginning of ozonation (t=0 min), after having treated the ODC with each type of seawater so that a fraction of organic substances dissolved into the liquid phase. Evidently, as the SDS concentration increases (especially if its value exceeds the critical micelle concentration) the solubilization of organic species in seawater also increases (Figure 5). After 2 h of ozonation, the TOC vanished totally from ODC in all cases (Figure 5). It seems that the higher TOC removal efficiency, observed for the seawater with the maximum SDS concentration (0.5%), is associated with the enhanced dissolution of organic species, particularly with reference to early times, given that the SDS may also be oxidized by ozone at long times (Figure 5).

Figure 5. Transient variation of the TOC removal efficiency from ODC for the three cases of seawater.
Eventually, the degradation of TOC may be attributed to two general oxidation pathways: (i) the ozone contained in the injected gas dissolves from the bubbles to the liquid phase and reacts with dissolved organic species; (ii) the rising bubbles come in contact with suspended solid particles and ozone reacts directly with the organic matter. As the dissolved organic substances are depleted from liquid phase, the dissolution of extra organics in seawater is triggered. On the other hand, the bubble flow mixing regime favors the continuous re-suspension of precipitated solid particles, the recirculation of suspended particles, and the increased frequency of O₃ contact with dissolved and undissolved organic species.

4. Conclusions

Ozonation was combined with surfactant-enhanced dissolution in seawater to remediate oil-drilling cuttings (ODC), heavily contaminated with hydrocarbons. The remediation efficiency was assessed by estimating the percentage of the total organic carbon (TOC) in dried ODC using the Walkley-Black titration method. The TOC is a quantitative measure of the all organic substances that still have not been converted to carbon dioxide. The pre-treatment of ODC with seawater contributes to the dissolution of 13-28% of TOC, the presence of SDS facilitates the fluidity of the ODC suspended in seawater, and may enhance the hydrocarbon solubilization from ODC to seawater. Regardless of the type of seawater, with the supply of pure oxygen at flow rate 0.5 L/min in a bubble column reactor, and generated ozone concentration at 40-60 g/Nm³, the TOC was eliminated totally after 2 hrs of treatment of 450 g of suspension (ODC diluted with seawater at weight ratio 1:5).

Ozonation seems a well-promising advanced oxidation technique able to oxidize high TOC content from water-saturated ODC, but further studies are required to optimize the conditions of treatment to minimize the seawater to ODC mass ratio, energy consumption, and ozone production.

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