



REMEDIATION OF SULFOLANE IMPACTED SOIL BY INTEGRATING SOIL WASHING/FLUSHING AND ADVANCED OXIDATION PROCESS

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Abstract: Sulfolane in soil is an emerging problem in oil and natural gas processing sites. This study investigates remediation of sulfolane contaminated soil through the application of soil flushing followed by UVC/H₂O₂/O₃ and soil washing followed by four different advanced oxidation processes (AOPs) including UVC/H₂O₂, UVC/O₃, alkaline ozonation and neutral Fenton reagent. Results showed that sulfolane can be effectively removed from the soil using water as a flushing/washing solvent. Furthermore, sulfolane in the soil flushing/washing solution was effectively degraded by the following AOP treatment.

1 INTRODUCTION

Remediation of contaminated soils and sites using environmentally sustainable and efficient technologies has been a major challenge. Despite the high cost, ex-situ procedures generally require less time to achieve contaminant cleanup when compared to in situ approaches. It is also easily monitored and uniform, offering greater prospects (Kupuna et al, 2016). Soil flushing/washing has previously been employed as a pre-treatment technique to extract contaminants from polluted soils and further facilitate advanced treatments. Soil flushing/washing is a mechanical process based on desorption of contaminants from soil through the action of water with or without surfactants (Mao et al, 2015). It has been applied to remediate soils contaminated with organic compounds including polychlorobiphenyls, polycyclic aromatic hydrocarbons and pesticides (Trellu et al. 2016). Although soil washing/flushing has shown promising results, this process only transfers the contaminants from the soil phase into aqueous phase, resulting in wash solution still containing contaminants which require further treatment. There are many post treatment options available for soil washing/flushing solutions such as bioremediation, chemical oxidation, advanced oxidation processes (AOPs) and electro-kinetic remediation. Among these options, AOPs have attracted more interests in recent years due to its capacity to degrade a large group of organic contaminants. AOPs are processes designed to degrade recalcitrant organic compounds using highly reactive species such as hydroxyl radicals (\bullet OH). They have been considered as highly efficient processes to treat emerging contaminants including pharmaceuticals and personal care products (PPCPs), pesticides, herbicides, surfactants, steroids and hormones, endocrine disrupting compounds etc (Andreozzi et al. 1999; Esplugas et al. 2007; Parsons 2004).

In this study, soil washing/flushing integrated with advanced oxidation processes was evaluated to treat soils contaminated with an emerging industrial pollutant, sulfolane. Sulfolane (C₄H₈O₂S) is a polar organosulfur solvent well known for sweetening sour gas in the Sulfinol® process as well as used to extract aromatics from hydrocarbon mixtures. Due to leaks and spills, soil and underground water have been contaminated with sulfolane. The highly polar nature of sulfolane makes it extremely mobile in water

enabling it to easily enter soil and groundwater of nearby gas refinery plants through different routes posing a threat for aquatic life and soil environment.

Previous published works (Yu et al. 2016a; Mehrabani et al. 2016; Izadifard et al. 2017) have shown that AOP is a feasible technology for sulfolane degradation in aqueous medium. However, in contrast to aqueous spiked medium, the composition of flush/wash water is heterogeneous as other compounds are also washed from the soil. Therefore, this paper reports on the effectiveness of AOPs on treating these solutions containing sulfolane. Both soil washing, and flushing were investigated to remove sulfolane from soil. The soil washing solution was treated with UVC/H₂O₂, UVC/O₃, alkaline ozonation and neutral Fenton while the soil flushing solution was treated with UVC/H₂O₂/O₃, which was reported as one of the more effective methods in degrading sulfolane (Yu et al., 2016a).

2 METHOD AND MATERIALS

2.1 Chemicals and Contaminated Soil.

Sulfolane (99% purity) and hydrogen peroxide (30% purity) were purchased from Sigma Aldrich, Canada, sodium hydroxide with 97% purity was purchased from EMD; EDTA chelated iron (III) with 99% purity was purchased from J.T. Baker and milli-Q water was used to conduct soil washing experiments and sample dilutions. Contaminated soil samples were provided by Bonavista Energy Corporation.

2.2 Experimental Procedure

The experimental setup for the integration of soil washing/flushing and AOPs is shown in Figure 1. The soil samples were firstly treated by soil washing or soil flushing with milli-Q water as the solvent. The collected soil washing, and flushing solution samples were then treated with different AOPs.

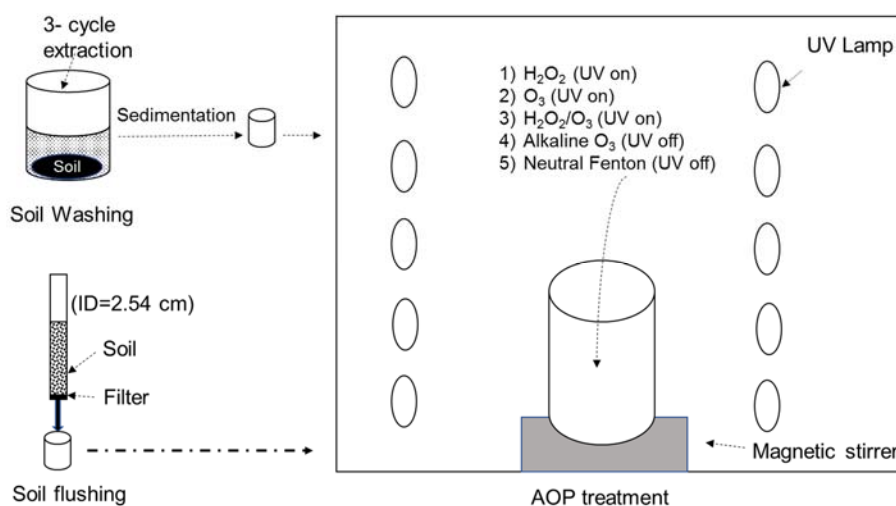


Figure 1. Experimental setup

2.2.1 Soil Washing and AOP

Processed soil weighing 1.5 kg and containing 900 mg/L of sulfolane was washed by water using a 3-cycle procedure. Three litres of water were applied for each cycle. The soil washing solution collected from each cycle was then combined in a settling column. After 24 hr of sedimentation, the supernatant was separated by siphon and kept in the fridge for AOP treatments. The AOP treatments included UVC/H₂O₂, UVC/O₃, alkaline ozonation and neutral Fenton. The details of each AOP experiment including chemical dosage, pH and light condition are listed in Table 1. All experiments were conducted in a 150 ml quartz beaker containing 100 ml of soil washing solution. Luzchem photoreactor (LZC ORG) equipped with 10 germicidal

lamps (LZC-UVC) were used to provide UVC irradiation if necessary. The light intensity was determined to be 5.3×10^{17} photon/s through ferrioxalate actinometry. For experiments with ozone, an O₃ generator (A2Z 3-G LAB, A2Z O3 systems Inc.) connected to the beaker through a glass diffuser was used. The ozone flow rate was kept at 3.7 g/h. For alkaline ozonation, the pH of solution was adjusted to 13 by adding sodium hydroxide before ozone exposure. For neutral Fenton experiments, FeEDTA and H₂O₂ were introduced into the solution at a molar ratio of 1:10.

Table 1: Details of AOP experiments

Type of AOP	UVC Light Intensity (photon/s)	[H ₂ O ₂] (mg/L)	O ₃ (g/h)	[FeEDTA] (mg/L)	pH
UVC/H ₂ O ₂	5.3×10^{17}	200	-	-	No adjustment
UVC/O ₃	5.3×10^{17}	-	3.7	-	No adjustment
Alkaline O ₃	-	-	3.7	-	13
Neutral Fenton	-	3400	-	3670	No adjustment

2.2.2 Soil Flushing and AOP

A glass column with 1 inch inside diameter was filled with 45 g of processed soil containing 8000 mg/L of sulfolane. Water was added from the top of column and the leachate was collected from the bottom of soil column at different time intervals. The collected leachate (first 68 mL) was diluted 40 times with milli-Q water. The diluted sample was then treated with UVC/H₂O₂/O₃. The H₂O₂ concentration was set at 1000 mg/L, ozone flow rate was controlled at 3.7 g/h and the light intensity was about 5.3×10^{17} photons/s.

2.2.3 Sample Extraction and Sulfolane Analysis

Sulfolane was extracted from water samples by liquid/liquid extraction. A ratio of 5:3 of each water sample to dichloromethane (DCM) was used. Samples were shaken for 30 mins in a shaker (Model: SI-1100, Roto-Shake Genie) at 35 rpm. The extracted samples were left to stand for 5 mins to allow separation of water and DCM. Extracted sulfolane in DCM was then analyzed with gas chromatography equipped with flame ionization detector (Yu et al. 2016a).

3 3. RESULTS AND DISCUSSION

3.1 Integration of Soil Washing and AOP

Using water as the washing solvent, three consecutive cycles of soil washing resulted in more than 99% of sulfolane removal from the contaminated soil. The solution, obtained from soil washing, containing sulfolane was treated with different AOPs including (UVC/H₂O₂, UVC/O₃, alkaline ozonation and neutral Fenton) and the results are presented in Figure 2. The four AOPs can be classified into two major categories: UV assisted processes and non-UV assisted processes. All four AOPs showed their capabilities to degrade sulfolane in the soil washing solution. Based on the degradation of sulfolane, the four AOPs in descending order were: alkaline ozonation > UVC/O₃ > UVC/H₂O₂ > Neutral Fenton. The percentage of sulfolane removal after 20 mins of retention time was 97%, 83%, 70% and 43% for alkaline ozonation, UVC/O₃, UVC/H₂O₂ and neutral Fenton respectively. The degradation of sulfolane is due to its reaction with the highly reactive hydroxyl radicals generated during AOPs. Each AOP has a distinct pathway for the generation of hydroxyl radicals which are summarized in Table 2.

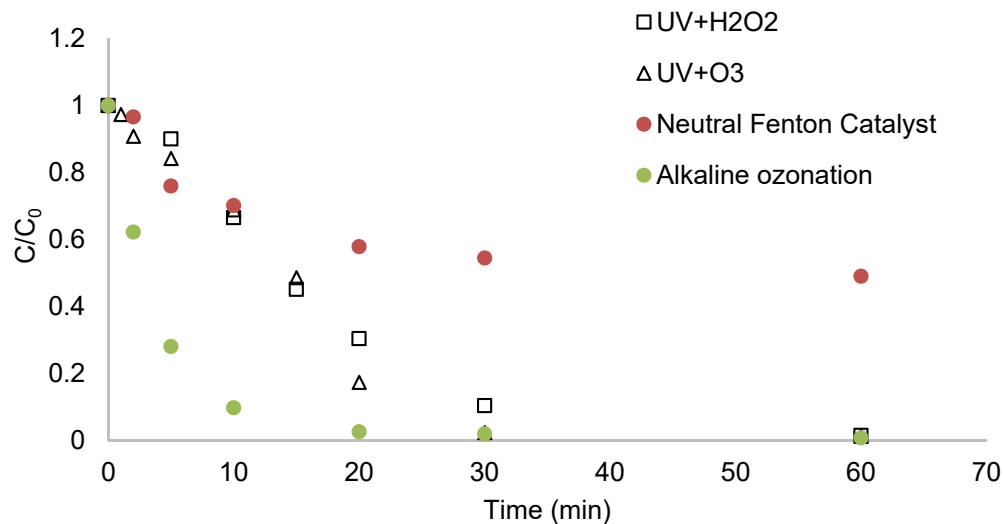


Figure 2. Sulfolane degradation in the soil washing water solution under different AOPs

Table 2: Reaction of different AOPs

Categories	Type of AOPs	Reactions
UV-based	UV/H ₂ O ₂	$H_2O_2 \xrightarrow{h\nu} HO \cdot + HO \cdot$
UV-based	UV/O ₃	$O_3 \xrightarrow{h\nu} O(D) + O_2$ $O(D) + H_2O \rightarrow H_2O_2$ $H_2O_2 \xrightarrow{h\nu} HO \cdot + HO \cdot$
Non-UV based	Alkaline Ozonation	$HO^- + O_3 \rightarrow O_2 + HO_2^-$ $HO_2^- + O_3 \rightleftharpoons HO_2 \cdot + O_3 \cdot^-$ $HO_2 \cdot \rightleftharpoons H^+ + O_2 \cdot^-$ $O_2 \cdot^- + O_3 \rightarrow O_2 + O_3 \cdot^-$ $O_3 \cdot^- + H^+ \rightarrow HO_3 \cdot$ $HO_3 \cdot \rightarrow HO \cdot + O_2$ $HO \cdot + O_3 \rightarrow HO_2 \cdot + O_2$
Non-UV based	Fenton process*	$Fe^{2+} + H_2O_2 \rightleftharpoons FeO^{2+} + H_2O$ $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH \cdot$ $Fe^{3+} + H_2O_2 \rightleftharpoons FeOOH^{2+} + H^+$ $FeOOH^{2+} \rightarrow HO_2 \cdot + Fe^{2+}$

During UVC/H₂O₂ process, each molecule of hydrogen peroxide can generate two moles of hydroxyl radicals under UV irradiation. The UVC/O₃ process produces hydroxyl radicals through initiating the reaction between ozone and UV photons. Both processes achieved more than 99% of sulfolane removal in 60 minutes, which are lower than the sulfolane degradation rate in ultrapure water reported by Yu et al. (2016a). In this study, the residual soil particles in the soil washing solution and other co-washing contaminants reduced the light intensity received by the target chemicals (H₂O₂, O₃ and sulfolane) as well as competed for hydroxyl radicals. In addition, hydrogen peroxide and ozone are strong oxidizers, they can be consumed by other organics. Ozonation with pH = 13 showed that 70% of sulfolane can be degraded within 2 mins. This is due to instant formation of hydroxyl radicals from the reaction between ozone and

hydroxide ions as shown in Table 2. For full scale applications, a pH adjustment step is required after this AOP treatment. Neutral Fenton reagent removed 45% of sulfolane in the first half hour but further exposure of 30 mins only improved the removal by 5%. The formation of yellow precipitate was formed during the degradation of sulfolane. As reported by Yu et al. (2016b), the catalytically active iron species precipitated out during the reaction and stopped the degradation of sulfolane. The advantages and disadvantages of these four methods are summarized in Table 3. It is noted that, each method is not optimized in this study. The comparison of these technologies was based on current experimental conditions.

Table 3. Comparison between different AOPs

Type of AOPs	pH Adjustment	UV requirement	Degradation rate	Formation of precipitates
UVC/H ₂ O ₂	No	Yes	Fast	-
UVC/O ₃	No	Yes	Fast	-
Alkaline Ozonation	Yes	No	Very fast	-
Neutral Fenton process	No	No	50% removal	Yes

3.2 Soil Flushing and AOP

Soil flushing is a more practical approach than soil washing processes for high conductivity soils as it does not require a soil/water separation step. The pictures of soil flushing solution during different periods are presented in Figure 3. From the images, it is observed that the color of soil flushing solution is dense yellow in the first few samples. The color of the collected leachate in the vials showed in Figure 3 is attenuated as the volume of water flushed accumulates from 2 mL to 152.9 mL. It means the organic matter in the soil, responsible for the strong yellow colour, is being flushed, as well as sulfolane. In that sense, it's important to consider that high organic load in the leachate can potentially affect pollutant degradation efficiency when conducting AOP in the presence of UV irradiation (Bandala et al, 2008). According to Figure 4, sulfolane concentration in the collected leachate dropped from 25000 mg/L to 200 mg/L after 68 mL of water had passed through the soil column. The equivalent sulfolane removal can be calculated from Equation [1].

$$[1] X_i(\%) = \frac{\int_0^{V_i} C dv}{\int_0^{V_T} C dv} \times 100$$

Where C (mg/L) is the concentration of sulfolane in the soil flushing solution; V_i (L) is the volume of water that passed through the soil column, V_T (L) is the total volume of water required to achieve 100% sulfolane removal, X_i (%) is the percentage of sulfolane removal from soil after V_i (L) of water passed through the column.

Figure 5 shows that more than 99% of sulfolane can be removed from the soil after flushing with 67 mL of water. The water/soil mass ratio to achieve 99% sulfolane removal is calculated to be 1.5, which is much lower than soil washing process. However, the flushing process is time-consuming for soils with low conductivity. In this study, it took more than 24 hours for 67 mL of water to pass through the soil column.




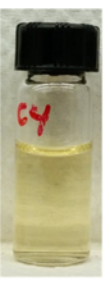


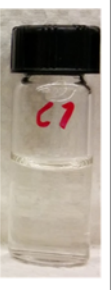

Color of water								
Cumulative volume of water flushed	2.0 ml	5.8 ml	8.9 ml	24.2 ml	67.6 ml	112.1 ml	136.9 ml	152.9 ml

Figure 3. Color change of soil flushing water

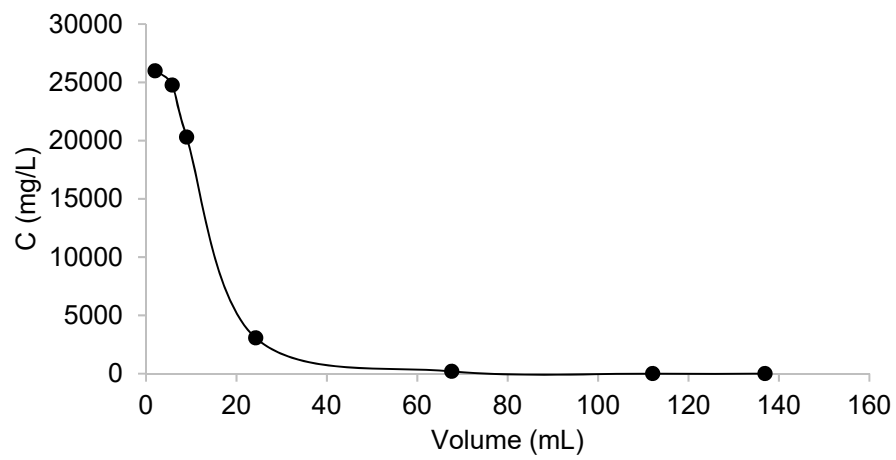


Figure 4. Change in sulfolane concentration in the flush water.

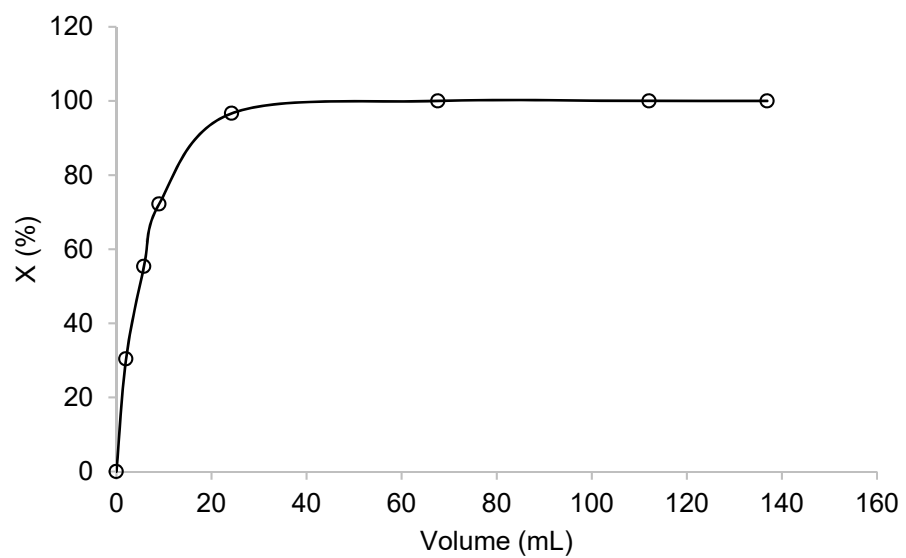


Figure 5. Percentage of sulfolane removal calculated based on Equation [1].

The collected leachate (soil flushing solution) was then exposed to UVC/H₂O₂/O₃ for degrading sulfolane. As a comparison, a similar experiment was conducted in ultrapure water and both results are reported in Figure 6. After 60 mins, more than 99% of sulfolane was degraded in the soil flushing samples. Sulfolane degradation in the ultrapure water was much faster, where it only took 30 mins to achieve 99% sulfolane removal. The soil flushing solution contains not only sulfolane, but all the inorganics and organic compounds found in the soil, such as metals, carbonates, humic substances and others. These co-elutes can reduce the UV light transmittance, consume oxidants and compete with hydroxyl radicals, all these leading to a less efficient sulfolane degradation.

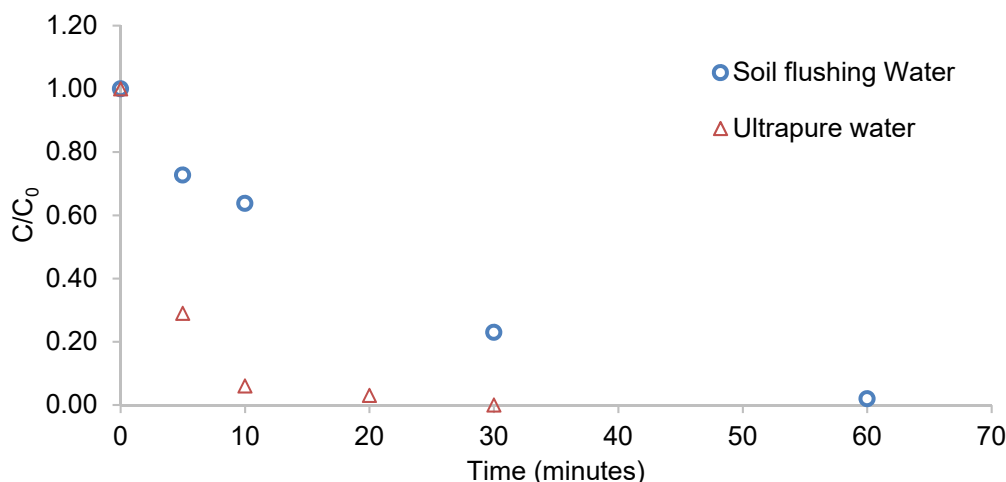


Figure 6. Degradation of sulfolane in the soil flushing solution and ultrapure water by using UV/H₂O₂/O₃; Light intensity = 5.3×10^{17} photon/s; O₃ flow rate = 3.7 g/h; H₂O₂ = 1000 mg/L

4 CONCLUSIONS

The soil washing/flushing processes integrated with AOPs are promising technologies to treat sulfolane contaminated soil. The specific conclusions drawn from this study are provided below:

- Three cycled soil washing can remove more than 99% of sulfolane from soil.
- 68 mL of water can remove more than 99% of sulfolane from 45 grams of soil.
- Alkaline ozonation yield the fastest sulfolane degradation in soil washing solution although it requires pH adjustment before and after treatment.
- UV combined with H₂O₂, ozone or H₂O₂/Ozone can completely degrade sulfolane from wash/flush water within one hour.
- Neutral Fenton reagent was not effective as a post soil washing/flushing treatment.
- Co-contaminants present in the soil washing/flushing samples decrease the AOP treatment efficiency.

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