

Article

# Advanced Oxidation Based Treatment of Soil Wash Water Contaminated with Sulfolane

Mariana Brandão <sup>1</sup>, Linlong Yu <sup>2,\*</sup>, Carlos Garcia <sup>1</sup> and Gopal Achari <sup>2</sup>

<sup>1</sup> Department of Water Resources, Federal University of Sergipe, Av. Marechal Rondon, São Cristóvão 49100-000, Brazil; mdjbrandao@gmail.com (M.B.); cgarcia@ufs.br (C.G.)

<sup>2</sup> Department of Civil Engineering, University of Calgary, 2500 University Drive NW, Calgary, AB T2N 1N4, Canada; gachari@ucalgary.ca

\* Correspondence: linyu@ucalgary.ca; Tel.: +1-403-220-5014

Received: 22 August 2019; Accepted: 9 October 2019; Published: 16 October 2019



**Abstract:** This study investigates advanced oxidation processes (AOPs) as post-treatment techniques to degrade sulfolane in soil washing water. Soil washing experiments were conducted with different soil/water ratios, shaking times, and number of extraction cycles. The soil wash water containing sulfolane was treated with four AOPs including H<sub>2</sub>O<sub>2</sub>/ultraviolet (UV), O<sub>3</sub>/UV, alkaline ozonation, and neutral Fenton reagent. Results show that sulfolane can be effectively removed from the soil using water as a washing solvent, where optimum conditions were found with 30 min of vigorous shaking, using 1:2 soil/water mass ratio, and a three-cycle extraction procedure. Moreover, the sulfolane in the soil wash water was also effectively degraded using appropriate AOPs. Among the four AOPs investigated, neutral Fenton was the least effective method to treat sulfolane in the wash water, while H<sub>2</sub>O<sub>2</sub>/UV, O<sub>3</sub>/UV, and alkaline ozonation can achieve more than 99% of sulfolane degradation within 1 h.

**Keywords:** advanced oxidation process; remediation; soil washing; sulfolane; UV

## 1. Introduction

Soil washing processes integrated with post-treatment technologies like bioremediation, phytoremediation, chemical oxidation, photocatalytic degradation, and electrokinetic remediation have been reported to effectively eliminate organic pollutants, such as polycyclic aromatic hydrocarbon (PAH), total petroleum hydrocarbons (TPH), polychlorinated biphenyls (PCBs), and other contaminants commonly found around oil and gas facilities sites [1–5]. However, this has never been attempted for sulfolane contaminated sites. Sulfolane (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>S) is a polar organosulfur solvent used for sweetening sour gas in the sulfinol® process. It is also used to extract aromatics from hydrocarbon mixtures. Due to its high aqueous solubility, and high mobility in the subsurface, sulfolane contamination can easily spread to significant distances. Although no studies have yet reported on sulfolane's effect on human health, it has been shown to be a toxic compound for rats and guinea pigs and has shown indicative signs of central nervous system (CNS) stimulation and/or depression at acute concentrations in mammals [6,7]. Leaks and spills of sulfolane and its consequent migration through the subsurface have led regulatory agencies to create guidelines for monitoring and treatment, while significant research is still being conducted [8–11]. So far, the only effective full-scale treatment technology for sulfolane contaminated soil is aerobic biodegradation which can be impacted by the availability of oxygen, nutrients, and the need of moderate temperature [12]. For cold places like Alaska and Canada, there is a need to develop abiotic methods to treat sulfolane in the soil. Thus, an ex situ soil washing integrated with advanced oxidation processes (AOPs) to treat the wash water was investigated.

AOPs are chemical oxidation methods used in water treatment to degrade organic chemicals due to the strong oxidizing potential of hydroxyl radicals (·OH) generated during reaction [13,14].

It has the ability to degrade sulfolane in water, producing non-toxic by-products and complete mineralization [9,15]. To facilitate the treatment, soil washing is used to extract the contaminants by water or organic surfactants [16]. Despite the higher cost, ex-situ treatment processes generally require less time to achieve contaminant cleanup when compared to in situ approaches. It is also easily monitored and uniform, offering greater control over the process [17]. In addition, the versatility of AOP is enhanced as it offers different possible processes for  $\cdot\text{OH}$  radical generation, which allows better compliance with specific treatment requirements. AOP represents a more reactive and therefore, more effective system when compared to conventional purification processes like biodegradation [18]. Yu et al. [8] demonstrated at laboratory scale that AOP was a feasible technology for sulfolane degradation in aqueous medium. The authors tested both synthetic water and contaminated groundwater samples, where the ultraviolet-C (UVC) combined with different oxidants (UVC/O<sub>3</sub>, UVC/H<sub>2</sub>O<sub>2</sub>, and UVC/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) led to up more than 99% sulfolane degradation. In contrast to aqueous spiked waters and contaminated groundwater, the composition of wash water is heterogeneous, as other compounds in soil might be present in the wash water.

This paper reports on sulfolane degradation in soil washing water by using AOP. The study initially focused on the evaluation of sulfolane removal efficiency by using water as a washing solvent. The impact of operational parameters such as water/soil ratios, mixing period, and number of cycles of soil washing was also determined. The soil washing technique with selected operational parameters were then integrated with four different AOPs including UVC/H<sub>2</sub>O<sub>2</sub>, UVC/O<sub>3</sub>, alkaline ozonation, and neutral Fenton. For each AOP treatment, the sulfolane degradation in different soil washing samples was studied. Chemical consumptions and degradation rate are two key evaluation factors for a cost-effective treatment technology. Therefore, the impact of different parameters (e.g., pH, concentration of H<sub>2</sub>O<sub>2</sub> and Ethylenediaminetetraacetic acid (EDTA) chelated iron, and O<sub>3</sub> flow rate) on the sulfolane degradation rate were also investigated in this study.

## 2. Materials and Methods

### 2.1. Chemicals

Sulfolane with 99% purity, dichloromethane (DCM) with 99.5% purity, ferric chloride with 97% purity, and hydrogen peroxide (ACS grade, 30%) were obtained from Sigma Aldrich, Canada; EDTA chelated iron (III) with 99% purity was purchased from J.T. Baker; sodium thiosulfate with 99.5% purity was obtained from British Drug Houses (BDH); sodium hydroxide with 97% purity was purchased from EMD Millipore. Milli-Q water was used to conduct soil washing experiments and to dilute the samples.

### 2.2. Experimental Procedure

#### 2.2.1. Soil Washing Standalone

The soil collected from a site contaminated with sulfolane contained 8.3% sand, 43% silt, and 48.6% clay. The soils were stored in an insulated container with the minimal headspace under ambient conditions. The soil washing experiments were conducted 7 days after soil collection from site. The impact of soil/water ratio, extraction period as well as number of cycles on sulfolane removal was investigated. The soil was hand crushed to fine particles with less than 0.2 cm in diameter. The fine soil samples were dried at 50 °C for two days. The dried contaminated soil was then passed through a size-20 sieve (850 micron) and homogenized by further mixing. Each 10 g of dried soil sample was placed in a 40-mL glass vial. Each vial was filled with a known amount of Milli-Q water and shaken for varying periods as shown in Table 1. The investigated soil/water (*w/w*) ratios were 1:1, 1:2, 1:3, while the investigated shaking periods were 30, 60, and 90 min. After shaking, each vial was centrifuged for 15 min at 1500 rpm. Following centrifugation, 2 mL of supernatant was then passed through a 0.45 μm filter to remove trace particles and then stored at 4 °C for sulfolane analysis. The remaining

solids in the vial were subjected to Soxhlet extraction with DCM. After Soxhlet, the extracts were carefully transferred into 250-mL beakers. The beakers containing extract were then placed inside of a well-ventilated fume hood, at room temperature, and evaporated to dryness. A total of 10 mL of the water was used to re-dissolve the dried solid in each beaker. After dissolution, the water was passed through a 0.22  $\mu\text{m}$  filter and kept for sulfolane analysis. For multiple-cycled soil washing, the same amount of water as the first cycle was added to the remaining soil in each cycle and extracted with the same shaking time. The extracts (supernatant) for each cycle were collected and kept for sulfolane analysis. All soil washing experiments were conducted in duplicates and the results were reported as averages with error bars.

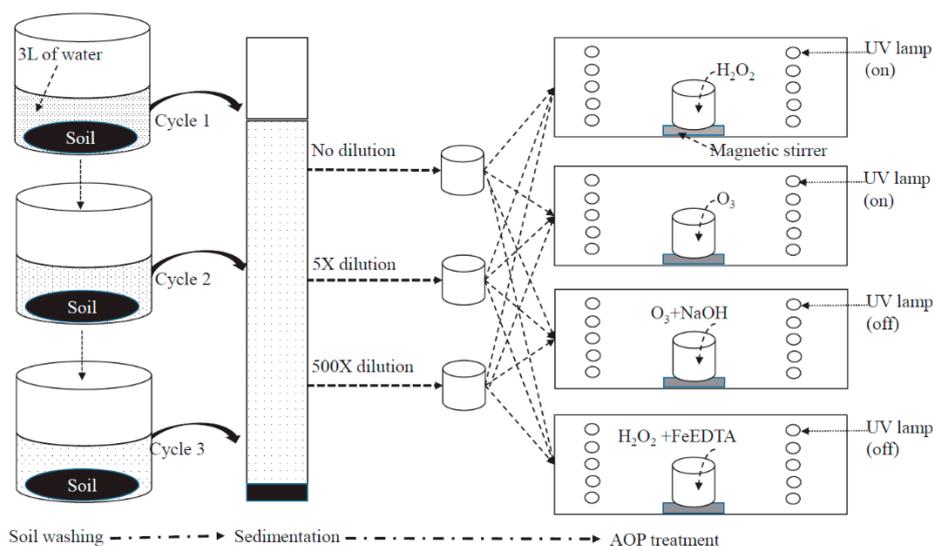
**Table 1.** Details of soil washing experiment.

Experiment No.	Soil/Water Ratio	Extraction Time per Cycle	No of Cycle
SW1	1:2	30 min	1
SW2	1:2	60 min	1
SW3	1:2	90 min	1
SW4	1:1	30 min	1
SW5	1:2	30 min	1
SW6	1:3	30 min	1
SW7	1:2	30 min	3

### 2.2.2. Advanced Oxidation Process Treatment of Soil Washing Water

The integration of soil washing and AOP treatment was conducted after one year of the original soil washing experiments. The original soil had been frequently exposed to the atmosphere during that period and no sulfolane was detected then due to aerobic biodegradation. Therefore, it is necessary to spike the soil with sulfolane to conduct this research. The soil with a 10% moisture was hand crushed into particles of less than 0.5 cm in diameter and passed through a size-4 sieve (5 mm). One and a half kilograms of sieved soil was then spiked with 900 mg of pure sulfolane and homogenized. The spiked soil was then sealed in a storage bag and kept in a freezer at  $-18\text{ }^{\circ}\text{C}$  for one week before soil washing/AOP integration study was initiated.

The experiment setup for soil washing-AOP integration is shown in Figure 1. One and a half kilograms of soil spiked with sulfolane was mixed with water vigorously (500 rpm) in a mechanical mixer (Velp F201A0152 Laboratory Mixer) through a three-cycle extraction procedure. For each cycle, water/soil ( $w/w$ ) ratio was set at 2:1 and the shaking time was set at 1 h. The soil wash water from each cycle was collected and combined in a 10-L column (ID = 15 cm) for sedimentation. After 24 h of sedimentation, 5 L of the supernatant was separated from the settled soil by a siphon. The supernatant was then placed in 1-L jars and stored at  $4\text{ }^{\circ}\text{C}$ . This supernatant is referred to as undiluted sample. One liter of undiluted sample was diluted five times, and another 1 L of undiluted sample was diluted 500 times. The soil washing solution with different dilutions were then treated with four different AOP technologies as shown in Figure 1.



**Figure 1.** Soil washing-advanced oxidation process (AOP) integration setup.

The investigated AOPs include UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, ozonation in alkaline condition, and neutral Fenton reagent. The details of each experiment including chemical dosage, pH, light condition, and sulfolane concentration are listed in Table 2 and described below:

- For UV/H<sub>2</sub>O<sub>2</sub> experiments, a Luzchem photoreactor equipped with 10 germicidal lamps (8 Watt LZC-UVC, Luzchem), was used. The photoreactor has a 30 cm wide, 30 cm deep, and 22 cm high chamber as shown in Figure S1. The chamber is made of aluminum alloy (Al 5052-H32), which can serve as good reflector. There are five lamps on each side of the chamber. The number of photons received by 100 mL solution in the quartz beaker per unit time was measured to be  $5.3 \times 10^{17}$  photon/s through ferrioxalate actinometry [19]. Four different H<sub>2</sub>O<sub>2</sub> dosages were applied to each diluted sample.
- For UV/O<sub>3</sub> experiments, ozone was generated through an O<sub>3</sub> generator (A2Z 5-G LAB, A2Z O<sub>3</sub> systems Inc.), which was introduced into the solution through a glass diffuser. Samples for each dilution were treated with four different ozone flow rates (1.9, 2.9, 3.7, and 4.3 g/h). The ozone flow rates were calculated based on ozone concentration in ozone generator outlet and the gas volumetric flow rate.
- For alkaline ozonation, sodium hydroxide was gradually added into the solution to adjust the pH from 10 to 13 before exposure to ozone. Ozone flow rate was kept at 3.7 g/h.
- For neutral Fenton experiments, FeEDTA and H<sub>2</sub>O<sub>2</sub> were introduced into the solution at a molar ratio of 1:10. The FeEDTA concentrations were 0.4 mM (147 mg/L), 2 mM (734 mg/L), and 10 mM (3670 mg/L). A total of 100 mg of sodium thiosulfate was used to quench the reaction.

Table 2. Details of AOP experiments.

Type of AOP	Dilution Factor	[Sulfolane] (mg/L)	Photon Flux * (photon/s)	[H <sub>2</sub> O <sub>2</sub> ] (mg/L)	O <sub>3</sub> (g/h)	[FeEDTA] (mg/L)	pH	
UVC/H <sub>2</sub> O <sub>2</sub>	1	100	$5.3 \times 10^{17}$	100	-	-	7	
				200				
				500				
				1000				
	5	20	$5.3 \times 10^{17}$	20	-	-	7	
				40				
				100				
				200				
	500	0.2	$5.3 \times 10^{17}$	5	-	-	7	
20								
40								
100								
UVC/O <sub>3</sub>	1	100	$5.3 \times 10^{17}$	-	1.9	-	7	
					2.9			
					3.7			
					4.3			
	5	20	$5.3 \times 10^{17}$	$5.3 \times 10^{17}$	-	1.9	-	7
						2.9		
						3.7		
						4.3		
	500	0.2	$5.3 \times 10^{17}$	$5.3 \times 10^{17}$	-	1.9	-	7
2.9								
3.7								
4.3								
Alkaline O <sub>3</sub>	1	100	-	-	3.7	-	10	
							11	
							12	
							13	
Alkaline O <sub>3</sub>	5	20	-	-	3.7	-	10	
							11	
							12	
							13	
Neutral Fenton	1	100	-	3400	-	3670	7	
				680		734		
				136		147		
	5	20	-	3400	-	3670	7	
				680		734		
				136		147		
	500	0.2	-	3400	-	3670	7	
				680		734		
				136		147		

\* the number of photons entering the 100 mL solution per unit time.

Each AOP experiment was conducted in batch mode in a 150 mL quartz reactor (D  $\frac{1}{4}$  59.0 mm) with 100 mL solution. A magnetic stirrer was used to keep the solutions homogeneous during experiments. For each experiment, 2.5 mL of duplicate water sample at different reaction periods was collected in 4-mL glass vials and stored for sulfolane analysis. The results are presented as the average with variation.

### 2.2.3. Extraction and GC Analysis

A total of 2.5 mL of water sample was extracted with 1.5 mL of DCM in a shaker with a shaking speed of 200 rpm. After 1 h vigorous shaking, 1 mL of the DCM layer at the bottom of the vial was analyzed with either a gas chromatography (GC) equipped with flame ionization detector (FID) or a GC equipped with mass spectrometry (MS). Extracts with high sulfolane concentrations were analyzed using an Agilent 6890 GC equipped with FID, while extracts with low sulfolane concentration (<1 mg/L) were analyzed with a Shimadzu QP2010SP GC-MS. The parameter settings for GC-FID and GC-MS are provided in Table 3.

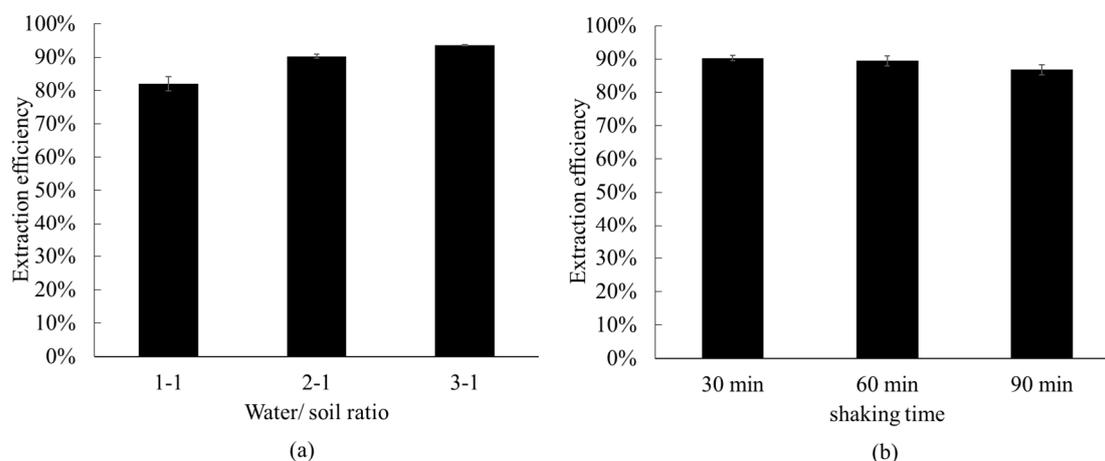
**Table 3.** Parameters setting for gas chromatography equipped with flame ionization detector (GC-FID) and GC equipped with mass spectrometry (GC-MS).

Parameters	GC-FID	GC-MS
GC column	ZB 5MSI (Phenomenex)	ZB 5MSI (Phenomenex)
Carrier gas type	helium	helium
Carrier gas program	constant pressure at 250 kPa	constant flow rate at 1.07 mL/min
Injection temperature	165 °C	250 °C
Injection volume	1.00 µL	1.00 µL
Mode of injection	splitless	splitless
Oven program	90 °C hold for 2 min; 10 °C/min to 175 °C; 175 °C hold for 3 min.	90 °C hold for 2 min; 10 °C/min to 160 °C; 20 °C/min to 280 °C; 280 °C hold for 2 min.
FID temperature	330 °C	\
Mode of MS	\	SIM
m/z	\	41, 56, and 120

## 3. Results and Discussions

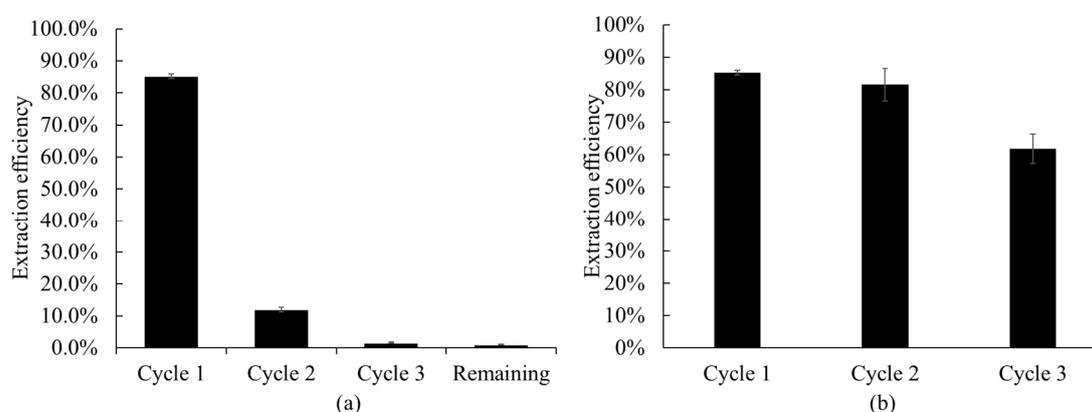
### 3.1. Soil Washing

The effect of water/soil ratio and shaking time on sulfolane removal is presented in Figure 2. The results show that more than 80% of sulfolane can be removed from soils by using water as a washing solvent. The increase of water/soil ratio from 1:1 to 3:1 improved the extraction efficiency from 82% to 93%. The variation in shaking period had almost no effect on extraction efficiency, indicating that sulfolane partition between soil and water reached equilibrium within 30 min.



**Figure 2.** Sulfolane removal by soil washing; (a) different water/soil ratios with 30 min shaking; (b) different shaking periods with water/soil ratio = 2:1. The error bars represent the variation of duplicates.

Sulfolane removal using a three-cycle soil washing is shown in Figure 3. Figure 3a presents the sulfolane removal for each cycle and Figure 3b summarizes the extraction efficiency for each cycle. The overall sulfolane removal after three cycles was about 99%. The percentage removal for cycle 1, cycle 2, and cycle 3 were 85.2%, 12%, and 1.7% respectively and the extraction efficiency for cycle 1, cycle 2, and cycle 3 were 85.2%, 81.6%, and 61.8%. The highest extraction efficiency was reported after cycle 1 when sulfolane was removed from the largest pores in the soil. In the following cycles the extraction became more difficult since the residual sulfolane must be removed from smaller pores. It is noted that the treated soil consisted of 48.6% clay and sulfolane can be adsorbed into the outside surfaces as well as the interlayer space of clay minerals [20]. It is understood that after the first wash the structure of the soil changes and soil particles become redistributed [21], therefore, the interaction between water and the smaller pores is facilitated. Many organic pollutants need a surfactant to enhance solubility and enable the use of soil washing technology [22], but considering that sulfolane is highly miscible in water, repeating the wash procedure can achieve good results.



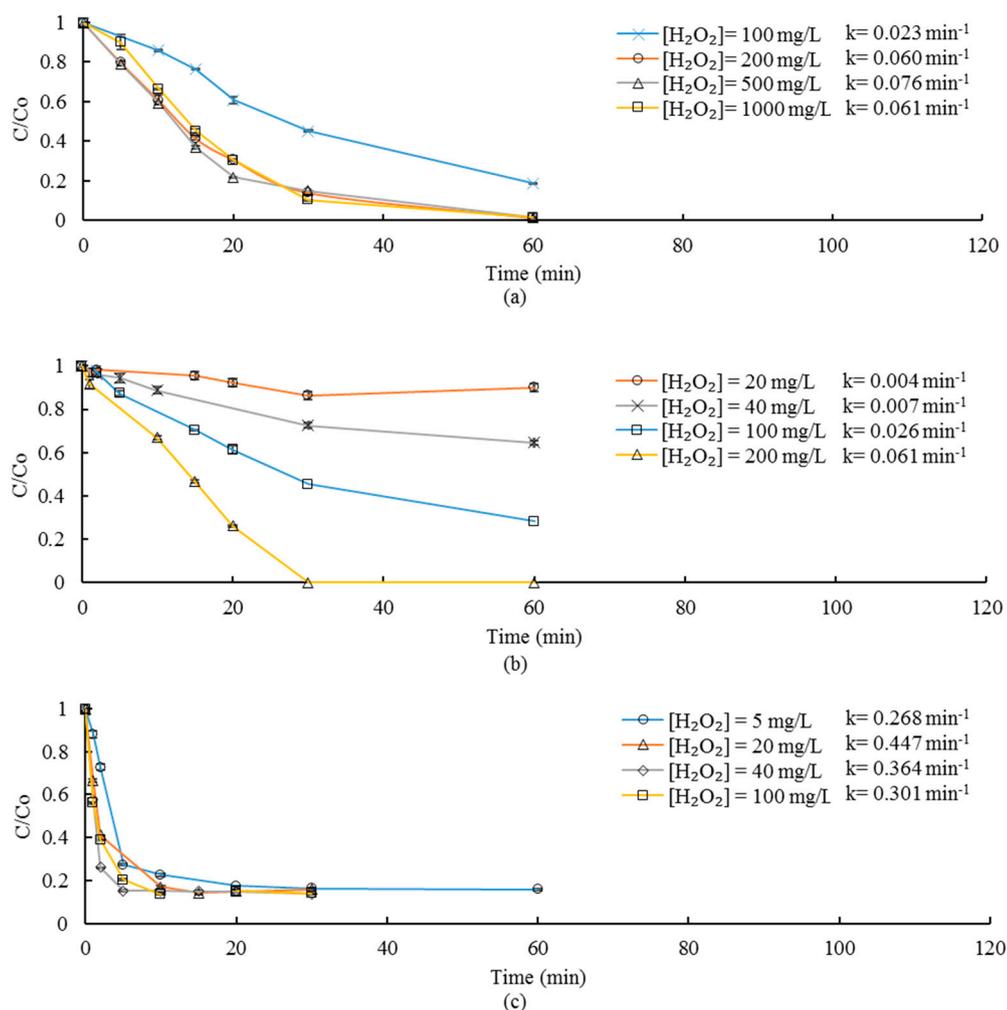
**Figure 3.** Sulfolane removal using a three-cycle soil washing; (a) the percentage sulfolane removal for each cycle and (b) the extraction efficiency for each cycle. The error bars represent the variation of duplicates.

### 3.2. AOP as a Post Soil Washing Treatment

The soil washing results in Section 3.1 indicate that water wash of sulfolane is feasible and most of the sulfolane was transferred to aqueous phase. Four different AOPs including UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, alkaline ozonation, and neutral Fenton were evaluated in this study as treatment options for the sulfolane in the wash water. It is noted that our previous results showed that no sulfolane degradation was observed in UV alone, H<sub>2</sub>O<sub>2</sub> alone, ozone alone, or FeEDTA alone within 1 h (data not published here). To evaluate the impact of dilution on AOP treatment, each AOP was evaluated with three different diluted soil wash water (SWW). They were (a) undiluted, (b) 5 × diluted, and (c) 500 × diluted.

#### 3.2.1. UV/H<sub>2</sub>O<sub>2</sub>

The degradation of sulfolane in different diluted SWW with varied H<sub>2</sub>O<sub>2</sub> concentrations are shown in Figure 4. The results show that sulfolane in different diluted SWW can be completely degraded in 1 h by UVC in combination with 200 mg/L of hydrogen peroxide. It was found that sulfolane degradation was not complete when H<sub>2</sub>O<sub>2</sub> concentration was less than 100 mg/L, in which cases only 72% to 85% sulfolane was degraded. In this study, the hydrogen peroxide was not continuously introduced into the system but added once in the beginning. Hydrogen peroxide can decompose upon UVC irradiation and therefore not be available after a certain period of UVC exposure.



**Figure 4.** Sulfolane degradation in soil wash water (SWW) with UV/H<sub>2</sub>O<sub>2</sub>; (a) no dilution, Co = 100 mg/L; (b) 5 × dilution, Co = 20 mg/L; (c) 500 × dilution, Co = 0.2 mg/L. The error bars represent the variation of duplicates.

As shown in Figure 4, the initial sulfolane degradation rates depended on hydrogen peroxide concentration and the optimal H<sub>2</sub>O<sub>2</sub> concentration varied with dilution factors. In Figure 4a, where SWW was not diluted, sulfolane degraded three times faster when H<sub>2</sub>O<sub>2</sub> concentration increased from 100 to 200 mg/L. However, further increase of hydrogen peroxide did not significantly increase the sulfolane degradation rate. The optimal concentration of H<sub>2</sub>O<sub>2</sub> was determined to be 200 mg/L. Yu et al., [8] degraded 100 mg/L of sulfolane in ultrapure water with UVC /H<sub>2</sub>O<sub>2</sub> (from 25 to 500 mg/L) and reported similar findings. Their peak rate was found at 100 mg/L of H<sub>2</sub>O<sub>2</sub> which is lower than ours. The presence of soil particles, carbonates, and humic matter and other co-contaminants led to a higher hydrogen peroxide requirement in this study. In Figure 4b, where SWW was diluted five times, sulfolane degradation rate increased with H<sub>2</sub>O<sub>2</sub> concentration, indicating that the optimal H<sub>2</sub>O<sub>2</sub> concentration is 200 mg/L or higher. In Figure 4c, where SWW was diluted 500 times, the optimal H<sub>2</sub>O<sub>2</sub> concentration was found to be 20 mg/L, which was much lower than undiluted or five-time dilution. Higher degradation rates are usually observed at higher hydrogen peroxide concentrations due to reactive radical species (hydroxyl radicals) generation through H<sub>2</sub>O<sub>2</sub> molecules decomposition [23]. Studies have reported that at high doses the excess H<sub>2</sub>O<sub>2</sub> did not enhance the degradation rate, sometimes even inhibit the reaction [24]. The negative impact of excess H<sub>2</sub>O<sub>2</sub> on degradation rates can be related to its scavenging effects [25,26]. The excess H<sub>2</sub>O<sub>2</sub> molecules can react with hydroxyl radicals to form hydroperoxyl radicals [26,27].

The impact of dilution on sulfolane degradation was determined by comparing the sulfolane degradation rates in different diluted samples with 100 mg/L of H<sub>2</sub>O<sub>2</sub>. It was found that low dilutions did not impact the degradation kinetics, but a high dilution factor can significantly increase the degradation rate. The initial degradation rates for undiluted, 5 × diluted and 500 × diluted samples were 0.023, 0.026, and 0.301 min<sup>-1</sup>. It is noted that through dilution the concentration of both co-contaminant and sulfolane decreased. The reduction of co-contaminant led to faster sulfolane degradation. Furthermore, the sulfolane degradation kinetics were impacted by sulfolane concentration. Higher initial contaminant concentrations have been reported to decrease degradation rate constants with UV/H<sub>2</sub>O<sub>2</sub> systems [28].

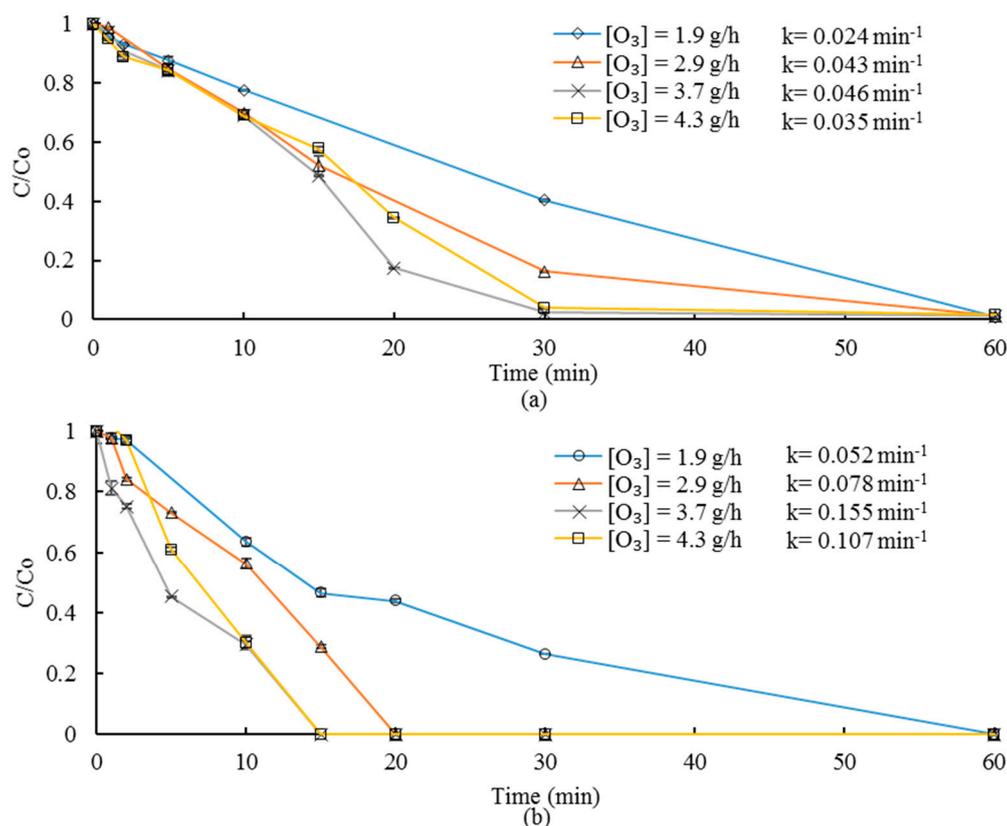
To determine whether dilution can reduce the overall photon energy consumption in this study, the photon energy required to remove 90% of sulfolane (one order reduction) from original SWW was calculated for different dilution scenarios and summarized in Table 4. As shown in Table 4, with 20 mg/L of H<sub>2</sub>O<sub>2</sub>, the photon energy requirement slightly decreased (from 186.45 to 171.71 kWh/m<sup>3</sup>) as the dilution factor increased. However, with 40, 100, and 200 mg/L of H<sub>2</sub>O<sub>2</sub>, the amount of energy required to treat sulfolane increased as the dilution factor increased. Dilution can be a practical approach to treat the waters containing high organic content and low UV transmittance. Nonetheless, it leads to higher volumes of water to be treated. The overall impact of dilution on photon energy requirement for sulfolane degradation depends on (1) how much can the degradation rates be improved as a result of dilution and (2) how much more water needs to be treated through dilution.

**Table 4.** Photon energy required to remove 90% of sulfolane from the original soil wash water under different dilution scenarios.

[H <sub>2</sub> O <sub>2</sub> ] mg/L	Photon Energy Required to Remove 90% of Sulfolane from the Wash Water (kWh/m <sup>3</sup> )		
	Undiluted	5× Dilution	500× Dilution
5	/	/	286.39
20	/	186.45	171.71
40	/	103.96	210.85
100	6.52	29.26	254.99
200	2.54	12.58	/
500	2.02	/	/
1000	2.50	/	/

### 3.2.2. UV/O<sub>3</sub>

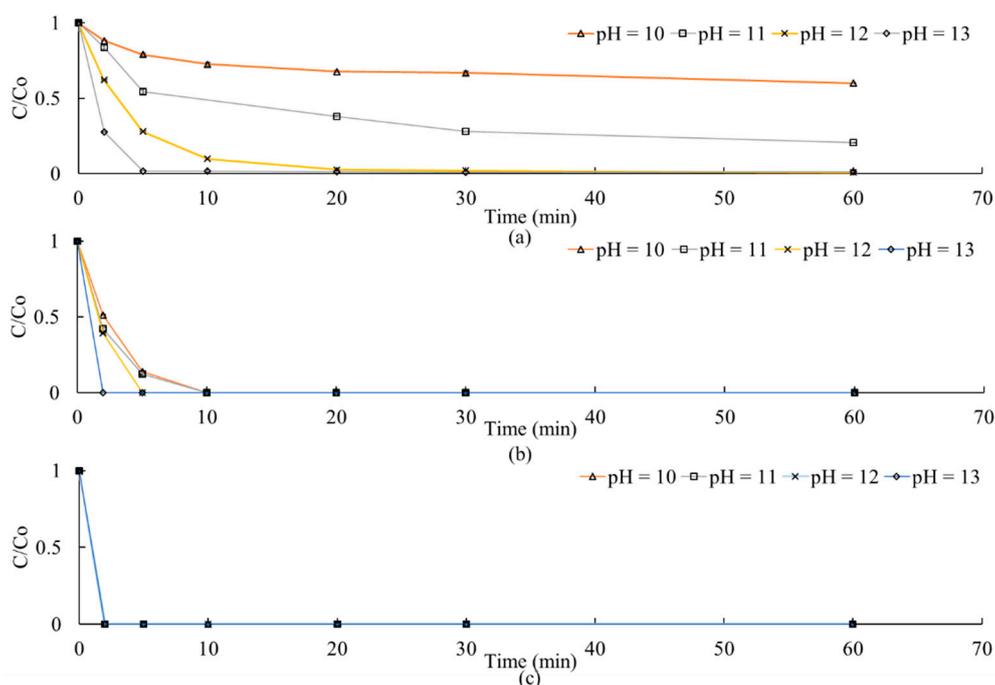
The degradation of sulfolane in SWW with different O<sub>3</sub> flow rates is shown in Figure 5. No sulfolane was detected in the soil washing solutions after 1 h of ozonation with UVC irradiation. In Figure 5a, where SWW was not diluted, sulfolane degradation rate doubled when O<sub>3</sub> flow rate increased from 1.9 to 3.7 g/h. Nonetheless, further increase of ozone decreased the sulfolane degradation rate. Usually, higher ozone flow rate with UVC irradiation provides more available radicals for sulfolane and its degradation by-products. However, in a batch reactor with a small space (200 mL), high ozone flow rate generated numerous ozone/oxygen bubbles. These bubbles reflected UV photons and changed the direction of radiation, both leading to less UV photons entering the water phase where the sulfolane degradation occurred. Therefore, an optimal ozone flow existed for a small batch reactor. The optimal flow rate of ozone for this study was determined to be 3.7 g/h and the corresponding degradation rate was 0.043 min<sup>-1</sup>. Similarly, in Figure 5b, where SWW was diluted five times, sulfolane degradation rate continuously increased until it peaked at 3.7 g/h. The sulfolane degradation rate with 3.7 g/h ozone was 0.155 min<sup>-1</sup>, which was higher than undiluted samples. This is because in undiluted samples, the co-contaminants competed with sulfolane for ozone and hydroxyl radicals.



**Figure 5.** Sulfolane degradation in SWW with UV/O<sub>3</sub>; (a) no dilution,  $C_0 = 100$  mg/L and (b) 5 × dilution.  $C_0 = 20$  mg/L. The error bars represent the variation of duplicates.

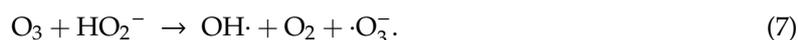
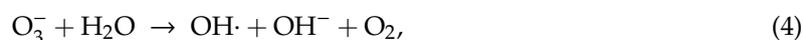
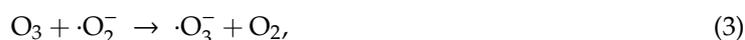
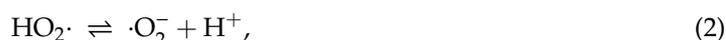
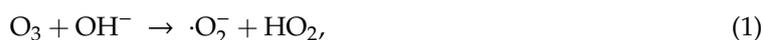
### 3.2.3. Alkaline Ozonation

The degradation of sulfolane by ozone under different alkaline conditions ( $pH = 10\sim 13$ ) is presented in Figure 6. Generally, a higher pH leads to a higher sulfolane degradation rate. In undiluted SWW with  $pH = 10$ , 33% of sulfolane degradation was observed after 30 min of ozone bubbling. The percentage degradation increased to > 99% when the pH was adjusted to 13. A similar trend is observed for 5 × diluted SWW samples. For 500 × diluted SWW samples, the degradation of sulfolane was quite fast and no sulfolane was detected in the waters after 2 min. Like other AOPs, sulfolane degradation rate can be increased through dilution. At  $pH = 10$ , the percentage of sulfolane degradation was 12%, 45%, and 100%, respectively for undiluted samples, 5 × diluted samples, and 500 × diluted samples.



**Figure 6.** Sulfolane degradation in SWW with alkaline ozonation; (a) no dilution, (b) 5 × dilution, and (c) 500 × dilution. The error bars represent the variation of duplicates.

Ozone can degrade the contaminants through two major routes: (1) direct oxidation by ozone, and (2) through the generation of hydroxyl radicals. High pH can cause a short half-life of ozone in water and result a low degradation rate controlled by the first mechanism [29,30]. Staehelin and Hoigne [30] reported that the half-life of ozone in water can be reduced from 4000 to 40 s, when pH is increased from 8 to 10. On the other side, high pH can enhance the generation of hydroxyl radicals and increase the degradation rates controlled by the latter mechanism. Staehelin and Hoigne [30] proposed two possible pathways on the reaction between ozone and hydroxide ion as shown in Equations (1)–(4) and Equations (5)–(7).

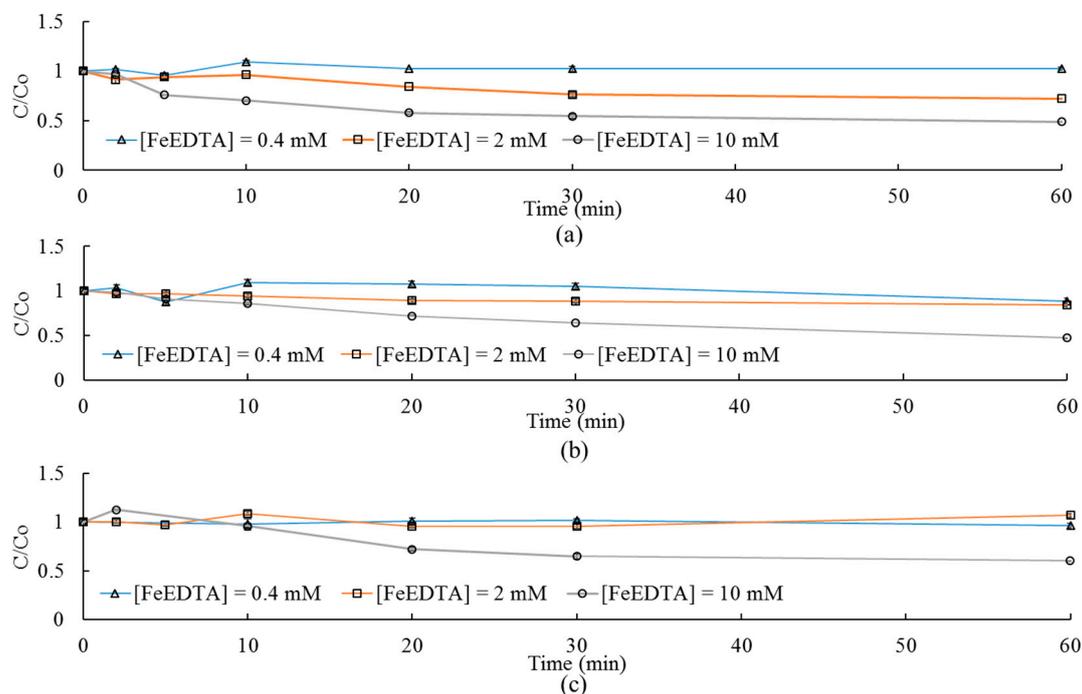


Both reaction pathways lead to the generation of hydroxyl radicals. The stoichiometric yield of hydroxyl radical with ozone and hydroxide was determined to be 0.55 at pH = 14. The results in this study indicate that sulfolane degradation by ozone is mainly through the reaction with the generated hydroxyl radical and not direct oxidation. An alkaline condition is required for fast sulfolane degradation. Under neutral or acidic condition, ozone cannot effectively breakdown sulfolane. Yu et al. [8] reported on the degradation of 100 mg/L of sulfolane in ultrapure water with ozone without pH adjustment and achieved a much lower degradation rate compared to other AOPs based on the hydroxyl radicals.

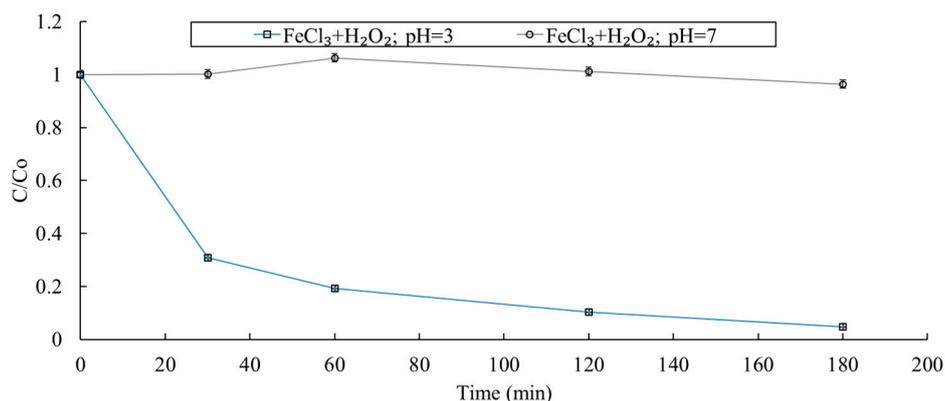
### 3.2.4. Neutral Fenton

The original Fenton reaction uses iron as a catalyst in acidic conditions to generate hydroxyl radicals from hydrogen peroxide. To facilitate real applications at near neutral pH, modified processes have been developed, which uses chelated iron for catalyzing the reaction. EDTA is one chemical used to chelate iron that has indicated promise [31]. In this study, sulfolane degradation in SWW with different levels of FeEDTA were investigated and the results are presented in Figure 7. In addition, as control experiments, the degradation of sulfolane in the spiked water using Fenton-like reagents were conducted at different pH and the results are reported in Figure 8. The results indicated that sulfolane can be degraded by  $\text{FeCl}_3 + \text{H}_2\text{O}_2$  when pH of water was kept at 3. Approximately 60% of sulfolane degraded after 1 h and more than 95% of sulfolane degraded after 3 h at pH of 3. The degradation of sulfolane was due to the generated hydroxyl radicals through Fenton-like reactions. No sulfolane degradation was observed at neutral pH using  $\text{FeCl}_3 + \text{H}_2\text{O}_2$ . For soil washing samples, the results (Figure 7) with low FeEDTA/ $\text{H}_2\text{O}_2$  dosage were very similar to control experiments at neutral pH. However, with 10 mM of FeEDTA and 100 mM  $\text{H}_2\text{O}_2$ , 40%~50% of sulfolane was degraded after 1 h for different dilutions of SWW. In general, better results are obtained at higher quantities of chelated iron as more catalytic Fe(III) is solubilized in the water and enables the Fenton reaction to occur. The sulfolane removal with neutral Fenton was relatively low in this study. Therefore, the neutral Fenton method is not suggested as a post soil washing treatment.

Yu et al. [32] also found low degradation when treating sulfolane contaminated groundwater with EDTA chelated iron and hydrogen peroxide at neutral conditions [32]. In their study, around 50% of sulfolane was removed after 30 min and then the reaction ceased. The author explained that the reaction ceased due to precipitation of catalytic iron which was also observed in this study.



**Figure 7.** Sulfolane degradation in SWW with neutral Fenton; (a) no dilution, (b) 5 × dilution, and (c) 500 × dilution. The error bars represent the variation of duplicates.



**Figure 8.** Degradation of sulfolane using Fenton like reagent in synthetic water:  $[\text{FeCl}_3] = 1 \text{ mM}$ ;  $[\text{H}_2\text{O}_2] = 15 \text{ mM}$ ,  $[\text{sulfolane}] = 100 \text{ mg/L}$ . The error bars represent the variation of duplicates.

#### 4. Conclusions

This study demonstrated that soil washing using water as a washing solvent integrated with appropriate AOP technologies can effectively treat sulfolane in contaminated soils. A total of 82%–93% of sulfolane can be removed through soil washing with the investigated water/soil ratios (1:1, 1:2, and 1:3) and shaking times (30, 60, and 90 min). The extraction efficiency for each cycle decreased as the number of wash cycles increased. A three-cycle soil washing procedure can remove about 99% of sulfolane from soil. Sulfolane degradation in soil wash water with different AOPs are summarized as below:

- UVC irradiation combined with appropriate  $\text{H}_2\text{O}_2$  concentration can remove more than 99% of sulfolane within 1 h. The suitable  $\text{H}_2\text{O}_2$  concentration was determined to be 200 mg/L in undiluted sample, leading to a  $k$  value of  $0.06 \text{ min}^{-1}$ . UVC assisted ozonation can effectively degrade sulfolane within 30 min. The suitable ozone flow rate was determined to be 3.7 g/h.
- Ozonation with higher pH can increase the sulfolane degradation in soil wash water.
- Neutral Fenton reagents perform poorly in sulfolane removal. Less than 50% of sulfolane removal were observed within 1 h.
- Dilution can increase sulfolane degradation kinetics for all AOP treatments. Neutral Fenton is least sensitive to dilution effect, whereas alkaline ozonation is highly sensitive to dilution.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4441/11/10/2152/s1>, Figure S1: Diagram of the photoreactor.

**Author Contributions:** Methodology, M.B., L.Y. and G.A.; Investigation, M.B. and L.Y.; Data Curation, M.B. and L.Y.; Writing—Original Draft Preparation, M.B. and L.Y.; Writing—Review and Editing, L.Y., G.A. and C.G.; Supervision, G.A. and C.G.; Project Administration, G.A.

**Funding:** This research was funded by Natural Sciences and Engineering Research Council of Canada, grant number 10012306 and the APC was funded by Natural Sciences and Engineering Research Council of Canada.

**Acknowledgments:** The authors acknowledge the financial support provided by NSERC, MITACS, and Bonavista Energy Corporation to conduct this research.

**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. Gan, S.; Lau, E.V.; Ng, H.K. Remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs). *J. Hazard. Mater.* **2009**, *172*, 532–549. [[CrossRef](#)] [[PubMed](#)]
2. Mousset, E.; Huguenot, D.; van Hullebusch, E.D.; Oturan, N.; Guibaud, G.; Esposito, G.; Oturan, M.A. Impact of electrochemical treatment of soil washing solution on PAH degradation efficiency and soil respirometry. *Environ. Pollut.* **2016**, *211*, 354–362. [[CrossRef](#)] [[PubMed](#)]

3. Lee, M.; Kang, H.; Do, W. Application of nonionic surfactant-enhanced in situ flushing to a diesel contaminated site. *Water Res.* **2005**, *39*, 139–146. [[CrossRef](#)] [[PubMed](#)]
4. Baziar, M.; Mehrasebi, M.R.; Assadi, A.; Fazli, M.M.; Maroosi, M.; Rahimi, F. Efficiency of non-ionic surfactants-EDTA for treating TPH and heavy metals from contaminated soil. *J. Environ. Health Sci. Eng.* **2013**, *11*, 41. [[CrossRef](#)] [[PubMed](#)]
5. Ma, X.-H.; Zhao, L.; Lin, Z.-R.; Dong, Y.-H. Soil washing in combination with homogeneous Fenton-like oxidation for the removal of 2,4,4'-trichlorodiphenyl from soil contaminated with capacitor oil. *Environ. Sci. Pollut. Res.* **2016**, *23*, 7890–7898. [[CrossRef](#)]
6. Gordon, C.J.; Dyer, R.S.; Long, M.D.; Fehlner, K.S. Effect of sulfolane on behavioral and autonomic thermoregulation in the rat. *J. Toxicol. Environ. Health* **1985**, *16*, 461–468. [[CrossRef](#)]
7. Zhu, Z.H.; Sun, M.L.; Li, Z.S.; Yang, Z.C.; Zhang, T.B.; Heng, Z.C.; Xiao, B.L.; Li, Q.Y.; Peng, Q.Y.; Dong, Y.H. [An investigation of the maximum allowable concentration of sulfolane in surface water]. *Hua Xi Yi Ke Da Xue Xue Bao* **1987**, *18*, 376–380.
8. Yu, L.; Mehrabani-Zeinabad, M.; Achari, G.; Langford, C.H. Application of UV based advanced oxidation to treat sulfolane in an aqueous medium. *Chemosphere* **2016**, *160*, 155–161. [[CrossRef](#)]
9. Izadifard, M.; Achari, G.; Langford, C.H. Degradation of sulfolane using activated persulfate with UV and UV-Ozone. *Water Res.* **2017**, *125*, 325–331. [[CrossRef](#)]
10. Khan, M.F.; Yu, L.; Achari, G.; Tay, J.H. Degradation of sulfolane in aqueous media by integrating activated sludge and advanced oxidation process. *Chemosphere* **2019**, *222*, 1–8. [[CrossRef](#)]
11. Khan, M.F.; Yu, L.; Tay, J.H.; Achari, G. Coaggregation of bacterial communities in aerobic granulation and its application on the biodegradation of sulfolane. *J. Hazard. Mater.* **2019**, *377*, 206–214. [[CrossRef](#)] [[PubMed](#)]
12. Saint-Fort, R. Sulfolane attenuation by surface and subsurface soil matrices. *J. Environ. Sci. Health A* **2006**, *41*, 1211–1231. [[CrossRef](#)] [[PubMed](#)]
13. Ayoub, K.; van Hullebusch, E.D.; Cassir, M.; Bermond, A. Application of advanced oxidation processes for TNT removal: A review. *J. Hazard. Mater.* **2010**, *178*, 10–28. [[CrossRef](#)] [[PubMed](#)]
14. Rosas, J.M.; Vicente, F.; Santos, A.; Romero, A. Soil remediation using soil washing followed by Fenton oxidation. *Chem. Eng. J.* **2013**, *220*, 125–132. [[CrossRef](#)]
15. Mehrabani-Zeinabad, M.; Yu, L.; Achari, G.; Langford, C.H. Mineralisation of sulfolane by UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> in a tubular reactor. *J. Environ. Eng. Sci.* **2016**, *11*, 44–51. [[CrossRef](#)]
16. Mao, X.; Jiang, R.; Xiao, W.; Yu, J. Use of surfactants for the remediation of contaminated soils: A review. *J. Hazard. Mater.* **2015**, *285*, 419–435. [[CrossRef](#)]
17. Kuppusamy, S.; Palanisami, T.; Megharaj, M.; Venkateswarlu, K.; Naidu, R. Ex-Situ Remediation Technologies for Environmental Pollutants: A Critical Perspective. In *Reviews of Environmental Contamination and Toxicology*; de Voogt, P., Ed.; Reviews of Environmental Contamination and Toxicology; Springer: Cham, Germany, 2016; Volume 236, pp. 117–192. ISBN 978-3-319-20013-2.
18. Andreozzi, R.; Caprio, V.; Insola, A.; Marotta, R. Advanced oxidation processes (AOP) for water purification and recovery. *Catal. Today* **1999**, *53*, 51–59. [[CrossRef](#)]
19. Goldstein, S.; Rabani, J. The ferrioxalate and iodide–iodate actinometers in the UV region. *J. Photochem. Photobiol. A Chem.* **2008**, *193*, 50–55. [[CrossRef](#)]
20. Luther, S.M.; Dudas, M.J.; Fedorak, P.M. Sorption of sulfolane and diisopropanolamine by soils, clays and aquifer materials. *J. Contam. Hydrol.* **1998**, *32*, 159–176. [[CrossRef](#)]
21. Kemper, W.D.; Rosenau, R.C. Aggregate Stability and Size Distribution 1. In *Methods of Soil Analysis: Part 1—Physical and Mineralogical Methods*; The American Society of Agronomy and Academic Press: New York, USA, 1986; pp. 425–442.
22. Trellu, C.; Mousset, E.; Pechaud, Y.; Huguenot, D.; van Hullebusch, E.D.; Esposito, G.; Oturan, M.A. Removal of hydrophobic organic pollutants from soil washing/flushing solutions: A critical review. *J. Hazard. Mater.* **2016**, *306*, 149–174. [[CrossRef](#)]
23. Legrini, O.; Oliveros, E.; Braun, A.M. Photochemical processes for water treatment. *Chem. Rev.* **1993**, *93*, 671–698. [[CrossRef](#)]
24. Zanta, C.L.P.S.; Martínez-Huitle, C.A. Degradation of 2-hydroxybenzoic acid by advanced oxidation processes. *Braz. J. Chem. Eng.* **2009**, *26*, 503–513. [[CrossRef](#)]
25. Watts Richard, J.; Teel Amy, L. Chemistry of Modified Fenton's Reagent (Catalyzed H<sub>2</sub>O<sub>2</sub> Propagations–CHP) for In Situ Soil and Groundwater Remediation. *J. Environ. Eng.* **2005**, *131*, 612–622. [[CrossRef](#)]

26. Christensen, H.; Sehested, K.; Corfitzen, H. Reactions of hydroxyl radicals with hydrogen peroxide at ambient and elevated temperatures. *J. Phys. Chem.* **1982**, *86*, 1588–1590. [[CrossRef](#)]
27. Pignatello, J.J.; Oliveros, E.; MacKay, A. Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry. *Crit. Rev. Environ. Sci. Technol.* **2006**, *36*, 1–84. [[CrossRef](#)]
28. Muruganandham, M.; Swaminathan, M. Photochemical oxidation of reactive azo dye with UV–H<sub>2</sub>O<sub>2</sub> process. *Dye. Pigment.* **2004**, *62*, 269–275. [[CrossRef](#)]
29. Forni, L.; Bahnemann, D.; Hart, E.J. Mechanism of the hydroxide ion-initiated decomposition of ozone in aqueous solution. *J. Phys. Chem.* **1982**, *86*, 255–259. [[CrossRef](#)]
30. Staehelin, J.; Hoigne, J. Decomposition of ozone in water: Rate of initiation by hydroxide ions and hydrogen peroxide. *Environ. Sci. Technol.* **1982**, *16*, 676–681. [[CrossRef](#)]
31. De Luca, A.; Dantas, R.F.; Esplugas, S. Assessment of iron chelates efficiency for photo-Fenton at neutral pH. *Water Res.* **2014**, *61*, 232–242. [[CrossRef](#)]
32. Yu, L.; Achari, G.; Langford, C.H.; Keir, I. A feasibility study on sulfolane degradation in groundwater using neutral fenton catalysts. In Proceedings of the CSCE 2016, London, ON, Canada, 1–4 June 2016.



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).