EFFICIENCY OF SOIL WASHING IN HYDROCARBON REMOVAL: THE ROLE OF TEMPERATURE, SURFACTANT CONCENTRATION AND SOIL MINERALOGY

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INTRODUCTION

The object of this work is to evaluate the effect of variations in the type and concentrations of surfactants, washing temperature and, most importantly, mineral composition of the soil on the efficiency of soil washing with specific reference to the soils of the Marche Region.

In the Marche Region, the four main types of contaminated sites are industrial sites (35.8%), gas stations (28.4%), waste disposal sites (2.8%) and other (33%, comprising fuel spills linked to traffic accidents and underground storage tank leaks). With gas stations representing almost one third of contaminated sites in the Marche Region, understanding the best way to tackle this type of contamination in reference to soils present in the Region is of paramount importance. In a soil-water system, hydrocarbon compounds, such as those present in gasoline and diesel, tend to adsorb to mineral surfaces. Although the most common method of treating contaminated sites across Europe and Italy continues to be landfilling, increasing restrictions and the availability of viable alternative methods have resulted in a rise in the use of other *in situ* and *ex situ* treatments methods, such as soil washing (Van Liedekerke *et al*., 2014).

Soil washing is an *ex situ* water-based remediation technology that utilizes a combination of physical processes to concentrate the contaminants in a smaller soil volume and chemical processes to extract them. The contaminant classes successfully removed by this process include petroleum and fuel residues, radionuclides, heavy metals, PCBs (polychlorinated biphenyls), PCP (pentachlorophenol), pesticides, cyanides, creosote, semivolatiles, and volatiles. Despite the great adaptability of soil washing plants, the technology has limitations associated with the physical and chemical characteristics of the soils and the type(s) of contaminant. The two most important physical parameters that must be evaluated are the soil grain size distribution and the cation exchange capacity (CEC). Some contaminants tend to preferentially bind to clay surfaces, hence the treatment of soils with clay contents greater than 30% is generally not cost effective. The higher the CEC, the ability of soils to exchange cations, the more tightly the soil will tend to bind pollutants, making removal progressively more difficult. Another important parameter is the organic content, as many contaminants tend to form progressively stronger bonds with organic matter as weathering processes take hold. In order for soil washing to be a viable option, organic contents should be below 2 wt.% (US EPA, 1991, 1993). Currently, the efficiency of soil washing installations allows the recovery of about 75% of contaminated material but it has been shown that recoveries of up to 90-95% can be achieved for heavy metal and hydrocarbon contaminants when heat and chemical compounds (such as surfactants and chelating agents) are added (US EPA, 1993). The primary additives used in the treatment of soils contaminated with hydrocarbons are surfactants (Delle Site, 2001; Muller *et al*., 2007).

Surfactants are generally classified based on the charge of their hydrophilic head group after dissociation in water into non-ionic, cationic, anionic and zwitterionic. When added to a solution, surfactants preferentially position themselves along interfaces found in the system (*e.g.*, water-oil, water-soil) in the form of monomers, orienting themselves such that their hydrophilic heads are in the water. As these interfaces fill up, and the surfactant monomers are pushed into solution, their hydrophobic heads tend to clump together forming agglomerates, called micelles. The surfactant concentration at which micelles first begin to form is called the Critical Micelle Concentration (CMC; Mao *et al*., 2014; Shah *et al*., 2016).

Surfactant-enhanced soil washing of hydrocarbons occurs via two distinct mechanisms: *i*) soil roll up, or mobilization, and *ii*) solubilization.

Soil roll-up occurs below the CMC. As the surfactant monomers accumulate along the oil/water interface, the repulsion between the head group and mineral surface results in an increase in the contact angle and a reduction of the capillary force holding the oil to the surface, effectively pushing it off the soil surface.

Solubilization, on the other hands, takes place above the CMC and consists of the incorporation of oil droplets into the hydrophobic core of micelles. This mechanism is more effective because the contaminant is less likely to re-adsorb to the surface. However, the same process that contributes to the efficiency of soil mobilization can also cause a delay in the improvement of hydrocarbon removal with concentrations above the CMC. The greater the attraction between the surfactant monomers and the mineral surfaces, the greater the amount of surfactant that will be lost to adsorption and hence not participate in solubilization.

In line with this reasoning, the adsorption of a cationic surfactants onto soil particles was observed to increase linearly with the cation exchange capacity of the soil, *i.e.* to be a function of the net negative charge of the mineral surface (Mao *et al.*, 2014), which makes them more suitable for soils dominated by minerals such as the negatively-charged calcite. For this reason, anionic surfactants are generally the surfactants of choice for sandstone dominated soils (Negin *et al.*, 2017). For non-ionic surfactants, it has also been found that sorption loss decreases with increasing soil maturity and is mainly governed by clay contents, as opposed to organic matter (Shen, 2000). Furthermore, several studies have shown that although most surfactants show an improvement in hydrocarbon extraction efficiency with increasing concentrations, some, such as saponin and tannin, do not (Abdul *et al.*, 1990; Deshpande *et al.*, 1999; Urum & Pekdemir, 2004). This behavior has been attributes to the instability of micelle shape in size observed in bulkier surfactants (Elvers *et al.*, 1994).

Despite a great volume of studies on the topic of surfactant-assisted soil washing, very little research has been done addressing the application of soil washing to soils contaminated with gasoline/diesel, and even less specifically addressing the influence of soil characteristics beyond grain size and CEC, such as mineralogy, on the efficiency of the process, despite the growing demand for viable and cost-effective solutions to soil contamination in vicinity of gas stations.

Consequently, the fundamental aim of this project was to evaluate the efficiency of two commercially available surfactants, SDS (anionic) and TWEEN80 (non-ionic), in the removal of diesel from soils of different mineral composition representative of the Marche Region. Additional parameters that were evaluated were temperature and surfactant concentration. To overcome the inherent complexity of *in situ* contaminated soils, clean soils were contaminated in the lab. The study was articulated into three distinct phases: *i*) soil sampling, characterization and selection; *ii*) fine-tuning of the laboratory batch washing procedure; *iii*) batch soil washing experiments.

SOIL CHARACTERIZATION

The aim of the first stage of the project was to characterize the most common soils found in the Marche Region and to select at least two end-member soils having markedly different mineralogical compositions while meeting the minimum requirements for soil washing in the event of contamination. In line with this aim, fourteen samples representative of the various soils present in the Marche Region were collected and their grain size distributions, organic contents, cation exchange capacity, mineral composition and Atterberg limits were determined. On the basis of grain size distribution analysis, the soils were found to be characterized by sand fractions between 7% and 49%, silt fractions between 2% and 49% and clay fractions between 2% and 52%. They had organic contents of 0.21 to 6.37 wt.%, CEC's of 7.2 to 35 cmol/kg and plasticity indexes that ranged from non-determinable (for non-plastic soils) to 25. The studied soils resulted rich in calcite, quartz and mica, and have minor amounts of clay minerals, feldspars and plagioclases.

The selection of soil samples to be used in laboratory soil washing experiments was carried out in two steps. First, soils meeting the minimum requirements for successful soil washing had to be identified.

Specifically, the cation exchange capacity, organic content and clay percentages of the soils, which should be below 10 cmol/kg, and 2 wt.% and 30 wt.%, respectively. In addition, soils with lower plasticity index values (an additional indicator of clay content) were given preference.

Second, since one of the goals of this study was to evaluate the efficiency of certain surfactants in washing soils of different mineral compositions, the mineral phase abundances were considered. In addition, the locations of the sampling sites were kept in mind to ensure that areas and soils at greatest risk of future contamination were included in the study. Hence, soils sampled from areas with the greatest population density were also given preference.

It was concluded that, in the event of contamination, most of the sampled soils would be unsuitable for surfactant-enhanced soil washing due to their high clay and organic contents. Of the remaining soils, sample MF-05 had equal proportions of quartz, calcite and mica minerals, whereas MF-10 had no calcite and lower CEC, organic contents and plasticity index. Consequently, based on their different mineralogy and locations in close proximity to population centers, these two samples were chosen for the experimental phase of the project.

FINE-TUNING THE EXPERIMENTAL SOIL WASHING PROTOCOL

In the second phase of the project benchmark values such as background soil contamination and contaminant compositions, were determined and the batch washing and analysis procedures were developed and fine-tuned using the procedure described in Urum *et al*. (2004) as a setting off point. The initial soil washing experimental procedure consisted of four broad phases: soil contamination, washing, extraction of residual contaminants (performed using n-Hexane) and analysis of the extracts. Due to differences in the chosen analytical method, contaminant used and available laboratory equipment, every step of the procedure described in Urum *et al*. (2004) had to be verified and modified where necessary before beginning the washing experiments.

Once the presence of background hydrocarbon contamination in the soils was ruled out, several contamination procedures were considered and tested. To assure a similar initial degree of loss of the more volatile hydrocarbon compounds, it was decided to spike the samples shortly before each washing experiment instead of performing a bulk contamination. Subsequently, a series of tests was carried out to determine the concentration (wt.%) of the contaminant that would result in the most homogeneous distribution within the soil samples. The percent contamination adopted was 15 wt.%. Since the washing containers used in the procedure described in Urum *et al*. (2004) proved unsuitable for this study, several washing containers were tested to ensure uniform and continuous agitation of the samples during washing and 500 ml Erlenmeyer flasks were chosen.

The use of Gas Chromatography-Mass Spectrometer (GC-MS) for analyzing the residual hydrocarbon contents of contaminated soils meant that a drying step following washing had to be added to the procedure. Consequently, drying conditions (temperature and duration) that would minimize the potential for additional loss of hydrocarbon compounds prior to extraction and analysis had to be determined. The percent recovery values of the n-Hexane extraction method were determined for each hydrocarbon compound considered. The recovery values range from 43 to 108% for sample MF-05 and 50 to 95% for sample MF-10 with percent experimental relative standard deviation (n = 3) ranges of 3.3 to 9.2 and 0.5 to 4.5, respectively. Recovery values below 60% were obtained for the heaviest of the quantifiable compounds, *i.e.* C27-C28. The last step before experiments could begin was to determine the concentration of n-Alkanes present in the contaminant. The chromatogram of C12 to C35 n-Alkanes in diesel showed a characteristic bell-shaped distribution curve with n-Tridecane being the most abundant n-Alkane. As a result of these tests, n-Alkane compounds with chain lengths below C14 were excluded from further consideration because of excessive loss during the drying stage of the washing protocol. Compounds with chain lengths above C26 were also excluded, due to their relatively low concentrations with respect to the lighter compounds and lower recovery percentages.

All n-Alkane analyses were carried out using an Agilent Technologies gas chromatographer and inert XL MSD mass spectrometer. Data collection was carried out in the Selected Ion Monitoring (SIM) mode with an acquisition window of 5-24 min. Five to six-point calibration curves for each n-Alkane compound analyzed were prepared using standard mixtures in order to define the linearity range within which quantification could be carried out. Calibration curves were repeated every month to correct for any changes in instrument response and each analysis was triplicated to determine instrumental error.

The adopted washing procedure was as follows: 5 grams of each sample were weighed out and transferred into 500 ml Erlenmeyer flasks. Then, each sample was contaminated with 15 wt.% diesel and allowed to rest for about 30 minutes. Subsequently, 20 ml of washing solution were added and the Erlenmeyer flasks sealed with aluminum foil. They were then placed into a temperature controlled, shaking water bath previously brought up to temperature and agitated for 30 minutes to simulate washing. After washing, the samples were transferred into 50 ml borosilicate glass test tubes and centrifuged to remove as much of the washing solution as possible. Then, they were rinsed with 20 ml of deionized water to remove any residue of the washing solution. The rinsed samples were transferred into glass plates and dried at 60°C for three hours. Once dry, the samples were transferred back into the test tubes and the residual hydrocarbons were extracted using n-Hexane. To accomplish this, 10 ml of n-Hexane were added to the samples and the test tubes agitated manually for 5 minutes. This process was repeated four times with the supernatant being removed each time. Following the last n-Hexane addition, the samples were centrifuged to remove as much of the supernatant as possible. The total supernatant thus obtained was then analyzed using GC-MS.

SOIL WASHING BATCH EXPERIMENTS

Once the sampling, characterization and selection of typical soils of the Marche Region were completed and a laboratory-scale soil washing simulation procedure was fine-tuned, it was possible to pass on to the comparison of the relative efficiencies of an anionic and non-ionic surfactants, SDS and TWEEN80 respectively, in the removal of diesel from two soils of different physical, mineralogical and chemical properties, MF-05 and MF-10.

The two soil samples were contaminated with 15% diesel and washed with SDS and TWEEN80 washing solutions, following the procedure described above. To establish a baseline for comparison, samples MF-05 and MF-10 were first washed with a washing solution containing only deionized water. Then, each sample was washed with three solutions of increasing concentrations of either SDS or TWEEN80.

The concentrations were 0.25, 1.5 and 2 times the CMC for each surfactant: SDS - 1.75mM, 10.5mM and 14mM; TWEEN80 - 0.003mM, 0.024mM and 0.18mM. In addition to varying surfactant concentration, each series of experiments was carried out at two washing temperatures, 30°C and 40°C. Stock solutions of both SDS and TWEEN80 were prepared and used to obtain all three concentrations of each surfactant via dilution. All experiments were performed in triplicates and analyzed three times to ensure experimental and instrumental repeatability.

It was found that for sample MF-05, washing with SDS-based washing solutions had little effect on extraction efficiency at concentrations below the CMC, but improved it drastically once the CMC was exceeded; in sample MF-10, on the other hand, a drastic improvement in washing efficiency was already evident at concentrations below the CMC and continued to increase, albeit at a lower rate, as the SDS concentrations increased (Fig. 1a). The initial delay in washing efficiency improvement in sample MF-05 is likely due to the adsorption of the negatively charged surfactant molecules to the positively charged calcite surfaces, absent in sample MF-10.

For both samples, washing with TWEEN80-based solutions resulted in a significant improvement in efficiency at concentrations below the CMC, followed by less significant improvement at intermediate concentrations and a decrease in efficiency at the highest concentrations of TWEEN80 (Fig. 1b). The similar

performance of the TWEEN80 washing solutions in samples MF-05 and MF-10 was consistent with its neutral charge.

When the efficiency of the two surfactants was compared to each other, for sample MF-05, TWEEN80 was found to be generally more efficient at removing n-Alkanes at concentrations below the CMC.
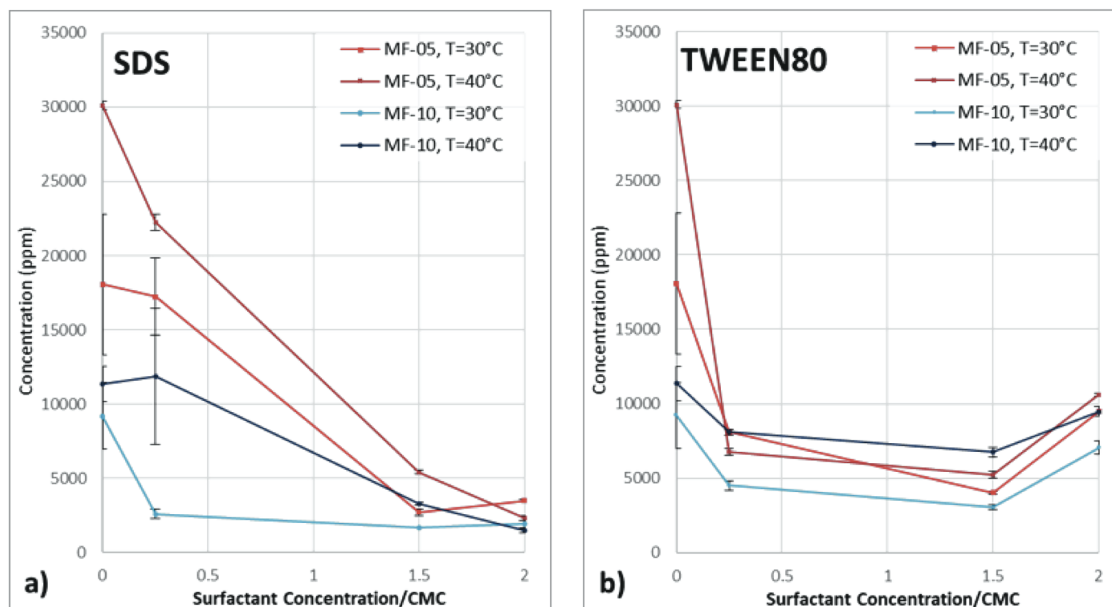

Fig. 1 - Plots of residual n-Alkane concentrations *versus* the ratio of surfactant concentrations to CMC for a) SDS and b) TWEEN80. Error bars represent Relative Standard Deviation of the experimental method (n = 3).

As the surfactant concentrations were increased above the CMC however, SDS became equally effective and then surpassed TWEEN80, which showed a drop off in efficiency at the highest concentration studied (Fig. 2a).
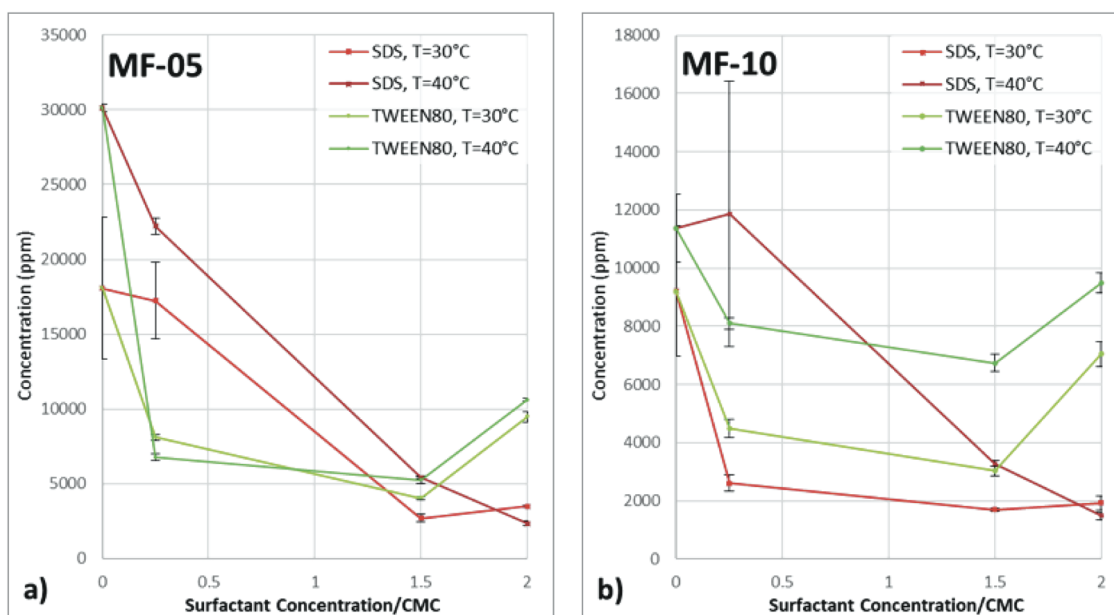

Fig. 2 - Plots of residual n-Alkane concentrations *versus* the ratio of surfactant concentrations to CMC for a) MF-05 and b) MF-10. Error bars represent Relative Standard Deviation of the experimental method (n = 3).

For sample MF-10, SDS and TWEEN80 showed similar trends of washing efficiency improvement with increasing surfactant concentrations. The lag in efficiency improvement with increasing surfactant concentration observed for SDS in sample MF-05 was no longer present. SDS was more effective at extracting n-Alkanes than TWEEN80 at the same temperature and for all concentrations (Fig. 2b).

Increasing temperature had little effect on the efficiency of n-Alkane removal for both MF-05 and MF-10, and for both surfactants. For both samples, the increase of the washing temperature from 30°C to 40°C for SDS-based washing solutions only improved the washing efficiency at concentrations 2 times greater than the CMC. Although slight, this improvement means that the improvement rate of washing efficiency with increasing concentration no longer flattens out but continues to rise. This means that if temperature and surfactant concentrations are increased concurrently, a continued improvement in washing efficiency can be achieved for SDS. For TWEEN80-based solutions, a slight improvement in efficiency with temperature was observed only for sample MF-05 at surfactant concentrations below the CMC. Consequently, varying the washing temperature by 10°C is either insufficient to result in an improvement or not an effective way of improving washing efficiency for this surfactant.

All of these observations can be explained by taking a closer look at the differences in mineralogical composition of the studied samples and the expected effect these differences would have on interactions with surfactant molecules. SDS is an anionic surfactant containing a negatively charged head group. When it was used to extract n-Alkanes from sample MF-05, which contains 30 wt.% calcite, the negatively charged surfactant molecules were adsorbed to the surface of calcite crystals effectively taking them out of solutions. This was the source of the poor improvement in extraction efficiency observed for sample MF-05 at SDS concentrations below CMC. Once the calcite surface was saturated and no more surfactant molecules were taken out of solution, the rate of improvement in extraction efficiency with increasing surfactant concentrations rebounded. As expected, for sample MF-10, which is composed mostly of quartz (62 wt.%), a mineral with a negatively charged surface, this trend was not observed. The mineral composition of sample MF-10, along with its slightly lower clay and organic matter contents (which can also result in loss of surfactants to adsorption), was the reason behind both surfactants being more effective at removing n-Alkanes from this sample. Unlike SDS, TWEEN80 is a neutral molecule that is not attracted to charged mineral surfaces. Consequently, no difference in the trends in the rate of improvement of extraction efficiency with increasing surfactant concentrations was either expected or observed for samples MF-05 and MF-10. The observed reversal in the extraction efficiency observed at the highest TWEEN80 concentrations analyzed requires further study. A possible explanation is the destabilization of micelles due to a change in their shape.

As illustrated in this study, understanding the mineralogy of the soils in need of remediation is of crucial importance to establishing the correct formulation of washing solutions. In addition to the standard grain size distribution and physical-chemical parameters, case by case evaluations of the mineralogy of contaminated soils will help maximize efficiency while minimizing costs and mitigating environmental impact.

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