

# Potential benefit of surfactants in a hydrocarbon contaminated soil washing process: Fluorescence spectroscopy based assessment

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## ABSTRACT

Soil washing is an ex situ soil remediation treatment process. The purpose of soil washing is to clean the major gravel and sand fractions, concentrating contamination into the fine silt and clay fractions. The addition of surfactants can improve the efficiency of this method. Here we report the use of UV fluorescence spectroscopy to assess the hydrocarbon cleaning process as a rapid and cost effective alternative to gas chromatography. Three wash solutions were tested on a total petroleum hydrocarbon contaminated soil: water, Sea Power 101 (SP101) at 1% (v/v) and Tween80 at 0.5% (w/v). The most effective to wash the gravel and sand was SP101 (54 and 65% improvement over the water only wash, respectively) which moved contamination to the silt fraction (94% of contaminants). Tween80 appeared not to enhance TPH removal efficiency from the gravel and sand fractions but did concentrate TPH in the effluent (95% more than water wash). In addition to TPH removal from gravel and sand, SP101 also showed potential benefit in the soil washing sedimentation process, enhancing sludge/water volume separation by 10% over the water only wash. In summary, fluorescence spectroscopy proved an effective technique to compare TPH removal efficiencies as part of soil washing laboratory based treatability testing.

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## 1. Introduction

Soils contaminated with aromatic hydrocarbons, including polycyclic aromatic hydrocarbons (PAH) are often slow to remediate by techniques such as bioremediation [1]. Soil washing, on the other hand is a comparatively rapid soil remediation technique [2–4], however, the hydrophobic nature of aromatic hydrocarbons can impede the effectiveness of the water only wash process to clean gravel and sand fractions and thereby concentrate contamination in the fine solid fractions [5]. Therefore, particularly where contaminants are coated or adsorbed onto gravel and sand fractions, surfactants are of potential interest to improve the cleaning process.

Many articles researching the use of surfactants in the soil washing process refer to removal efficiency as the ability to concentrate contaminants into the liquid phase (effluent) [6,7]; however, these are in the main based on soils consisting of a single (sand) fraction only. Contaminant removal efficiency in soils consisting of multiple fractions such as gravel, sand, silt and clay are more complicated. Specifically, contaminant removal efficiency can be considered in

terms of the removal from a particular solid fraction or, the transfer from the soil to the liquid effluent. Given that the objective of soil washing is to recover the gravel and sand fractions, contaminant removal efficiency should address these fractions specifically. In addition, as the silt and clay fractions are usually heavily contaminated and often require disposal, it may be better to concentrate contamination in silt and clay rather than the liquid effluent. As such, surfactants which primarily enhance the desorption of contaminants from gravel and sand fractions, without necessarily increasing contaminant water solubility are of interest.

Numerous studies have assessed the potential of chemical surfactants such as SDS, Brij 35 or Tween80 to improve removal efficiency of contaminants in the soil washing process; the results of which are that surfactants show varying contaminant removal efficiencies. With the relative performance of a particular surfactants being soil specific, laboratory based treatability tests are beneficial to decide the most appropriate surfactant for a specific soil and site. For example, Surfapcol has been shown to be more effective than Tween80 or SDS in sand [8], whereas, Tween80 and Brij35 had similar removal efficiencies in a sandy loam soil [9].

In addition to the choice of surfactant, many studies have focused on defining optimal washing parameters for the surfactant, for example, the influence of washing time, temperature, as well as surfactant concentration [7,10]. In these previous articles, washing times varied from 5 min to 48 h; however, in order to have

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a time-efficient treatability test and to mimic currently available soil washing plant, washing duration should last minutes rather than hours. Finally, artificial ageing of pollution has also been studied, although in reality, ageing of pollution is not a variable in soil washing treatability testing. There are few articles to date using soils which have not otherwise been artificially contaminated.

In recent years, biosurfactants have increasingly been considered for potential application in soil washing processes. Biosurfactants have been isolated from various sources including microorganisms (such as bacterial rhamnolipid), animals (frog saliva) and even plants [11,12]. In the relatively few studies to date, biosurfactants have shown similar or better results when compared with chemical surfactants in terms of contaminant removal efficiency. For example, rhamnolipid showed a better TPH removal than Tween80 [13] and a similar removal efficiency to SDS [14,15]. Furthermore, biosurfactants have a lower toxicity, excellent biodegradability, are less influenced by environmental conditions (such as pH and temperature) and are more cost-effective [16].

In addition to contaminant removal from the gravel and sand fractions, the use of surfactants in a soil washing process will have an influence on sedimentation of the fine solid component. Flocculating agents may be used as part of the sedimentation process and so the influence of surfactants on flocculating agents also needs to be considered. Amongst other properties surfactant can reduce suspension viscosity [17]. Interactions between surfactants and flocculants can be positive or negative depending on chemical type(s) [18,19]. Therefore, soil washing treatability testing involving surfactants should also consider effects on sedimentation processes.

Finally, in the majority of articles, assessment of surfactant performance has been made using gas chromatography [9,10] or gravimetric method [8,20]. As an alternative to gas chromatography in particular, Ultra-Violet fluorescence (UVF) spectroscopy is of interest as a comparatively rapid and cost-effective technique that retains a high degree of sensitivity.

The aim of this study was to determine the effects of two surfactants (the chemical surfactant Tween80 and a biosurfactant Sea Power 101) on soil washing of a historically contaminated soil. Specifically, their potential benefit on hydrocarbon removal from gravel/sand and, effects on the sedimentation process when compared to the water only wash process. The washing process efficiency was assessed using UV fluorescence spectroscopy as a rapid, cost effective technique of benefit for soil washing remediation treatability testing.

## 2. Materials and methods

### 2.1. Solutions for soil washing

The three wash solutions were:

- (1) Deionised water (hereafter referred to as 'water').
- (2) Sea Power 101 at 1% (SP101); a bio-stimulant and biosurfactant product (supplied by Sea-Chem Ltd, Shropshire, UK). The concentration was based on previous washing experiments by ourselves which demonstrated that 1% was effective when compared to higher concentrations. In addition, the critical micelle concentration (CMC), was determined with a UV fluorescence method using pyrene as described previously [21,22]. Briefly, emission (EM) scans were undertaken using a UV fluorescence spectrophotometer (see Section 2.6 for details) in order to excite pyrene at 334 nm and record its emission at 373 and 384 nm.

**Table 1**  
Soil characteristics.

|  |        |
|--|--------|
| Moisture content                                   | 16.8%  |
| pH   | 6.2    |
| <i>Soil distribution</i>                           |        |
| Silt/clay  | 23.6%  |
| Sand   | 70.6%  |
| Gravel   | 6.5%   |
| <i>TPH aromatic – whole soil (mg/kg)</i>           |        |
| UVF  | 283.85 |
| GC-FID   | 549.95 |
| <i>TPH aromatic – gravel only fraction (mg/kg)</i> |        |
| UVF  | 90.85  |
| GC-FID   | 230.75 |

- (3) Tween80 at 0.5% (Tween80); a non-ionic surfactant (Fisher Scientific, Loughborough, UK). The concentration was chosen based on previous articles [8].

The solutions were prepared in a 2.5 L container with deionised water.

### 2.2. Solutions for flocculation test

The solutions were:

- (1) Deionised water (hereafter referred to as 'water'),
- (2) Ferric chloride at 0.5% (v/v) (FeCl<sub>3</sub>); a flocculating agent,
- (3) Sea Power at 1% (v/v) (SP101),
- (4) Sea Power at 1% (v/v) and ferric chloride at 0.5% (SP101&FeCl<sub>3</sub>),
- (5) Tween80 at 0.5% (w/v) (Tween80),
- (6) Tween80 at 0.5% (w/v) and ferric chloride at 0.5% (v/v) (Tween80&FeCl<sub>3</sub>).

### 2.3. Soil

A historically hydrocarbon contaminated soil was taken from a former oil refinery located in Ayrshire, Scotland, UK. Soil characteristics can be found in Table 1.

### 2.4. Soil washing procedure

For each wash solution, three replicate experiments were conducted following the stages below:

- 1 kg of fresh soil, previously sieved through 8 mm, was mixed with 1 l of wash solution and stirred for 20 min. A wash time of 20 min was chosen based on previous reports [8]. This mixture was passed through two sieves (3.35 mm and 63 µm aperture) and washed with an additional 500 ml of wash solution.
- The <63 µm fraction was allowed to settle for 5 h (corresponding to time where no significant reduction in sediment height observed). After which, the resulting supernatant was removed. The three soil fractions were oven-dried.
- The three resulting solid fractions; gravel (>3.35 mm), sand (>63 µm) and silt/clay (<63 µm), as well as effluent were analyzed as indicated below (Section 2.6).

### 2.5. Procedure of flocculation test

For each wash solution, three replicate experiments were conducted following the stages below:

- Soil aliquots of 200 g, previously sieved through 3.35 mm, were mixed with each wash solution generating 500 ml of soil/wash solution mix; this mix was stirred for 20 min.
- Flocculating agent was added and stirred for 5 s.

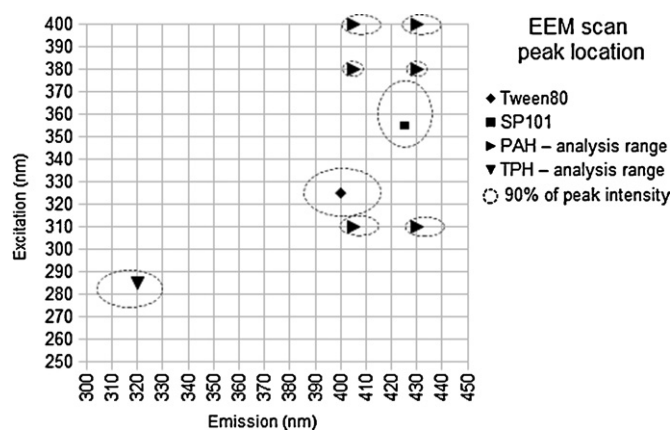


Fig. 1. Peak location on the excitation emission matrix (EEM) map of TPH, PAH, Tween80 and SP101.

– The experiment lasted 3 h. During this time the evolution of different parameters was studied. At each chosen time (0, 10 min, 30 min, 1 h, 2 h and 3 h) the sludge height was taken, and from 30 min onwards, total suspended solids (TSS) was analyzed using a spectrophotometer (Hach DR 2800 Portable Spectrophotometer).

### 2.6. Ultraviolet fluorescence (UVF) spectroscopy analysis

The petroleum products have a specific location within the EEM fingerprint [23,24]; but the peak can move in the map with the concentration [23]. However, within a specific calibration range, the intensity can be used to find the contaminant concentration [24].

UVF spectroscopy was carried out using a FluoroSENS fluorimeter (Gilden photonics Ltd, Glasgow, UK). Soil, 5 g<sub>dryweight</sub> was mixed with 10 ml HPLC fluorescence grade methanol (Fisher Scientific, Loughborough, UK) and shaken for 5 min using a reciprocating shaker. The resulting supernatant was filtered using a 0.45 μm PTFE filter. Effluent samples were filtered in the same manner as soils. Initial characterization of hydrocarbon in the soil extract and wastewaters was carried out using excitation–emission matrix (EEM) scan, after which an emission (EM) scan was used. Specifically, total petroleum hydrocarbon (TPH) was analyzed at an excitation wavelength of 285 nm and emission 300–355 nm with step of 5 nm. The area under the resulting curve was calculated with the rectangle method. A linear relationship between area and concentration was found with a coefficient of  $R^2 = 0.959$ . This relationship was used to determine the total aromatic TPH concentration in studied samples. Maximum fluorescence intensity was consistent at the wavelengths employed within the calibration range. Sample extracts outside of this range were diluted as necessary. The calibration kit came from SiteLab Corporation (West Newbury, MA, USA) consisting of five standards between 0.1 and 5 ppm (EDRO Diesel Range Hydrocarbons; product #CAL-042).

## 3. Results and discussion

### 3.1. Surfactant effects on the analysis

Tween80 and SP101 both fluoresce when excited with UV light. Even though the surfactants maximum fluorescence intensities are in different locations to the soil extracted hydrocarbon contamination (Fig. 1), TPH analysis of surfactant washing solutions using the EM scan showed that both surfactants influenced hydrocarbon contaminant analysis at the 285 nm excitation wavelength. Therefore, to allow for the surfactant influence on UVF analysis, a

Table 2  
Compensation factors for the surfactant influence on TPH analysis.

|                               | Tween80                              |                              | SP101                                |
|-------------------------------|--------------------------------------|------------------------------|--------------------------------------|
| If $C < 0.005\%$              | 0.92                                 | If $C < 0.005\%$             | 0.95                                 |
| If $0.005\% \leq C < 0.03\%$  | 0.84                                 | If $0.005\% \leq C \leq 1\%$ | $\frac{1}{2.9357 \times C^{0.1993}}$ |
| If $0.03\% \leq C \leq 0.5\%$ | $\frac{1}{11.112 \times C + 1.2529}$ |                              |                                      |

compensation factor was determined experimentally as previously used [25]. The factor was specific to the surfactant and was concentration dependent (i.e. non-linear) presumably due to effects in addition to fluorescence emission (Table 2). The surfactant concentration was determined by the dilution used for the analysis; then the factor was applied on the calculated area described above. Given that the heat destroys the surfactant [26] the compensation was only used for the effluent analysis. Moreover, we found experimentally further justification for not applying the compensation factor to the solid fraction analysis (Fig. 2). In particular, with an excitation scan at fixed emission wavelength of 430 nm the surfactant influence was observed; the resulted curves were standardized before being compared. The results show that the sand fraction extracts of the surfactant washes had fluorescence profiles which associated more closely with the water only wash sand fraction extracts than the original surfactant solutions (Fig. 2a and b). By comparison, the fluorescence profiles of the surfactant effluent showed clear differences in the shape of the emission envelope relative to the water only wash effluent (Fig. 2c and d).

### 3.2. Effect of surfactants on TPH in a soil washing process

#### 3.2.1. Surfactant effects on TPH in solid fractions

The TPH concentration in the gravel fraction was significantly lower for the SP101 wash when compared to water only wash (Fig. 3a), with a 54% washing improvement. By comparison, Tween80 appeared not to have a significant effect on TPH removal in the gravel fraction. For the sand fraction (Fig. 3b), SP101 had an even greater effect on TPH removal with 65% washing improvement when compared to the water only wash. Although Tween80 appeared to enhance TPH removal in the sand fraction, the inherent variability in contaminant concentration in the historically contaminated soil prevented us from drawing this conclusion.

Although an improvement in contaminant removal efficiency was found when using surfactant SP101 for the gravel fraction, the biggest improvement was on the sand fraction. Despite generally few articles having studied the effect of particle size on the removal efficiency, Torres et al. [8] found removal was more effective for smaller particle size fractions, which corroborates with our results. By determining the initial TPH concentration in the gravel (Table 1) the specific removal efficiency on gravel was also calculated for all the wash solutions (this stage could not be done with the other fractions because of being unable to separate without a wet sieve process). The removal efficiencies for the gravel washed by water and Tween80 were similar ( $21 \pm 29\%$  and  $30 \pm 26\%$ , respectively), whereas, SP101 showed an enhanced removal efficiency ( $64 \pm 16\%$ ). As such, these results show the biosurfactant SP101 is effective at enhancing TPH removal efficiency from gravel, which contradicts comments on the inability of surfactants to improve the washing of gravel fraction [27].

By analyzing TPH concentration in all three major solid fractions (and the effluent), we observed apparent differences in behavior of the two surfactants (Fig. 3). Specifically, SP101 appeared more effective at moving contamination into the fine solid fraction (Fig. 3c), whereas, Tween80 was more effective at concentrating contamination into the effluent (Fig. 3d and 4). Given that the fine solid fraction is typically disposed of to landfill in soil washing projects, concentrating contamination in this fraction seems less

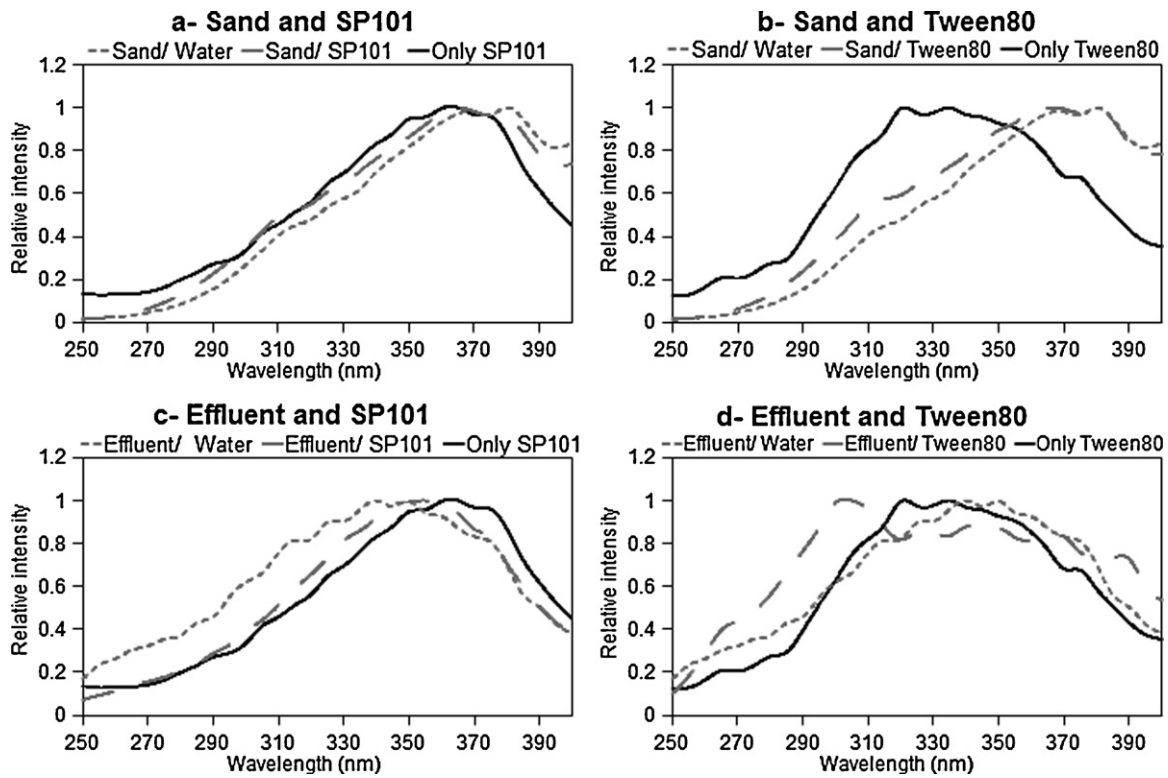


Fig. 2. Surfactant influences on soil fraction and liquid effluent analyses.

important than the improved cleaning of gravel and sand fractions where stringent site remedial targets apply. The contaminant distribution was different for the three wash solutions, but the purpose of soil washing, moving the contaminants from the gravel and sand,

was improved by the surfactant addition. In summary, SP101 was most effective at washing the gravel and sand fractions; with 6% contamination with SP101 in the gravel and sand, compared to 16% with Tween80 and 19% for water only (Fig. 4). Tween80 has already

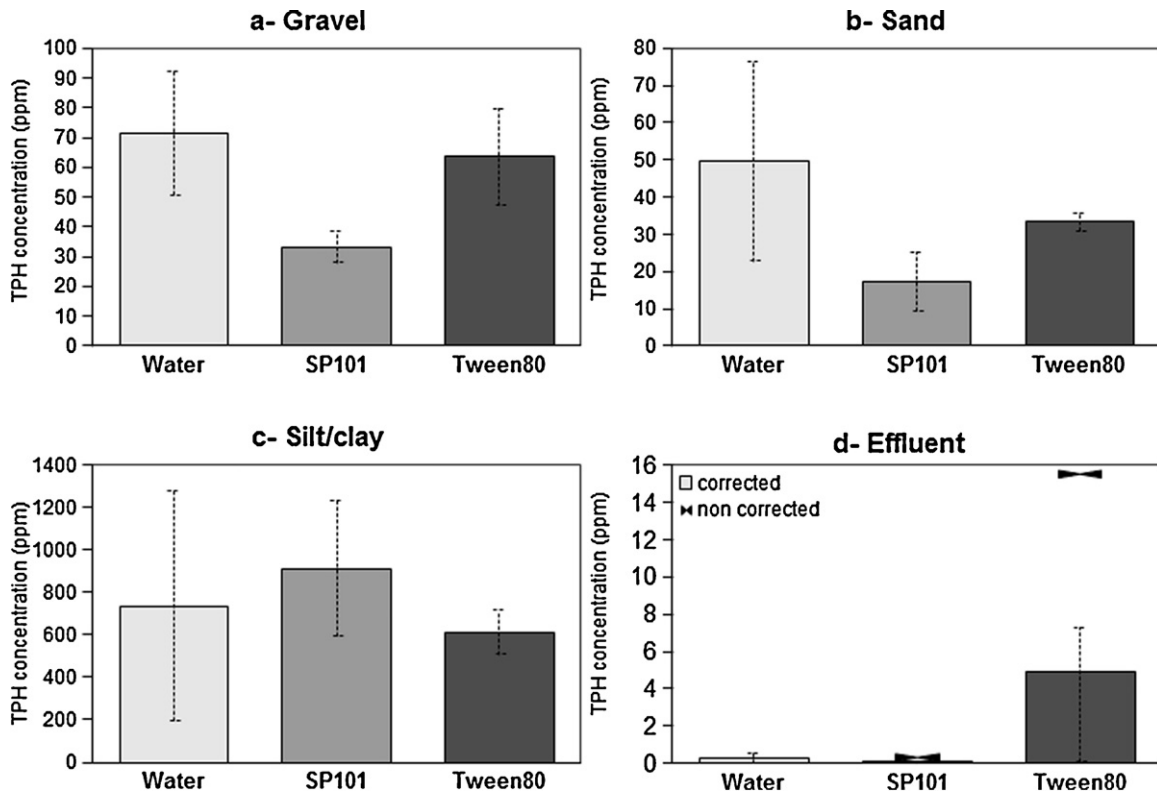


Fig. 3. TPH concentration in each fraction ( $n = 3$ ); with and without compensation for surfactant influence.

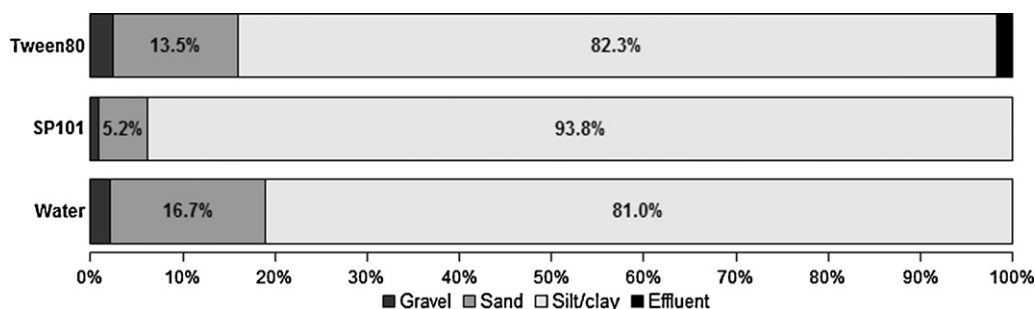


Fig. 4. Contaminant distribution.

been shown to be less effective than another biosurfactant (Rhamnolipid) [13]. Our results show that another biosurfactant, SP101, is also more effective than Tween80.

In terms of the contamination variability in the soil fractions, the results show reduced variability when surfactants were used. Specifically, a deviation of 62% was observed for the water only wash, 24% for the SP101 wash and 24% for the Tween80 wash; these deviations include the initial soil contamination deviation (23%). During treatability test experiments, where environmental parameters such as temperature may be less rigorously controlled, they have the potential for masking effects of other parameters of interest. As such, surfactants may be beneficially used to help reduce environmental influence from an analytical only perspective in assessing soil washing as part of treatability testing studies.

### 3.2.2. Surfactant effects on TPH in liquid effluent

As stated previously, Tween80 desorbed and concentrated more contamination into the liquid effluent than the other wash solutions (contaminant concentrations in Fig. 3d and distribution in Fig. 4). The enhanced contaminant solubility in the presence of Tween80 over both SP101 and water only wash is in part due to its ability to reduce water surface tension; reduction of 52% with Tween80 [28] and 44% [29] with SP101 in comparison to water. Despite the lesser performance of SP101 to enhance contaminant solubility, it again raises a question over methods used to evaluate the benefit of surfactants in soil (rather than sand only) washing. As stated earlier, in most articles removal of contamination in a two component (sand and water) system, performance is often assessed based on increasing uptake in the effluent [8]. However, as commercial soil washing plant produce sand and gravel outputs which are usually both intended to be used back on site (once they achieve site specific remediation targets), contaminant removal efficiency should be assessed in terms of the removal from these fractions rather than transfer from the soil to the liquid effluent. Therefore, surfactants which enhance desorption of contamination from sand and gravel fractions into the silt and clay fractions, such as SP101,

are potentially beneficial for hydrocarbon contaminated soil washing processes.

### 3.2.3. Effects of surfactants of sedimentation process

As part of most soil washing processes, a sedimentation process is usually used to removal solids prior to further effluent treatment and disposal or recycling of water back into the upstream soil washing process. Often flocculating agents are added at this stage to enhance sedimentation. Therefore, the purpose of this experiment was to determine the effect of the two surfactants, Tween80 and SP101, on the sedimentation process in the presence/absence of the common flocculating agent ferric chloride ( $\text{FeCl}_3$ ). Parameters that were measured were total suspended solids (TSS) and sludge height.

Evolutions of the two studied parameters (Figs. 5 and 6) were different; for TSS removal the most effective was  $\text{FeCl}_3$  and the less effective was Tween80, whereas for sludge reduction the less effective was water and the most effective were SP101 and Tween80. The interaction between SP101 and  $\text{FeCl}_3$  decreased the benefit of SP101 on TSS; with all the others solutions having a similar TSS result. For both surfactants,  $\text{FeCl}_3$  addition had a negative effect on their ability to reduce the sludge height.

The settling rate of each solution was also compared (Table 3); the rate calculated using the following formula:

$$R_{\text{settling}} = \frac{H_{\text{init}} - H_i}{T_i} \times 60$$

where  $R_{\text{settling}}$  in cm/h,  $H_{\text{init}}$  the initial height in cm,  $H_i$  the height at the inflection point of the curve of the sludge height evolution in cm and  $T_i$  the time at the same inflection point in min.

The table shows the improvement of the settling rate with surfactants and flocculating agent alone; the water was the least effective and  $\text{FeCl}_3$  the most effective. With this parameter, we can see clearly if the interaction between surfactants and flocculating agent has a positive influence; for Tween80 the addition of  $\text{FeCl}_3$  improved the efficiency but with SP101 it became less effective. Negative interactions between surfactant and flocculant on the

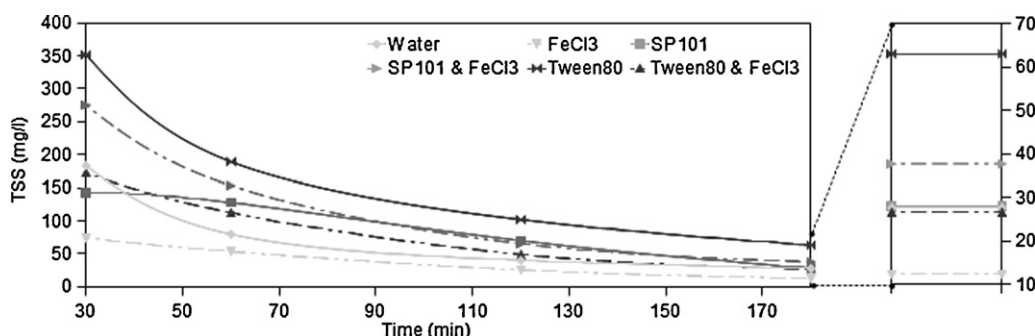


Fig. 5. Evolution of total suspended solids (TSS) with surfactants and flocculating agent ( $n=3$ ). Right-hand side of figure represents enlargement of data at 180 h.

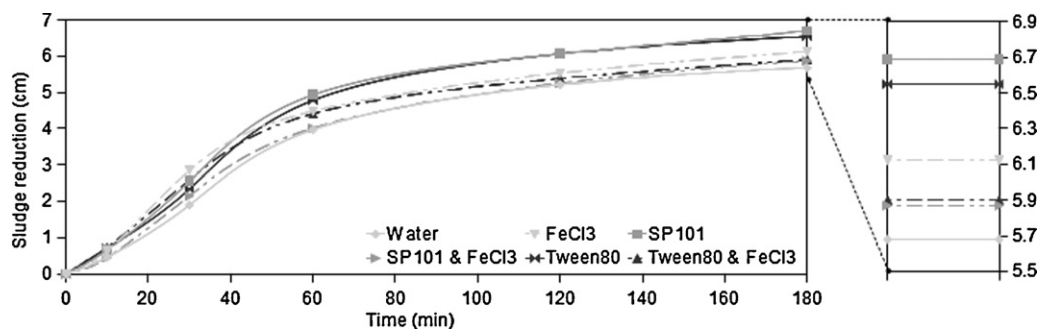


Fig. 6. Evolution of sludge reduction with surfactants and flocculating agent ( $n=3$ ). Right-hand side of figure represents enlargement of data at 180 h.

Table 3

Comparison of settling rates for the six solutions ( $n=3$ ).

| Solution             | Water      | SP101&FeCl <sub>3</sub> | Tween80     | SP101       | Tween80&FeCl <sub>3</sub> | FeCl <sub>3</sub> |
|----------------------|------------|-------------------------|-------------|-------------|---------------------------|-------------------|
| Settling rate (cm/h) | 3.94 ± 0.6 | 4.28 ± 0.4              | 4.70 ± 0.14 | 4.93 ± 0.23 | 5.27 ± 1.51               | 5.64 ± 0.43       |

settling rate and the sludge volume have been observed previously [19]. These results suggest that if the objective is to recover as much water as possible, surfactant addition to the soil washing process is also beneficial for the sedimentation process. However, if there is demand to reuse the water, a low TSS is recommended and so the choice can be FeCl<sub>3</sub>.

#### 4. Conclusions

The interactions between soil matrix, contaminants and chemical agents are complex resulting in the need for treatability testing on a site by site basis as part of the remediation design process. The purpose of this work was to conduct soil washing treatability tests mimicking (as far as possible) the full scale process for a historically contaminated soil and to evaluate contaminant removal efficiency using UV fluorescence spectroscopy. Specifically, the four outputs were the same as a full-scale plant: gravel, sand, silt/clay and effluent. In addition, a mixing time of 20 min was used to not only mimic full scale plant but ensure that treatability tests are processed as quickly as possible to aid practitioners in decision making.

By comparing the effects of the three wash solutions, SP101 appeared as the best surfactant in terms of contaminant removal efficiency from the gravel and sand fractions. Moreover, SP101 had a positive effect on the sedimentation process without flocculant addition. However, addition of the flocculant ferric chloride caused a decline in performances of sludge reduction in the presence of this surfactant.

In terms of the use of UV fluorescence spectroscopy, we found that it showed good reproducibility and demonstrated its value as a technique for rapid and cost effective analysis of hydrocarbon contamination for soil washing treatability trials. Further research is needed to understand the influence of surfactants, especially novel biosurfactants such as SP101, on enhancing and/or quenching fluorescence of measured parameters such as TPH.

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