Enhanced soil-washing treatment for soils which are highly contaminated with crude oil

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Abstract

Soil and water contamination due to hydrocarbon spills is a frequent problem worldwide. In the case of Mexico, even when programs oriented to the diminution of these undesirable events are in progress, in the year 2000 a total of 1,518 hydrocarbon spills (6,250 tons) were reported. Surfactant enhanced washing of soils is a remediation technology, which has been shown to be a high cost-effective process. The first step in the washing process development is the selection of suitable surfactants and doses. In this work, twelve anionic and nonionic surfactants and their mixtures were assessed in the remediation of highly contaminated crude oil soils. Moreover, the use of different amounts of NaCl and Na-silicate (10%), due to the high amount of Ca, Mg and Mn in the soils is shown and discussed. The studied soil was artificially contaminated with crude oil from the *El Batab* (Campeche, Mexico) perforation well in a concentration of 108,980 mgTPH/kg soil. SDS and E-600 surfactants at 1% concentration achieved higher TPH removal rates (20.4 and 32.9%, respectively). The surfactant-salt mixture that showed a TPH removal rate higher than those obtained with the best single surfactants was SDS+ EW600+Na_2SiO_3 10% (30.2%). Using a tensiometric technique, the SDS critical micelle concentration (CMC) was measured without any salt present and with 0.5, 1 and 2% of NaCl. These data were employed together with other surfactants CMC and HLB (hydrophilic-lypophilic balance) reported values in order to explain the surfactants performance during the soil washing assessments. In general, TPH removal values were higher when high HLB values-surfactants were employed.

Keywords: crude oil, hydrocarbon spills, ionic, nonionic, soil washing, surfactants.

1 Introduction

Soil and water contamination due to hydrocarbon spills is a frequent problem worldwide. For the case of Mexico, even when programs oriented to the diminution of these undesirable events are on progress, at year 2000 a total of 1,518 hydrocarbon spills were reported. The total amount of spilled hydrocarbons was around 6,250 tons. The main petroleum industry areas were those spills occurred were crude exploration and production, with 1,428 spills *(*1,097 tons), and crude refining, with 90 spills (5,155 tons)[1]. The main spills were in the refineries, pipelines and marine terminals. Among the soil remediation techniques applied to hydrocarbon contaminated samples, surfactant enhanced soil washing is one of the most promising. Surfactant enhanced washing of soils is a remediation technology, which has demonstrated being a high cost-effective process. The first step in the washing process development is the selection of the suitable surfactants and doses. In this work, twelve anionic and nonionic surfactants and their mixtures were assessed in the remediation of crude oil highly contaminated soils arising form a Mexican refinery.

2 Materials and methods

2.1 Soil

The sandy soil employed in this work was obtained form an old refinery located at North Mexico [2]. Soil was artificially contaminated with crude oil arising from *El Batab* perforation well (Campeche, Mexico). The crude-contaminated soil also was previously characterized [3]. Table 1 shows some oil-contaminated soil characteristics, regarding texture, metal contents, bulk density, porosity, and soil pH values. Note the high Ca+Mg+Mn/Na+K ratio value.

Table 1: Some oil-contaminated soil characteristics.

Parameter	Value	Unites	Parameter	Value	Unites
Porosity	0.37	-	Cd	1	mg/kg
Sand	92	%	Cr	10	mg/kg
Fines	7.9	%	Cu	23	mg/kg
Bulk density	1.82	mg/cm^3	Fe	9,085	mg/kg
pH, 1 M KCl	6.1	unites	Ni	12	mg/kg
Na	272	mg/kg	Pb	544	mg/kg
K	332	mg/kg	Zn	1,444	mg/kg
Ca	28,160	mg/kg	Na+K	605	-
Mg	996	mg/kg	Ca+Mg+Mn	29,246	-
Mn	90	mg/kg	Ca+Mg+Mn/Na+K	48.34	-

From [3]

2.2 Surfactants

Twelve commercial surfactants (nonionic and ionic, with different chemical nature, HLB and molecular weights spectrum) were assessed in the soil washing tests at 1% concentration Commercial surfactants employed along this work were, Emulgin 600, Emulgin 1000, Tween 20, Tween 60, Tween 80, Span 80, Texapon 40, Maranil lab, Brij 35, Brij 58 Brij 72 and SDS. The general properties of the surfactants are resumed at table 2. All solutions were prepared in distilled water and stored at 4°C until used. NaCl (0.5, 1, and 2%), and Na-silicate (10%) analytical grade were added in some assessments.

Table 2: Some surfactants characteristics.

Surfactant	Ionic nature	Chemical name	Mol weight (g/g mol)	HLB	CMC (mg/l)
SDS	Anionic	Sodium dodecyl sulphonate	288.4	40	400*
Texapon 40	Anionic	Sodium lauryl ether sulphate	442	NR	1,458 ***
Maranil Lab	Anionic	Sodium dodecyl-bencen sulphonate	348	NR	1,392
Emulgin 600	Non-ionic	Nonyl phenol (Poe 6)	483	11.0	45.06 **
Emulgin 1000	Non-ionic	Nonyl phenol (Poe 10)	NR	13.5	NR
Brij 35	Non-ionic	Lauric alcohol ether (Poe 23)	1,206	16.7	NR
Brij 58	Non-ionic	Stearilic alcohol ether (Poe 20)	1,122	5.6	NR
Brij 72	Non-ionic	Stearilic alcohol (Poe 2)	358	4.9	NR
Span 20	Non-ionic	Sorbitan monolaurate	214	8.6	NR
Tween 20	Non-ionic	Sorbitan monolaurate (Poe 20)	1,226	16.7	60.74 ***
Tween 60	Non-ionic	Sorbitan monostearate (Poe 20)	1,310	14.9	NR
Tween 80	Non-ionic	Sorbitan monoleate (Poe 20)	1,308	15.0	65.4**

*From this work, **from [5], ***from [6], NR, not reported.

2.3 SDS with and without NaCl-CMC measurement

Surfactant solutions were prepared with 0-2,000 mg/l of SDS in presence of 0, 0.5, 1 and 2% NaCl. Surface tensions ST were measured ten times in a Krüss automatic tensiometer (model K12). Measurements averages were plotted against surfactant concentration for every NaCl value. Deflection points*, i.e.*, where surface tension does not diminish anymore due to the increase in SDS concentration, are the CMC values for every NaCl concentration.

2.4 Soil washing efficiencies

Six grams of soil were put into 40 ml vials, and 20 ml of water, water, or a fixed concentration of a surfactant solution (with or without NaCl) was added. The assessed surfactant concentrations were 0.1, 0.5 and 1%. Assessed NaCl (JT Baker, USA) concentrations were 1, 2, and 3%. The flasks were kept at room temperature during 20 hours in reciprocating agitation. After this period, the flasks were allowed to sediment for 1 hour and samples were taken for TPH analysis. All assessments were carried out in duplicate and the average of the two tests was reported. Differences between duplicates were always less than 5%. After Soxhlet extraction, a gravimetric method was employed for TPH measurement.

3 Results and discussion

3.1 SDS CMCvalues

SDS solutions average ST values were plotted as shown in Figure 1, for every NaCl value. As mentioned in Materials and Methods section, CMC values are those where ST value did not diminish due to an augmentation in SDS concentration. CMC values for 0, 0.5, 1 and 2% NaCl resulted in values of 400, 300, 200 and 70 mg/l. For comparison the 1,586 mg/l value previously reported by Li-Zhong and Chiou [4] for CMC without any salt, was included.

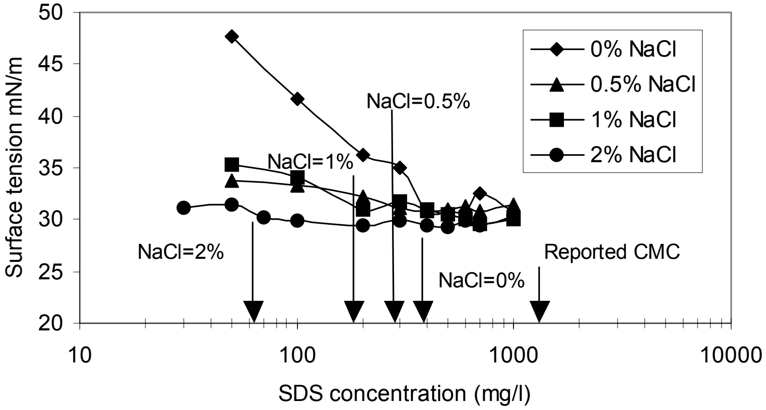

Figure 1: Surface tensions for the SDS solutions.

It is noteworthy when discussing the Na, K, Ca, Mg and Mn soil concentrations (table 1), that total monovalent cations are present in a total amount of about 600 mg/kg, while the correspondent divalent cations are present in more than 29,250 mg/kg. This value gave a Na+K/Ca+Mg+Mn of about 48. Some authors have reported the hardness tolerance of anionic surfactant solutions (*i.e.,* SDS), and underlined precipitation of these surfactants by the presence of divalent cations (Ca, Mg and Mn). It has been reported that hardness tolerance is increased by as much as a factor of 25 upon addition of 0.1M NaCl [7]. It was decide to use NaCl for enhancing the SDS performance and the SDS CMC values in the presence of 0, 0.5, 1, and 2% of NaCl was assessed. The CMC values were plotted ass a function of the NaCl concentration (%) at Figure 2. As observed they showed a lineal behaviour characterized by the equation (1):

$$\mathrm{CMC} = 386 - 164\,[\mathrm{NaCl}],\ \text{with } R^2 = 0.9859 \qquad (1)$$

This trend was also observed by Stellner and Schamerhon [7], when studying precipitation of sodium dodecyl sulphonate by calcium.

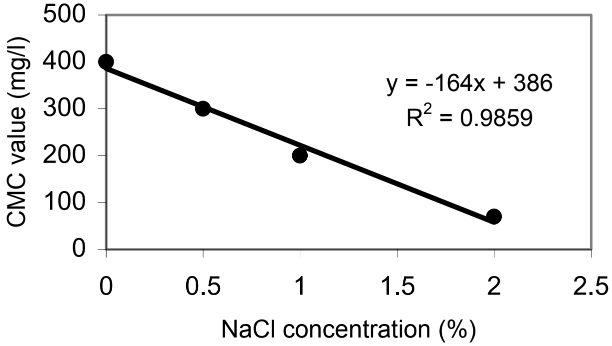

Figure 2: SDS CMC values as a function of NaCl concentration (%)

The equation found by these authors for describing that phenomenon is $\ln \mathrm{cmc}_{\mathrm{DS}} = -0.69832 \ln [\mathrm{Na}^+]\mathrm{eq} - 8.5134$, which is equivalent to results found in this work, employing a different Na concentration parameter. These authors reported that the Mg effect over the SD (the ionic SDS specie) CMC value is very similar. These values will be used in the next sections.

3.2 TPH removal values for single surfactants

The TPH removal for the blank test (water) gave a 3.52% value. Average results are reported. Standard deviations were lower than 5% of the total removals. As observed, values ranged from 0 to 32.9% for Brij 58 and Emulgin 600 (E-600), respectively. Other low TPH removal values were obtained for Brij 72, Texapon 40, and Span 20, with values of 0.4, 0.45, and 2.44%, respectively. Best results were obtained when using E-600 (32.9%), SDS (20.37), Brij 35 (16.86%), and Tween 80 (14.57%). Intermediate results were obtained when employing Emulgin 1000 (14.22%), Tween 20 (13.41%), Tween 60 (12.13%), and Maranil Lab (10.79%), see Figure 3. Note that regarding the initial TPH contaminated soil content of 108,980 mg/kg, these TPH removals correspond to high TPH values. For example, the E-600 32.9% value means that 32,905 mg TPH/kg soil was removed. The 20.37% removal achieved by SDS, means that 20,370 mg TPH/kg soil were removed. Even the lower values, means thousands of mg TPH removed per kg of soil. Torres *et al.* [5] reported the use of ethoxylated sorbitan monoleate and nonylphenol, and sodium lauryl ether sulphate for washing a soil contaminated with 20,00 mg/kg of TPH-diesel. They reached efficiencies between 41.9 and 88.2% when using doses between 0.5 and 300 x CMC for the products assessed. On the other hand, Lopez *et al.* [8] reported removal efficiencies between 16.1 and 69.4% when washing a soil contaminated with 17,200 mg/kg of PAHs and heavy petroleum fractions, using ethoxylated sorbitan monoleate, and nonylphenol, and sodium dodecyl sulphonate in concentrations between 0.1 and 1%. These authors reported the use of NaCl for SDS performance. Iturbe *et al.* [9], demonstrated that *in situ* flushing of soil contaminated with about 56,000 mg/kg of TPH (including some PAHs, gasoline, and diesel) was successful reaching a total removal of 98%. Polyethoxylated Sorbitan monoleate at a concentration of 0.5%. Finally, Iturbe *et al.* [10], reported that the same surfactant (TW80) was employed for washing soil contaminated with 3,800-17,200 mg/kg of TPH. Removal efficiencies with 0.5% surfactant solutions were between 50.3 and 92.8% regarding the initial contaminant concentration. A close look to the surfactants properties (table 1) shows that best TPH removal results were obtained when using a non-ionic (E-600) and an ionic (SDS) surfactant. There exist a trend when comparing TPH removal values and HLB surfactant values (see Figure 4). The higher the HLB value, the higher the TPH removal, but the correlation factor is not very high. Note that the highest point corresponds to E-600. Unfortunately there is no enough information for the set of surfactants regarding the CMC values. For the available values, including the CMC reported in this work, it seems that the lower the CMC value, the higher the TPH. A close look to the surfactants properties (Table 1) shows that best TPH removal results were obtained when using a non-ionic (E-600) and an ionic (SDS) surfactant. There exist a trend when comparing TPH removal values and HLB surfactant values. The higher the HLB value, the higher the TPH removal. Unfortunately there is no enough information for the set of surfactants regarding the CMC values. For the available values, it seem that the lower the CMC value, the higher the TPH removal (figure not shown). Due to the high divalent cation content of the soils (see Table 1) there is a detrimental effect over the ionic surfactants (SDS and Maranil Lab). There are different approaches to resolve this difficulty: 1) the use of NaCl, as suggested by Stellner and Scamerhon [7], 2) the use of a nonionic surfactant together with the ionic one, proposed by the previous authors and 3) the addition of divalent ions sequestrants like zeolites and phosphates (as in laundry detergents), or sodium silicate [11].

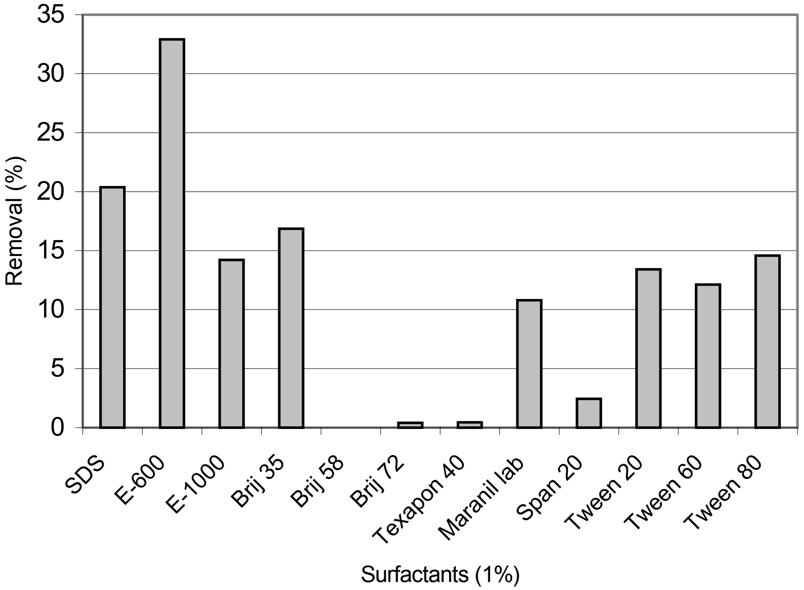

Figure 3: TPH removal values for the single surfactants assessments.

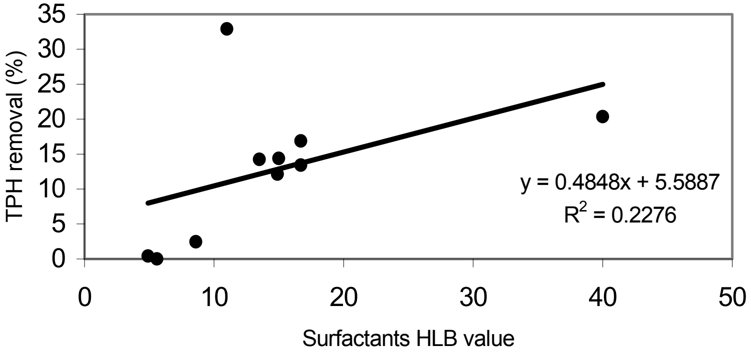

Figure 4: TPH removal (%) *versus* surfactant HLB values.

In this preliminary work, the three approaches were applied. SDS was selected between the two ionic surfactant employed because of its high initial TPH removal value. NaCl was added in amounts of 0.5, 1 and 2%. Besides, mixtures of SDS and a nonionic surfactant were assessed (always with a total surfactant concentration of 1%), *i.e.* SDS+ E-600, SDS+ TW80, SDS+ Brij35, and SDS+E1000. Sodium metasilicate analytic grade was employed as Ca sequestrants in a 10% concentration. Figure 5 shows the results of these assessments. It s remarkable that surfactant-surfactant and surfactant+salt assessments gave TPH removal efficiencies between 20 and 30%. In none of the assessments, TPH removal values higher than that found with E-600 at 1% was achieved. The addition of NaCl gave an increase in the TPH removal efficiency values of 21.97, 26.03 and 23.85% (for 0.5, 1 and 2% NaCl) in comparison with no salt (20.37%) assessments, since NaCl increases the SDS hardness tolerance and diminish the CMC value. This means 1.6, 5.66 and 3.48% of TPH removal enhancement due to NaCl addition. It seems that best choice is to add 1% NaCl addition. In the other hand, addition of 10% of Na-Silicate yielded in a TPH removal of 21.9%, in comparison with the SDS 1%, where 10.37% removal was achieved. At this point, results form the previous section can be helpful to explain this behaviour. Addition of NaCl promotes a diminution in the SDS CMC value. This effect was described before. An addition of 0.5% NaCl diminished SDS-CMC value from 400 to 300 mg/l (50%). An additional addition of 0.5% (up to 1%) yielded a CMC diminution from 300 to 200 mg/l (33%). Finally, an addition of a 1% more (up to 2%) yielded in a CMC value of 70 mg/l (a diminution of 65%). Since Na-silicate has been reported as a Ca sequestrants [11], but at the same time provides the Na^+ ion, both mechanisms *i.e.,* augmentation of SDS hardness tolerance and sequestration of Ca^{++} ions, are responsible by the enhancement in TPH removal. Regarding the SDS-nonionic assessments, it can be observed that all the combinations yielded TPH removal values higher than that found for SDS alone (all mixtures were prepared with a total of 1% surfactant, half and half). Differences were not quite enough high, but best results were obtained with the combination SDS+E-600. This fact is quite expectable, since both surfactants separately gave the best TPH removals. At this point it is important to remark the need of further experiments employing different surfactant doses (lower doses), and surfactant-surfactant proportions.

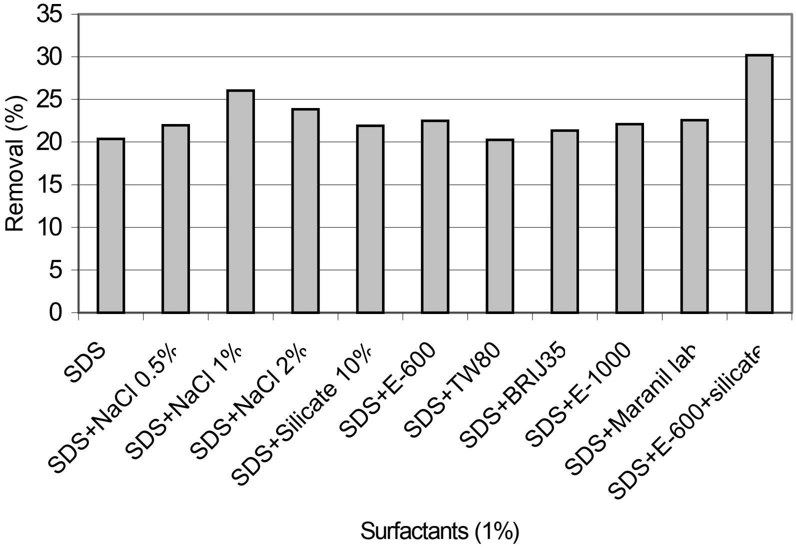

Figure 5: TPH removal values (%) for the mixed surfactant assessments.

The mixture SDS+Maranil lab is the only one anionic-anionic combination. It yielded a TPH removal of 22.57% higher than that obtained with only Maranil lab (10.79%) and SDS alone (20.37%), which indicates the existence of surfactants synergism. It is noteworthy that both products are very similar (dodecyl sulphonateand dodecyl-bencen sulphonate), except for the inclusion of the aromatic group.

At the end, the combination SDS-E1000+ Na-silicate yielded the best TPH removal value, *i.e.* 30.2%. It seems that Na-silicate augmented in a 7.7% the SDS+E-600 mixture performance (22.5%). It is very desirable to continue this work, employing different total surfactant doses and surfactant/surfactant/salt proportions. Since Na-silicate dose will impact the total washing process cost, it is necessary to evaluate the minimum amount required for the TPH removal enhancing.

4 Conclusions

Main conclusions of this work are the following:

1) It is possible to treat soils highly contaminated with crude oil (*c.a.* 109,000 mg/kg as TPH) employing surfactant-enhanced soils washing.
2) When washing with single surfactants (1%), best results were obtained with SDS, Brij 35 and E-600 (20.4, 16.8 and 32.9%, respectively).
3) Addition of NaCl to SDS solutions change the value of CMC, decreasing in a lineal proportion to the salt concentration in accord to the equation CMC = 386 – 164 [NaCl], with $R^2 = 0.9859$.
4) Mixtures of SDS+NaCl, SDS+nonionic surfactants and SDS-anionic surfactant (SDBS) gave better TPH removal rates that only SDS (for total surfactant concentrations of 1%). Best values were observed for SDS+NaCl 1% (26%), SDS+E-600 (22.5%), and SDS+Maranil lab (22.6%).
5) The mixture SDS+E-600+Na-silicate 10% gave the best TPH rate for the mixtures assessments, *i.e.* 30.2%.
6) These results are very promising, but more experimental work is necessary in order to optimise the surfactant and salt concentrations, and best TPH removal rate can be achieved with lower total surfactant and salts amounts.

Besides the surfactant and salts doses optimisation, evaluation of metal removals (Cu, Fe, Ni, Pb and Zn) is in progress.

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