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Investigation on the implementation of an in situ process for the treatment of coal tar using standard mixture of surfactants in different $CaCl_2$ concentrations

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ABSTRACT

This (qualitative) research focuses on the investigation of the implementation of standard mixture of Alfoterra® and Aerosol® with different concentrations of $CaCl_2$ as electrolyte, to be used in the future as in situ technique for the removal of polycyclic aromatic hydrocarbons from coal tar. The process will include the implementation of a standard mixture produced from two surfactants: Alfoterra 123-8S (3%) and Aerosol MA 80-I (1%) using $CaCl_2$ as electrolyte in the range of 0–20,000 ppm. The optimum conditions indicated that at 60°C ± 1°C the Winsor Type I system occurs between I1 and I3 samples (0–600 mg/L $CaCl_2$), a Winsor Type III system occurs between I4 and I9 samples (1,000–1,900 mg/L $CaCl_2$) and a Winsor Type II system occurs between I11 and I14 samples (2,500–10,000 mg/L $CaCl_2$). The final results point out that a three phase system (Type III—aqueous phase, oleic phase, micro-emulsion) appears between 1,000 and 1,900 mg/L of $CaCl_2$. Phase behaviour experiments are extremely important, in both surfactant enhanced aquifer remediation and enhanced oil recovery applications, for the selection of the best optimal mixture of surfactant solution to applied for soil remediation.

Keywords: Coal tar; PAHs; Surfactant; Soil remediation; In situ rehabilitation; Alfoterra; Aerosol

1. Introduction

The greatest significant environmental impact involves groundwater that becomes contaminated by contact with toxic liquids. Coal tar is a complex organic liquid mixture containing a wide variety of compounds. The polluted groundwater can then move away from the site into other areas and pollution is translated to organisms living on the bottom of nearby surface water bodies such as streams, rivers and lakes. The toxicity of coal tar varies according to both its constituent compounds and the route of exposure. Van Metre et al. [1] stated that a major source of polycyclic aromatic hydrocarbons (PAHs) in urban environments comes from road traffic and perhaps pavement sealants. Mahler et al. [2] determined that coal-tar sealants on roads and parking surfaces can significantly elevate PAHs in runoff. Zorpas et al. [3] indicated that storm runoff from urban area contains various pollutants and carries a large pollutant load, so it functions a great influence on receiving waters. Furthermore, under heavy traffic conditions the deposition of toxic substances such as PAHs after the first flush of runoff [3] is usually more important than those of other non-point pollutants, for example, phosphorous and nitrogen. Coal tar is a by-product of coal gas manufacture

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in the USA and Europe during the first half of the twentieth century [4,5]. At many coal gas manufacturing plants, coal tar entered sub-surface soils, sediments and rocks as a result of either accidental spillages or deliberate disposal practices [5,6].

PAHs are one of the most prevalent environmental pollutants, posing severe threats to human health wing to their mutagenic and carcinogenic nature and constitute a major concern for both U.S. Environmental Protection Agency and National Institute of Environmental Health Sciences [7]. Moreover, PAHs have low solubility in water due to their hydrophobicity. On the other hand, they are strongly sorbed onto soils and sediments, resulting in long-lasting environmental effects [8] and also due to PAHs chemical composition (containing from two to six benzene rings) are highly toxic, carcinogenic, teratogenic and thermally stable [9–11]. Sixteen PAHs have been recognized as priority carcinogenic compounds by the U.S. Environmental Protection Agency [3]. Generally, more than 150 PAHs compounds can be identified in coal tar among them are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(kl)xanthene, dibenzonaphthofuran, dimethylbenzopyrene, etc. [12,13].

Surfactant enhanced aquifer remediation (SEAR) is an in situ technology addressing the removal of immiscible phase liquid contaminants, from the saturated zone [14]. Compared with ex situ treatment, in situ technologies offer numerous benefits, such as addressing deep contamination and generally costing less [15]. This remediation technology may be used as enhancement to conventional pump and treat systems, which are often inefficient for recovering contaminants that are trapped as an immiscible phase liquid. By promoting the rapid removal of these contaminants, groundwater clean-up goals may be accomplished much more quickly.

Surfactants have shown great promise in remediating trapped non-aqueous phase liquid (NAPL) [7,16,17]. As Dong et al. [5] mentioned the addition of surfactant can reverse the spreading behaviour and with some surfactants the change in the spreading coefficient is sufficient for the coal tar to sink. Therefore, this behaviour corroborates the proposition that coal tar is a spreading NAPL in the unsaturated zone. Under such conditions, it seems proper to consider that one remediation goal for tackling coal tar in the unsaturated zone is to alter its spreading behaviour. This can be done to increase the volume of residually trapped coal tar which will significantly help to reduce off-site migration of mobile coal tar. Furthermore, changing the morphology of immobilized coal tar from a film to a compact lens will also alter the kinetics of mass transfer of NAPL components from residuals to infiltrating water.

This paper focuses on the implementation of an in situ process for the recovery of coal tar using different concentrations of surfactants using $CaCl_2$ as electrolyte. Through this research, the final results will be useful to be applied for the rehabilitation of heavy polluted soils.

2. Materials and methods

2.1. Experimental design

Distinction must be made between surfactant concentrations that are reported on an "active" basis or "as-received." The initial experiments were performed using active aqueous surfactant solution (26.8% active alcohol propoxylate sulphate sodium salt, Alfoterra® 123-8PO; 80.27% active sodium dihexyl sulfosuccinate, Aerosol® MA 80-I; 99% purity of secondary butyl alcohol and coal tar) and 4 wt% alcohol, and varying the salt concentration (0–20,000 mg/L $CaCl_2$). Secondary butyl alcohol was used as cosolvents to minimize gelling problems and reduce equilibration times according to Kostarelos et al. [6]. Moreover, calcium chloride (99.9% of purity $CaCl_2$) was used for electrolyte.

2.2. Batch experiment – phase behaviour test

All experiments were carried out using two types of surfactant and at a series of electrolyte concentration (0–20,000 mg/L Ca^{+2}). The batch studies reported in this paper were performed using a sample of coal tar from the market (with a CAS No.: 8007-45-2).

All batch experiments were conducted at 60°C ± 1°C temperature. Glass pipettes (25 mL) were used. The pipettes were sealed at the bottom end using a propane torch before fluids were added. Then 4.8 g of coal tar were added. After adding 4 mL of surfactant solution to each test tube, 2 mL of salt solution were added. Glass pipettes (tubes) were sealed with a propane torch; the samples were placed in water bath (60°C ± 1°C) for 30 min, shaken for 3 min using a vibrating shaker (IKA-Vibrax-VXR) and then allowed to equilibrate until the final results obtained after 8 weeks. The tubes contained an excess of coal tar, ensuring that the maximum solubilization of coal tar was achieved.

The samples were measured every week for a period of 2 months. Measurements included visual inspection of the samples, calculating the height of each column and colour recording of each column. Through the height it was indicated if evaporation occurs between the experiments. The same height indicated that our phases were stable.

Each week, heights were recorded, of each column and three different types were observed. Winsor Type I, II and III systems. The system is analogous to the solubilization surfactant systems in that the majority of surfactant resides in the aqueous phase, and contaminant recovery is promoted by partitioning of contaminant into surfactant micelles. This type of system has also been referred to as a single-phase micro-emulsion. A micro-emulsion is a thermodynamically stable solution of micelles and structured aggregates of micelles. There are (Fig. 1) three phases to consider in this system (water micro-emulsion and NAPL), and the surfactant micelles reside in only the micro-emulsion phase. The formation of this third phase is associated with achieving ultra-low interfacial tensions. The primary recovery mechanism in such systems is NAPL mobilization in response to the reduction of capillary forces. The middle phase micro-emulsion system is typically referred to as a Winsor Type III, or Type III, system that describes a middle phase micro-emulsion existing in equilibrium with excess aqueous and oil phase. The surfactant molecules comprising the micelles could be oriented with their hydrophobic tail groups pointing outward towards the NAPL phase. Such systems are typically referred to as Winsor Type II systems. The phase behaviour for non-ionic surfactant-based systems is especially sensitive to temperature in contrast to ionic surfactant-based systems, which are particularly sensitive to salinity.

3. Results and discussion

Coal tar has accumulated over decades in soils, is persistent to biodegradation, and persistent in soil and water [18–21] consequently, in recent years, coal tar or the related product is considered the fundamental PAHs source among all the known sources [2,22] and contributes to a major source of PAHs. It is mentioned by many researchers [13,23,24] that PAHs in particles can be easily transported by wind and rainwater to nearby soil sediments, water and air, lead to increased cancer risk for human beings. Numerous publications [25–28] indicated that in the USA, coal-tar-based pavement sealant is considered to be a major source of PHAs particularly in urban waterways. Coal tar can be transported in the sub-surface many decades after the initial release [5]. This happens due to coal tar which has a slightly larger density (1.18–1.23 g/cm^3 at 20°C) than that of water and a high viscosity [4].

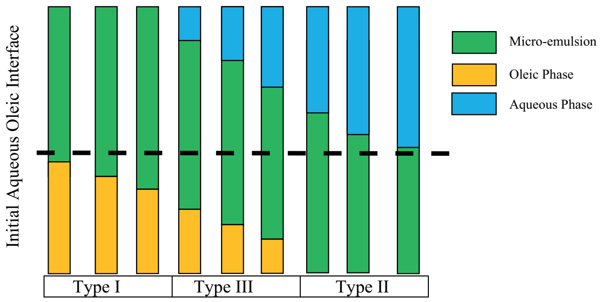

Fig. 1. Phase behaviour of equal volumes of surfactant solution and oil mixed in test tubes (after allowing time for equilibrium). At low salinity (Type I), a micro-emulsion and excess oil phase exist. At high salinity (Type II), a micro-emulsion and excess water form. All three phases (Type III) exist at intermediate salinities (Kostarelos et al. [6]).

Kostarelos et al. [6] mentioned that in previous studies in the same scientific area regarding the behaviour of surfactant phase was conducted and called Winsor Type I, II and III. Winsor Type I systems are typically oil-in-water micro-emulsions; Winsor Type II systems are typically inverted or water-in-oil micro-emulsions. Table 1 presents the results arising from the final measurement. It is obvious that a Winsor Type I system occurs between I1 and I3 samples (0–600 mg/L $CaCl_2$) (Figs. 2 and 3), a Winsor Type III system occurs between I4 and I9 (1,000–1,900 mg/L $CaCl_2$) samples and a Winsor Type II system occurs between I11 and I14 samples (2,500–10,000 mg/L $CaCl_2$).

Type I specifies surfactant-rich water phase (lower phase) that coexists with surfactant-poor oil phase (Winsor I), Type II

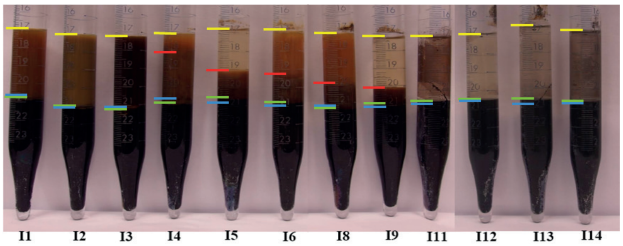

Fig. 2. Final results for the phase behaviour test (60°C ± 1°C) using as surfactant (2 mL): Alf 123 (3%) and MA 80-I (1%) (blue line indicates the initial interface, yellow line indicates the phase C, red line indicates the phase B and green line indicates the phase A).

Table 1
Final results for the phase behaviour test (60°C ± 1°C) using the proposed mixture of 26.8% Alfoterra® 123-8PO and 80.27% Aerosol® MA 80-I with 99% purity of secondary butyl alcohol

Sample	$CaCl_2$ (mg/L)	Phase A (coal tar)	Phase B		Phase C	
		Height (cm)	Height (cm)	Colour	Height (cm)	Colour
I1	0	20.8			16.85	Brown-white
I2	200	20.95			16.95	Grey-green
I3	600	21.2			17.11	Dark brown
I4	1,000	20.99	18.1	Brown-white	17.1	Brown-white
I5	1,500	20.6	18.85	Dark brown	16.65	Light clear
I6	1,600	20.85	19.5	Brown-white (milky)	16.85	Brown-white
I7	1,700	Broke				
I8	1,800	21.3	19.9	Brown-white (milky)	17.1	Brown-white
I9	1,900	21	20.1	Dark brown	17.28	Light clear
I10	2,000	Broke				
I11	2,500	20.48			16.88	Clear
I12	3,000	20.6			17	Clear
I13	5,000	20.6			16.6	Clear
I14	10,000	20.6			16.8	Clear
I15	20,000	Broke				

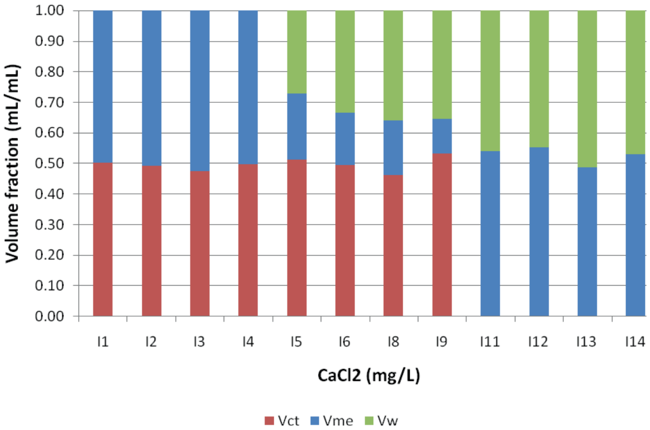

Fig. 3. Surfactant phase behaviour diagram for $CaCl_2$ (Winsor Type I 0–600 mg/L, II 2,500–10,000 mg/L, III 1,000–1,900 mg/L system) (Vct: coal tar volume, Vme: micro-emulsion volume, Vw: water volume).

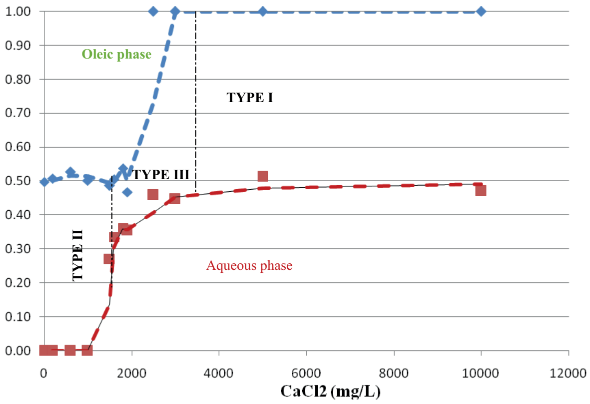

Fig. 4. Optimum salinity range for the formulation of the Type III micro-emulsion.

is surfactant-rich oil phase (the upper phase) that coexists with surfactant-poor water phase (Winsor II), Type III represents the surfactant-rich middle phase which coexists with both water (lower) and oil (upper) surfactant-poor phases (Winsor III; Fig. 4). A Type II system is undesirable because the partitioning of surfactant into the NAPL represents a significant loss mechanism [6].

Numerous other researchers [17,29,30] used several other mixtures of surfactants with other electrolytes in order to studied how PAHs can be removed from heavy polluted substrate. Couto et al. [29] investigated the remediation of sandy soils contaminated with diesel oil using sodium dodecyl sulphate (SDS) as surfactant solution, regular foams and colloidal gas aphrons. Foams have been investigated for soil remediation as a result of fact that they can improve the contact between the surfactant and the soil contaminant and reduce the interfacial tension between NAPL and the aqueous phase (Type III; Fig. 1). Foams were shown to be very effective fluids to remove diesel oil from sandy soils, demanding lower amount of surfactant and reaching removal efficiencies higher than 90%. López-Vizcaíno et al. [30] had studied the combination of surfactant-aided soil washing (SASW) process and coagulation treatment, using iron and aluminium salts, to remediate a low-permeability PAH-polluted soil. SASW is one of the standard technologies in the remediation of soils polluted with PAHs. This method involves washing the soils with an aqueous surfactant solution with the aim of enhancing the water solubility of the PAHs and forming O/W emulsions with micro-drops of PAHs. For the purpose of his study, three different types of surfactants were used as washing agents: SDS as a model anionic surfactant, alkylbenzyldimethylammonium chloride as a model cationic surfactant and polyoxyethylene sorbitan monooleate (Tween 80) as a model non-ionic surfactant. The result of this research indicates that: (i) SASW provide acceptable results for the remediation of low-permeability soils polluted with phenanthrene with the anionic surfactant to be the most efficient and gave pollutant removal percentages more than 90% while the non-ionic and cationic surfactant efficiencies were 70% and 30%, respectively, and (ii) the coagulation process appears to be a good alternative option for the treatment of SASW wastewater, which consists of an emulsion of phenanthrene in water stabilized by the surfactants. Additionally, Zhong-Yi et al. [16] studied the removal of PAHs in gas plant soils with four different types of surfactant: Triton X-100 (TX100 – non-ionic/synthetic surfactant), sodium dodecylbenzene sulphonate (SDBS – anionic/synthetic surfactant), rhamnolipid water solution (RWS – anionic/biological surfactant) and rhamnolipid fermentation broth (RFB – anionic/biological surfactant). The concentrations of acenaphthene (Ace) and fluorine (Flu) were very high in the two contaminated soils (more than 80% of PAHs presented). All aqueous solutions for the solubilization tests contained 0.01 mol/L NaCl (as electrolyte) to keep a constant ionic strength and 0.5 g/L $HgCl_2$ to inhibit microbial growth. After solubilization test, washing soil test and surfactant analysis the results indicated that: (i) in reverse series the solubilization efficiency for the PAHs was TX100 > SDBS > RWS > RFB, (ii) the maximum amounts of surfactants adsorbed (using Sm values) in the treated soil was in the order of RWS > RFB > SDBS > TX100 and (iii) the removal efficiency using the TX100 was >41% regarding the T-PAHs, followed by the SDBS (>36 indicating that TX100 surfactant can potentially be used for the remediation of contaminated soils from PAHs).

The experiments completed to characterize surfactant solutions for use in NAPL recovery can be termed phase behaviour experiments. Phase behaviour experiments with surfactant, water, alcohol and electrolyte are extremely important in both SEAR and enhanced oil recovery applications for the selection of optimal surfactant solution to applied for soil remediation and/or depuration. However, good understanding of surfactant phase behaviour in order to propose the best available concentration and conditions to be applied for the rehabilitation of heavy polluted soils, need experiments to be done.

4. Conclusion

Different types of surfactants (anionic, non-ionic, mixed surfactant, gemini surfactant, biosurfactant) in combination with others techniques (coagulation treatment, photo-Fenton oxidation) have been implemented over the years. Phase behaviour experiments with surfactant, water, alcohol and electrolyte are extremely important in SEAR for the selection of optimal surfactant and solution. In this qualitative research, the use of standard mixture from Alfoterra 123-8S and Aerosol MA 80-I as surfactants was used, using as electrolyte $CaCl_2$, indicated that it could be an acceptant solution for the removal of PHAs from coal tar or other polluted surface like agricultural soils. Further research could be done in the future focussing on the determination of the optimal $CaCl_2$ concentration. This will be helpful to evaluate the measurements of individual components of coal tar.

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