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Washing of field weathered crude oil contaminated soil with an environmentally compatible surfactant, alkyl polyglucoside

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ABSTRACT

Weathered crude oil contaminated soils (COCSs), which are much more difficult to remediate than those freshly contaminated, are widespread especially at the sites of oil fields and industries. Surfactant enhanced ex situ soil washing could be used to remediate COCSs, but surfactant toxicity becomes one of the major concerns. In this study, a class of green surfactants, alkyl polyglucosides (APGs), were tested in washing the field weathered COCS with relatively high oil concentration (123 mg g^{-1} dry soil) from Jilin Oilfield, Northeastern China. APG1214, characterized with longer alkyl chain, was more effective than APG0810 in crude oil removal. Adding inorganic sodium salts into APG1214 solution further improved the crude oil removal efficiency (CORE). Washing parameters (temperature, washing time, agitation speed and solution/soil ratio) were investigated and further optimized integratedly with an orthogonal design. At the optimum conditions, the CORE reached 97%. GC/MS analysis showed that the proportion of small *n*-alkanes (C_{16}–C_{23}) in residual crude oil gradually increased, which was helpful to interpret the oil removal mechanism. Moreover, eminent effect on removal of large *n*-alkanes was achieved from the synergy between APG1214 and inorganic salts, which was opposite to the effect when they were added separately. This study demonstrated a promising way to remediate COCS with ecologically compatible surfactant and provided guidelines for its practical application.

1. Introduction

Petroleum exploration and application result in serious soil contamination due to aboveground oil spills, storage tanks leakage and other accidents. Crude oil contaminated soils (COCSs) represent a considerable threat to the environment and human health (Li et al., 2008). The weathering procedure results in contaminants with higher molecular weight, viscosity and density, as well as greater binding strength of crude oil to soil (Urum et al., 2004; Chen et al., 2007). Therefore, weathered contaminated soils are usually much more difficult to remediate than recently contaminated soils (Cho et al., 1997).

Surfactant enhanced soil washing is an effective way to remediate COCSs. As amphiphilic molecule, surfactant removes crude oil from COCSs mainly by two mechanisms: mobilization induced by the reduced oil/water interfacial tension (IFT) and solubilization of the contaminants into the hydrophobic cores of the surfactant micelles (Mulligan et al., 2001). Soil washing has been widely studied to remediate soils and sands contaminated with crude oil components (Deshpande et al., 1999; Chang et al., 2000; Vreysen and Maes, 2005; Santa Anna et al., 2007). However, in most researches traditional synthetic surfactants were used, which have brought problems because of their toxicity and low biodegradability. Thus, surfactants of low toxicity and high biodegradability have received more and more interest in this field.

Some researchers have tested biosurfactants produced by microorganisms such as *Rhodococcus* and *Pseudomonas* species in the cleanup of COCSs (Kuyukina et al., 2005; Santa Anna et al., 2007). Urum and Pekdemir (2004) investigated the feasibility of five natural surfactants, including aescin, lecithin, rhamnolipid, saponin and tannin, for possible use in washing COCSs. Dwarakanath et al. (1999) employed three food grade surfactants in soil column flushing to remove nonaqueous phase liquids. However, these studies were mainly carried out on laboratory artificially contaminated soils. As the real contaminated soils are more complicated and difficult to remediate, the methods mentioned above may not be as effective in practical application.

As a class of relatively new nonionic surfactants, alkyl polyglucosides (APGs) are produced from renewable resources such as fatty alcohols and sugars (Fukuda et al., 1993). Due to their low toxicity, excellent biodegradability (Park et al., 2007) and outstanding properties (Fukuda et al., 1993), APGs have received considerable research interests and have been used in many fields

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(Weerawardena et al., 2000; Mehling et al., 2007) in recent years. Nevertheless, the application of APG in washing COCS has not been reported in open literatures.

In present work, APGs were employed in the washing remediation of COCS. Inorganic salts, which were commonly used in commercial detergents, were added into APG solution and the oil removal was significantly improved, which is uncommon for a nonionic surfactant. Some interesting results were obtained and discussed from the investigations of the co-effect between APG and the salts. Field weathered COCS was used as soil sample in current work to provide information for practical application. The objectives of this study can be summarized as: (1) to develop an optimized formula and to investigate the optimum conditions for washing field weathered COCS with the environmentally compatible surfactant, APG; (2) to investigate the variations of crude oil components in soil during the washing process and (3) to investigate the synergy between APG and inorganic salts. This work provided a demonstration of an environmentally compatible formula for the washing of real COCS.

2. Materials and methods

2.1. COCS

The COCS, which had been weathered for over a year, was collected from the surface soil of a contaminated site of Jilin Oilfield, Northeastern China. The soil was air-dried indoors at ambient temperature (25 ± 1 °C) for 1 week, screened through a 2 mm sieve to remove coarse fragments and then mechanically mixed to ensure homogeneity. The sieved soil sample was stored in airtight containers at 4 °C for further experiments. Major characteristics of the sieved COCS are shown in Table 1. The crude oil concentration is 123 mg g^{-1} dry soil, which is higher than those reported in soil washing literatures, though it is common for real COCSs.

Soil particle size distribution was analyzed with Mastersizer 2000 (Malvern Instrument Ltd., UK). The total organic carbon (TOC) was measured by burning the soil at 1300 °C with a Multi TOC/TN 3000 Analyzer (Analytik Jena AG Corporation, Germany). Soil pH was determined in distilled water at a solid/liquid ratio of 1:2.5 g mL^{-1} (pH-201, Hanna Corporation, Italy).

2.2. Surfactants and chemicals

Two commercial APGs were tested in washing the weathered COCS, $C_{8/10}$-APG (APG0810) and $C_{12/14}$-APG (APG1214) (Fig. 1a). They were obtained from China Research Institute of Daily Chemical Industry (Shanxi, China). Both of them have a polymerization degree of 1.5. The products were 50 wt% aqueous solutions (paste-like) with 0.3 wt% residual polyglucoses and less than 1 wt% residual fatty alcohols. The surfactants were used as received without further purification but the concentrations mentioned in this work are based on pure APGs. The critical micelle concentration (CMC) values of APG0810 and APG1214 were determined to be 0.08 wt% and 0.007 wt%, respectively at 25 °C by surface tension measurements using drop volume method.

Table 1
Major properties of the sieved COCS sample.

Properties		Value
Soil texture (vol.%)	Clay (<0.002 mm)	6
	Silt (0.002–0.02 mm)	16
	Sand (0.02–2 mm)	78
pH		8.1
TOC (%)		6.33
Crude oil concentration[a] (mg g^{-1} dry soil)		123

[a] Extracted with *n*-hexane.

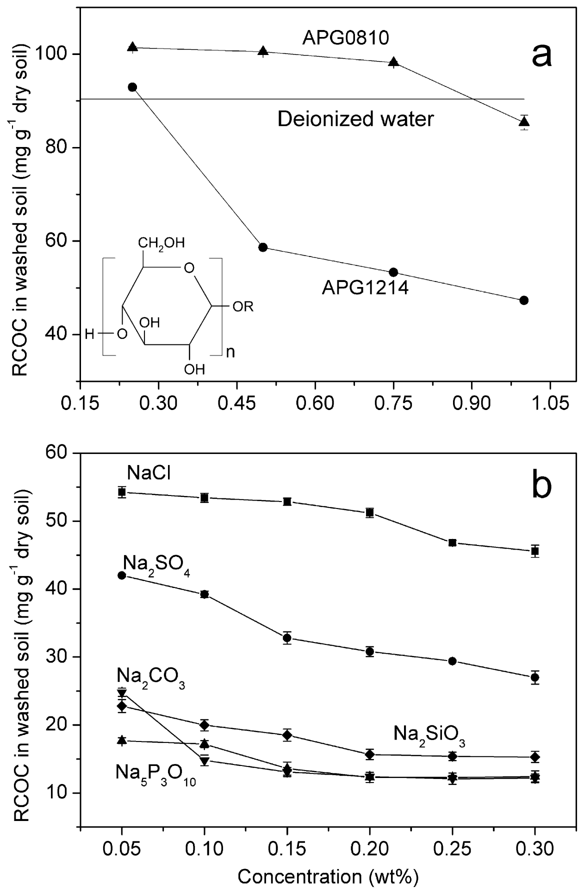

Fig. 1. (a) Residual crude oil concentrations (RCOCs) in the soils washed with APG0810 and APG1214 solutions of varying concentrations. General structure of the APGs is shown in the left corner. N: Degree of polymerization; R: alkyl chain (for APG0810, R = $C_{8/10}$; for APG1214, R = $C_{12/14}$). (b) Effect of adding inorganic salts into 0.75 wt% APG1214 solution on RCOCs. 10 g weathered COCS was washed with 50 mL solution at 70 °C for 30 min at an agitation speed of 130 rpm. Each experiment was carried out in triplicate and the error bars indicate standard deviations (SDs).

HPLC-grade *n*-hexane was purchased from Fisher Scientific, US. Other chemicals were of analytical grade and purchased from Beijing Chemical Reagent, Co. (Beijing, China). Deionized water was used for all tests.

2.3. Experimental procedures

2.3.1. Surfactant comparison

APG0810 and APG1214 of varying concentrations were tested in washing the weathered COCS. Soil washing was conducted by mixing 10 g weathered COCS with 50 mL surfactant solution in a 250 mL glass beaker at 70 °C, which was regulated with a water bath. The concentrations of the surfactants solutions ranged from 0.25 wt% to 1 wt%, which were all above the CMCs. Also a control sample with 10 g COCS in 50 mL deionized water was made. The slurries were mechanically agitated for 30 min with an accurate electric stirrer (Model JJ-1, 25 W, Hengfeng Instruments Co., Ltd., Jiangsu, China). At the end of each washing, the slurry was immediately cooled to the room temperature (25 ± 1 °C) with an ice-water bath before passed through a 0.3 mm sieve. The mixture passed through the sieve was centrifuged for 30 min at 4000 rpm. After removing the supernatant, the washed soil was rinsed with 40 mL of deionized water at room temperature (25 ± 1 °C) and then the wastewater was decanted after settled for 4 h. The soil was dried for 5 h at 60 °C, which could prevent contaminants from volatilizing. Afterwards, the soil was ground and