



Evaluation of naphthenic acids as a soil remediation agent: A physicochemical perspective



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HIGHLIGHTS

- Naphthenic acids tested as a surfactant for soil remediation.
- At low shear rates, washing efficiency improved with increasing surfactant addition.
- At high shear rates, washing efficiency worsened with increasing surfactant addition.
- Formation of bicontinuous microemulsion compromised washing performance.

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ABSTRACT

Removal of residual oil from reject sand grains is a major challenge in solvent-based bitumen extraction. A proposed solution is to wash the oil-contaminated sand grains with water and surfactants (the remediation agent). Due to the very favourable interfacial properties of naphthenic acids, namely, its ability to significantly reduce the oil–water interfacial tension and render the solid substrate hydrophilic, the surfactant has been proposed as a promising remediation agent. In this study, we evaluated the washing performance of naphthenic acids and demonstrated its inadequacy in sand remediation. The fundamental reason for the surfactant's poor performance was the inadvertent formation of a bicontinuous microemulsion which consumed much of the naphthenic acids, leaving little if any for remediation purposes.

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1. Introduction

At present, the primary method of extracting bitumen (extra heavy oil) from the Canadian oil sands is a flotation process which produces, as a by-product, contaminated water which must be kept in increasingly large tailings ponds [1,2]. To address this problem, recent efforts are under way to develop alternative *solvent-based* extraction methods which require little or no water [3,4]. Briefly, a solvent-based process involves mixing mined oil sand with a light hydrocarbon solvent, creating (i) a product in the form of diluted bitumen, and (ii) a reject stream which consists of the left-over sand grains. Owing to capillary forces, there will unavoidably be residual diluted bitumen that is trapped within the small crevices between the sand particles. As this residual oil has in it a volatile organic component (the solvent), it must be separated from the sand before the latter can be used for land reclamation. Indeed, the primary obstacle to any solvent-based extraction technology is the removal of residual oil from the reject sand grains.

In separating the residual oil, straightforward methods such as mechanical displacement and drying are effective only up to a point (the last portion of the oil is most difficult to remove). An alternative approach, one that we recently began to explore, is to wash the oil-laden sand particles with water–surfactant systems. This is a technique that is often employed in soil remediation [5,6], and shares many similarities with chemical enhanced oil recovery [7,8]. As the intent of solvent-based extraction is to avoid excessive consumption of water, the washing process must be in accordance with the principle of minimal water use (using an amount that is, for example, equal to that of the residual oil). With little water at one's disposal, the effectiveness of the surfactant becomes especially critical to the success of a washing operation. Unfortunately, no clear guideline can be found in the literature regarding the choice of surfactants for soil remediation: the 'optimal' surfactant appears to depend on the type of soil and the nature of the contamination; there is also no consensus on the chemical structure of the surfactant (e.g. whether it should be anionic or non-ionic) or the dosage that should be applied (e.g. whether it is above or below the critical micelle concentration) [9,10]. With little guidance from field-based experience, we

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turn our focus to the fundamentals of colloid and interface science. There are several conditions that a good washing agent should satisfy: Recognizing that the residual oil is held in place by capillary forces, the first requirement of a washing agent is its ability to significantly lower the oil–water interfacial tension γ . In addition, a small contact angle θ_c between the oil–water interface and the silica surface (angle measured through the aqueous phase) would greatly facilitate detachment of oil ganglia from the sand. Lastly, the surfactant should also be abundant and readily available to the operator. In an earlier paper, we had demonstrated that a particular class of surfactants, called naphthenic acids (NA), fulfils all of the above requirements [11]. Naphthenic acids is a class of anionic surfactants (consisting of cycloalkane carboxylic acids) that is indigenous to the Athabasca bitumen and many other types of crude oils [12–14]; it has an abundance of 1–2 wt% in Athabasca bitumen [15]. Our earlier study showed that NA had just the desired pore-scale interfacial properties for a washing process, i.e. it was able to create low γ and small θ_c [11]. Along with its ready availability, it appears naphthenic acids is an ideal candidate as a washing agent. In this study, we take the next logical step and evaluate the performance of naphthenic acids as an agent for cleaning oil-contaminated sand grains. We will demonstrate that, despite its promising interfacial properties, NA performs rather poorly as a washing agent. As such, we are reporting a negative finding. The main focus of this communication, however, is not on identification of a viable washing agent; rather, it is to reveal, from a fundamental perspective, the underlying mechanisms that led to NA's poor performance. The learning from this study, perhaps as a cautionary note, can be of relevance to many soil remediation and chemical enhanced oil recovery operations.

2. Experimental

2.1. Surface treatment of the sand

Before experiments, the sand grains were pre-treated under controlled conditions as follows: “Quack sand” (silica grinding sand with average diameter of 0.8 mm) was purchased from Quackenbush Company Inc. (Crystal Lake, Illinois) and used as the solid matrix. The sand was first thoroughly washed in toluene (HPLC grade) and dried under convective air flow. The particles are next surface-treated by dispersing them in 10 wt% diluted bitumen (i.e. 1 part bitumen + 9 parts toluene) to allow extensive exposure of the silica to bituminous materials—just as in the case of the waste sand grains in a solvent-based extraction operation. Bitumen samples (the so-called “DRU bottoms”) were obtained from Syncrude Canada Ltd. The sand particles were suspended and stirred in the diluted bitumen solution for two days, then washed multiple times with toluene until all residual diluted bitumen was rinsed away; the particles were again allowed to dry under a fume hood. This pre-treatment step was to render the sand particles hydrophobic through irreversible adsorption of bituminous materials onto the silica surface [16,17]. After such surface treatment, the sand grains may be considered “model particles” which mimic the interfacial properties of silica in an oil sand ore. In an earlier study [17], we had demonstrated, through wettability and XPS analyses, that the treated silica surface was indeed hydrophobic due to adsorbed materials from bitumen.

2.2. Surfactant solution and its surface tension

Naphthenic acids was the surfactant used in this study. Sodium naphthenates (SN), which is the salt form of naphthenic acids, was supplied by Eastman Kodak (practical grade) as a yellowish crystalline material. The Kodak SN was used without further purification.

Aqueous solutions of sodium naphthenates were prepared at various concentrations by dissolving the SN crystals in deionised and distilled water. To speed up the dissolution process, the mixtures were placed in a sonication bath for 1–2 min. It is known from an earlier study that the critical micelle concentration (CMC) of SN is roughly 10 g/L [11]. (The range of SN concentrations in this study was 0–100 g/L.) The surface tensions of SN solutions were measured by a Krüss K100 device with a Wilhelmy plate.

2.3. Washing protocol

We devised the following protocol to quantify the overall performance of a washing agent. Here, “overall performance” includes the ability of the surfactant to: liberate oil fragments from the sand grains, emulsify the oil in the aqueous phase, and facilitate transport of the oil/water mixture out of the porous sand matrix. In accordance with the principle of minimal water use (see Section 1), we also stipulated, somewhat arbitrarily, that the amount of water consumption would be equal to the amount of oil that was to be washed.

Fig. 1 shows a schematic of the washing procedures. As a first step, 50.0 g of surface-treated sand was placed in a PTFE (i.e. Teflon®) bottle. The bottle was gently tapped on a hard surface until the dry sand grains were more-or-less “close-packed” (i.e. with the sand level in the bottle at its lowest). Next, the sand was “contaminated” by slowly dripping toluene-diluted bitumen (again at 10 wt% concentration) into the PTFE bottle until the sand matrix was saturated with the liquid—and before the grains were completely submerged. The amount of diluted bitumen required for this step was very repeatable: it was 8.0 g. To remediate (i.e. clean) the oil-wetted sand, 8.0 g of an aqueous surfactant solution was introduced into the PTFE bottle containing the oil/sand mixture; the concentration of SN in the aqueous solution ranged from 0 to 100 g/L (recall that the CMC is ~ 10 g/L). Next, the oil/water/sand mixture was agitated in one of two ways: (a) gentle mixing with a spatula for 2 min, at a period of about 5 s per revolution; (b) vigorous shaking on an Excella E2 platform shaker (New Brunswick Scientific) at 300 rpm for 2 min. We will refer to these two manners of mixing as the low and high shear agitations, respectively; the corresponding shear rates are estimated to be of order 1 s^{-1} and 100 s^{-1} . Following agitation, the mixture was transferred to a glass vacuum filter holder (filtration area 9.6 cm^2 ; Fisherbrand, Fisher Scientific) and the oil/water mixture was allowed to drain through a stainless steel screen (100 mesh) and into a collecting flask until the dripping stopped. (Note that this filtration/drainage step was carried out without any filter paper or vacuum suction.) The drained liquid is a mixture of diluted bitumen, water and surfactants in various emulsified and/or free forms. To calculate the

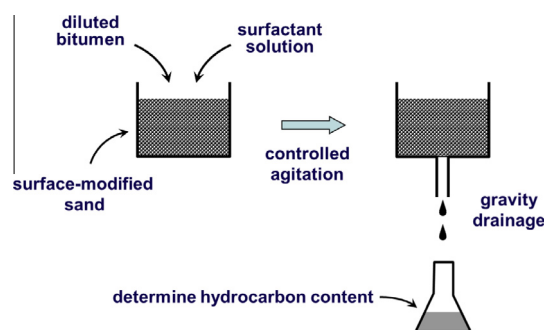


Fig. 1. A schematic of the washing protocol. Surface-modified sand was first “contaminated” with diluted bitumen, then washed with an aqueous surfactant solution that is equal in mass to the contaminant. The amount of hydrocarbon in the drained liquid is used as a measure of the washing performance.

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