Remediation of Diesel Contaminated Soil by Tween-20 Foam Stabilized by Silica Nanoparticles

R. Arun Karthick, and Pradipta Chattopadhyay

***Abstract*—Diesel oil spills into soil from petroleum storage areas, pipelines are a major environmental hazard. There is thus an increasing demand for new, efficient agents for remediation of diesel contaminated soil. The aim of this study therefore was to analyze the efficiency of application of nanoparticle stabilized nonionic surfactant foams for remediation of diesel contaminated soil. Stable foams were produced from dispersions of hydrophilic, hydrophobic silica nanoparticles with nonionic surfactant Tween-20. The foam generated was then transferred to a column containing the contaminated soil. The maximum diesel oil removal efficiency obtained by applying Tween-20 foam stabilized with 0.5 wt% hydrophobic silica nanoparticle was 78%- much higher than that obtained for Tween-20 foam stabilized with 0.5 wt% hydrophilic silica nanoparticles. The Tween-20 surfactant solution alone showed only 42% maximum oil removal efficiency.**

***Index Terms*—Diesel, nonionic surfactants, silica nanoparticles, soil remediation, stable foams.**

I. Introduction

Foam consists of gas phase dispersed in a continuous phase of liquid. The foamability and foam stability are crucial factors for the application of stable aqueous foam in removal of contaminants from soil [1]. It is a big challenge to apply suitable method and use efficient agents to treat contaminated soil [2], [3]. Diesel oil serves as major energy source in many countries. Fertile soil is prone to contamination with diesel seeping through pipelines during transport, leading to undesirable change in the subsurface of soil. This also leads to groundwater contamination. Diesel oil contamination was always a threat to environment thus causing a demand for robust contaminated soil remediation strategies with new, efficient agents [4]. It is thus very important to select a proper remediating agent that would completely solubilize the contaminants from soil. Surfactant remediation was earlier the primary technique to clear up the oil spills in land. Other methods such as using biological microbes to degrade diesel have also been reported [5]. The surfactants in water-soil heterogeneous system bring about removal of contaminant from soil by adsorbing on to the surface of soil. The amphiphilic nature of surfactant helped in solubilization of non-polar hydrocarbon contaminants on the soil surface. It has been possible to achieve satisfactory diesel removal efficiency by using nonionic surfactants like Tween-80 [6]-[9].

Aqueous foams have been identified as a better and effective tool to improve the removal of non-aqueous phase liquids (NAPLs) from contaminated soil. The foams occupy larger space and typically require less surfactant solution. This distinguishing behavior between surfactant solution and foam plus the higher cost of surfactants have led to foam being a better soil remediating agent. It was established that use of aqueous foam in contaminated soil remediation overcomes various problems associated with application of surfactant solution [10]. On comparing the various literature available, it was found that the application of nanoparticle stabilized nonionic surfactant foams for remediation of diesel contaminated oil have been investigated very rarely and not in proper depth. Thus the present work aims to analyze the efficiency of remediation of diesel contaminated soil by application of nonionic surfactant Tween-20 foams, stabilized with hydrophilic and hydrophobic silica nanoparticles.

II. Materials and Methods

A. Materials

Ultra-pure water prepared with Elix Millipore system was used throughout the study. The nonionic surfactant Tween-20 used for foam stabilization study was supplied by Himedia (India). Hydrophobic SiO_2 nanoparticle of average particle size of 55 nm and with specific BET surface area of 195-245 m^2g^{-1} and density of 2 gcm^{-3} was supplied by Evonik Canada Inc. Hydrophilic SiO2 nanoparticles (NanoLabs) used in the study had particle size in the range 50-80 nm, surface area of 630 $m2g^{-1}$ and a density of 2.5 gcm^{-3}. Tetrahydrofuran (THF) obtained from Spectrochem (India) was used as solvent to pre-wet the nanoparticles. All the glasswares were cleaned and dried with 70 vol% ethanol solution to prevent any contamination prior to experiments. Soil samples used in the study were collected locally and it was artificially contaminated with commercial diesel oil purchased from local petrol filling station.

B. Experimental Procedures

The silica nanoparticle and surfactant Tween-20 dispersion was prepared. The hydrophobic SiO_2 nanoparticles formed clumps in water. In order to prevent this, nanoparticles were initially wetted with 1 mL of THF and dispersed in water. The dispersion was then sonicated using ultrasonic probe sonicator (Johnson Plastosonic, Mumbai, India) at 20 kHz for 30 min [11], [12]. Tween-20 was dissolved in the prepared dispersion and used for further

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studies. Concentrations (vol%) of Tween-20 tested in the study include 0.02, 0.04, 0.06, 0.08 and 0.1%.

The foam properties of the prepared dispersion were analyzed using Dynamic Foam Analyzer DFA 100 (Kruss GmbH, Germany). The principle behind operation of DFA 100 lies in generation of foam by passing air through the sintered glass filter having pore size of 40-100 μm into the dispersion placed in a cylindrical glass column of length 250 mm and inside diameter of 40 mm. The air was passed at a flow rate of at 0.3 L/min for 12 s at the start of each run. This air flow rate and injection time was selected as it was the default setting for the Foam Analysis Software version 1.4.2.3 supplied by Kruss GmbH, Germany. For all the foaming measurements, 50 mL of sample was used with air injection time of 12 s and total run time was fixed to be 900 s arbitrarily [13]. The results attained using the Dynamic Foam Analyzer DFA 100 along with the Foam Analysis Software included foamability and foam stability. All the experiments were repeated thrice and arithmetic average was considered. All foaming runs were conducted at room temperature of 298 ± 2 K.

Soil sample used in the study was collected from non-contaminated agricultural field and characterized. Initially the collected soil was washed with water and dried at 128°C for 24h [14]. Soil was screened by sieving through mesh size 30 BSS (British Standard Specification) to remove any large particles such as debris of sand, stone and dry leaves [15]. The soil was placed in hot air oven at 128°C for 24 h to remove any microbial contamination. The type and texture of soil typically affects the remediation of soil to a greater extent. Hence the soil was characterized prior to the experiments [16]. The characteristics of the soil sample used in remediation study are given in Table I. The heat treated soil was contaminated with diesel oil at the rate of 200 μL per gram of soil and sealed tightly for 24 h prior to experiment so as to ensure complete adsorption of diesel oil on to the soil [17].

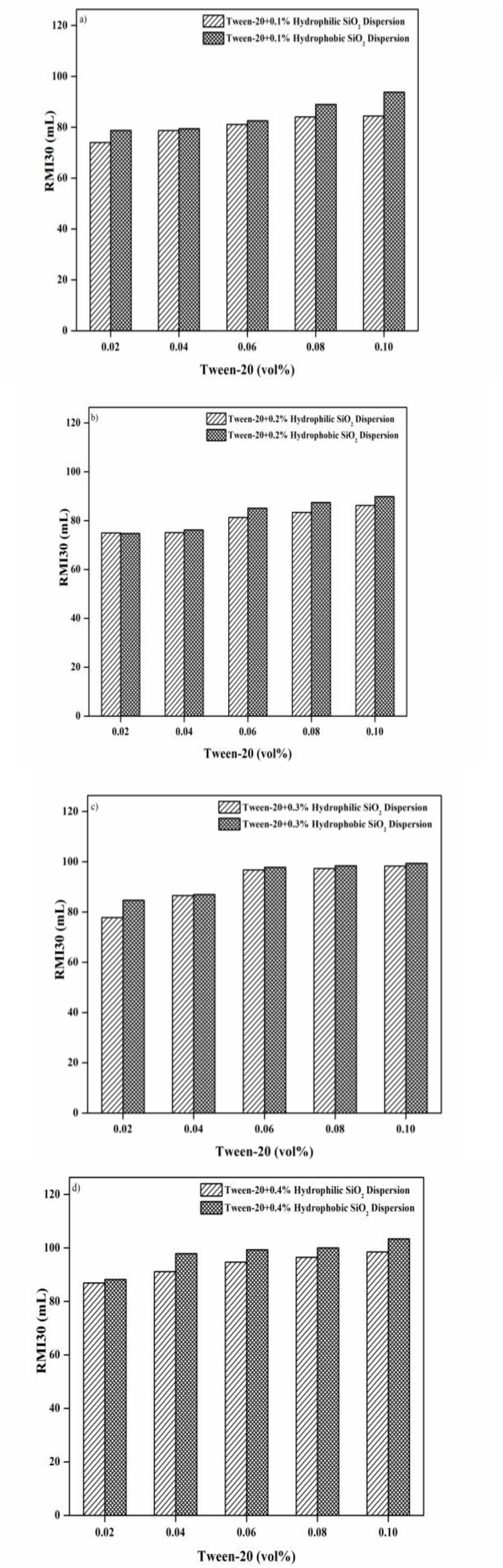
The soil remediation study was carried out in a column of 3 cm diameter and 30 cm length. A fine steel mesh was positioned at the exit of the column to trap the contaminated soil and to collect the effluent. The 100 g of contaminated soil was packed in layer by layer and tapped using glass rod [18, 19]. The foam generated using DFA 100 at a flow rate of 0.3 L/min was transferred to the soil column and allowed to penetrate into the contaminated soil. The drained liquid from the column was collected and separated using separating funnel [20]. The diesel oil removal efficiency obtained by applying silica nanoparticle and Tween-20 stabilized foam was compared with the application of pure surfactant Tween-20 solution. The oil removal efficiency by foam generated by only surfactant Tween-20 and foam stabilized by combination of Tween-20 and SiO_2 nanoparticles at 0.5 wt % were determined by:

$$\% = {}^{V_0}/_{V_R} \times 100 \qquad (1)$$

where, *Ƞ*%- Percentage of diesel oil removed from contaminated soil; V_0-Volume of diesel oil removed by surfactant foam and V_R-Volume of diesel oil present initially in the soil sample [21].

III. Results and Discussion

A. *Effect of Silica Nanoparticles on Foam Stability and Foam Volumes*



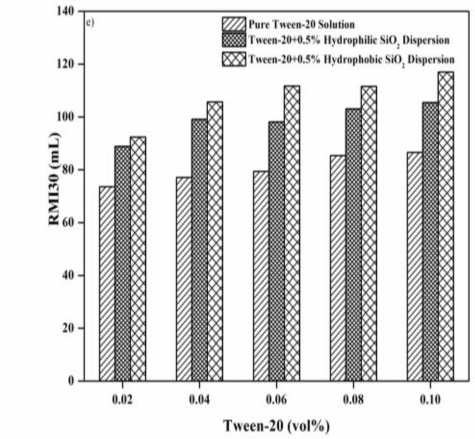


Fig. 1. Comparison of foam stability at various concentrations of hydrophilic and hydrophobic silica dispersions with Tween-20. a), b), c), d), e) represents the variations in RMI 30 values at 0.1, 0.2, 0.3, 0.4, 0.5 wt% of hydrophobic as well as hydrophilic silica nanoparticle concentrations respectively.

The foams were found to decay gradually at the end of air injection time of 12 s from the start of each run. Foam stability was measured in terms of Ross Miles Index (RMI 30) which described the volume of foam after 30 s collapse. The foam produced only with Tween-20 surfactant solution had very low RMI 30 value. As seen from Fig. 1, foam produced with 0.5 wt% hydrophobic SiO_2 and 0.1 vol% of Tween-20 had maximum RMI 30 of 117 mL whereas the foam produced with 0.5 wt% hydrophilic SiO_2 and 0.1 vol% of Tween-20 had maximum RMI 30 of 105.5 mL. Thus the foam stability is enhanced in the presence of hydrophobic SiO_2 nanoparticle. The foam generated with surfactant Tween-20 solution alone and 0.5 wt% silica nanoparticle dispersion with Tween-20 surfactant was subsequently used for the contaminated soil remediation study. The reason for selecting the foam produced from 0.5 wt% silica nanoparticle dispersion in combination with Tween-20 surfactant was that the dispersion showed maximum foam stability.

TABLE I: PROPERTIES OF SOIL SAMPLE USED FOR REMEDIATION STUDY

Properties of Soil sample	Values
Sand content (%)	95.1
Silt content (%)	4
pH	8.31
Density (kg m^{-3})	1399

B. *Dynamic Foam Properties*

Fig. 2 illustrates the results for dynamic foam volume for dispersions of 0.5% hydrophobic and hydrophilic silica nanoparticles and 0.1% Tween-20. The dynamic change in volume of foam produced by passing air at a flow rate of 0.3 L/min is plotted over a time period of 900 s. Nanoparticles being a good foam stabilizer tend to form a stable foam volume over a time period [22].The initial rise in foam volume occurs because of air being passed. 0.5% hydrophobic silica nanoparticle produced higher foam volumes than the surfactant only solution and hydrophilic silica nanoparticle. Also it can be noted that both hydrophilic and hydrophobic nanoparticle produced stable foam volumes over the stated time period. The reason for this lies in the fact that the size of both types of silica nanoparticle used was around 50 nm. It is known that the size of nanoparticles affects the generation of foam [23].

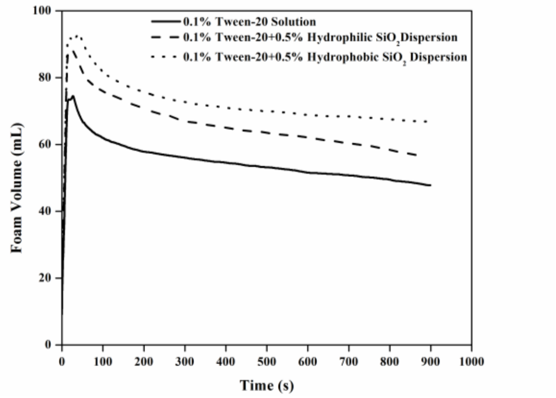


Fig. 2. Dynamic change in volume of foam generated using dispersion of 0.1 (vol%) of Tween-20 and 0.5 (wt%) of hydrophilic and hydrophobic silica nanoparticles.

The effect of silica nanoparticles on foam drainage was further investigated to describe the foam stability. Generally drainage is the phenomenon by which the liquid content in the foam drains by the effect of gravity. Not all the liquid from the foam drains due to capillary holdup until an equilibrium is reached. The liquid drainage pattern exhibited by dispersions of 0.5% hydrophilic and hydrophobic SiO_2 nanoparticles with 0.1% of Tween-20 as well as only 0.1% Tween-20 solution is shown in Fig. 3. The volume of liquid all the cases initially increases and remains nearly constant [24].

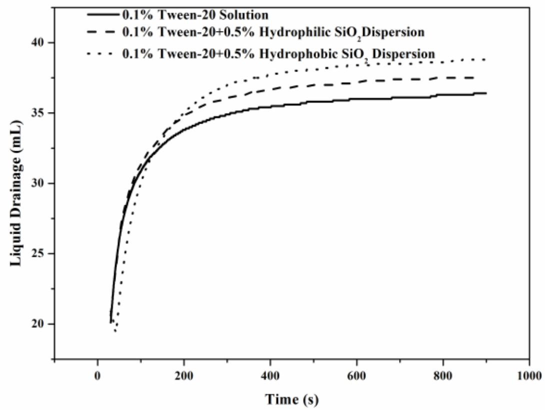


Fig. 3. Liquid Drainage using dispersion of 0.1 (vol%) of Tween-20 and 0.5 (wt%) of hydrophilic and hydrophobic SiO_2 dispersion.

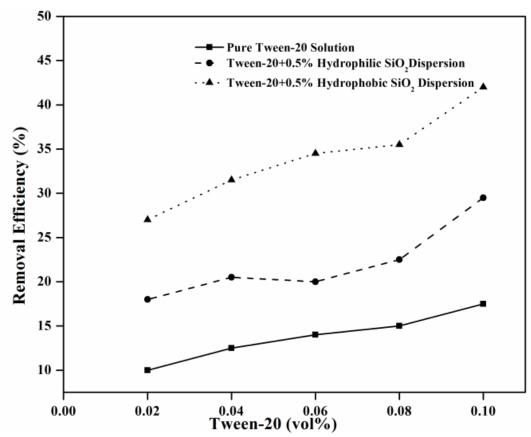


Fig. 4. Effects of application of surfactant Tween-20 solution and 0.5 wt% silica nanoparticle dispersions with Tween-20 on diesel oil removal efficiency from contaminated soil.

The amount of liquid drainage affects the foam stability which determines the removal of contaminants from soil surface. In the study conducted, the drainage of liquid from foam stabilized by 0.5% silica nanoparticles was found to be slower and higher diesel oil removal efficiency was noted. Though the mechanism by which silica hydrophobic particles affect drainage is unclear, the hydrophilic particles tend to adhere to the foam [25].

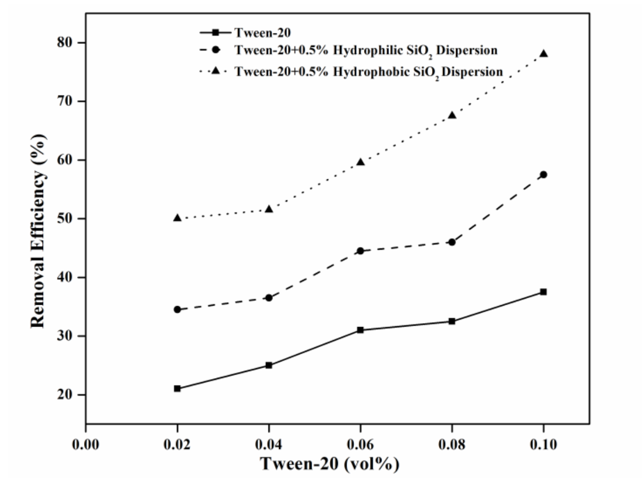


Fig. 5. Effects of application of surfactant foam stabilized by Tween-20 and 0.5 wt% silica nanoparticle dispersions with Tween-20 on diesel oil removal efficiency from contaminated soil.

C. Soil Remediation Study

With an objective to obtain higher oil removal efficiency from contaminated soil, the soil was treated with surfactant Tween-20 aqueous solution, dispersions of 0.5 wt% SiO_2 nanoparticles with Tween-20. The contaminated soil was subsequently treated with foams stabilized with Tween-20 solution as well as foams stabilized with dispersions of 0.5 wt% SiO_2 nanoparticles and Tween-20. The oil removal efficiency of both surfactant solution and surfactant foam was shown in Fig. 4 and Fig. 5 respectively. The Tween-20 surfactant solution alone only showed 42% maximum oil removal efficiency from contaminated soil. It was also observed that the Tween-20 surfactant foam stabilized with hydrophobic SiO_2 nanoparticle showed 78% maximum oil removal efficiency and the maximum oil removal efficiency obtained by Tween-20 surfactant foam stabilized with hydrophilic silica nanoparticles was only 57.5%. The availability of silica nanoparticles to interact with contaminants was an important factor in achieving better soil remediation. The absence of nanoparticle in surfactant solution made it difficult to interact with soil and hence less oil removal efficiency was observed in that case. Also it was found that the hydrophobic silica nanoparticles tend to adsorb efficiently and thus made the foam much more stable. Higher the foam stability, higher was the oil removal efficiency from contaminated soil as mentioned in literature [26].

IV. Conclusions

The applications of nanoparticles are vast in various fields in recent times. The process of stabilization of foam by using dispersions of nonionic surfactant (Tween-20) and different types of SiO_2 nanoparticles and its subsequent application in removal of diesel oil from contaminated soil was demonstrated. The most stable foam was used in the soil remediation study. The hydrophobic silica nanoparticle dispersion along with different concentrations of Tween-20 produced better foamability and foam stability than hydrophilic silica nanoparticle dispersion at 0.5 wt% concentration. A significant improvement in oil removal efficiency was also seen for Tween-20 surfactant foam stabilized by silica nanoparticle than that for Tween-20 surfactant solution alone. Hence Tween-20 surfactant foam stabilized by silica nanoparticles are better capable for contaminated soil remediation compared to Tween-20 surfactant solution. Higher percentage of diesel oil removal from contaminated soil was attained by using Tween-20 foam stabilized by hydrophobic silica nanoparticle. The results obtained will be compared in future with that obtained for important biosurfactant foams, used for soil remediation.

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