Extraction and Characterization of an Eco-Friendly Surfactant for Its Use in Enhanced Oil Recovery

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Abstract
Experimental studies have been performed to explore the suitability of an eco-friendly surfactant in enhanced oil recovery. In this respect, herbal surfactant has been isolated from soap nut and characterized by its morphology and physico-chemical properties. The extracted surfactant reduces the interfacial tension significantly over a wide range of concentrations. A series of flooding experiments have been carried out using the extracted surfactant and substantial incremental recoveries have been observed after the conventional water flooding. Use of alkali and polymer were found to improve the incremental recovery because of synergistic effects of surfactant, polymer and alkali.

Keywords: *Soapnut, surfactant, polymer, enhanced oil recovery, flooding*

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INTRODUCTION
Surfactant flood tertiary oil recovery schemes have been gaining importance in recent years as most of the oil reservoirs are depleted after primary and secondary recoveries. Several surfactants and their mixtures have been reported for enhanced oil recovery EOR [1–5]. In general, the mechanism by which surfactants enhance oil recovery is by reducing the interfacial tension or surface tension in the rock-water-oil. In particular, spontaneous imbibitions can be enhanced by adding surfactants [2]. On the other hand, surfactants also may lead the alteration of the rock's wettability [5]. In recent years, much attention has been directed towards natural surfactants owing to their different advantages such as lower toxicity, higher biodegradability, better environmental capability, higher foaming, high selectivity, specific activity at extreme temperatures, pH and salinity, and the ability to be synthesized from renewable feed stocks [6]. Many natural surfactants have been tested at the lab scale only. The discovery of new natural surfactants may open a new door to the petroleum industry to explore the use of low cost and environmental friendly natural materials [7] for enhanced oil recovery (EOR) during chemical flooding.

The Earth's ecosystem has evolved in presence of natural surfactants. Synthetic surfactants have many acutely toxic and subtle effects on the environment. The production and use of synthetic surfactants have several socio-economic, health and environmental impacts [8]. In the present work, an environmentally sustainable surfactant has been isolated from soapnut. Soapnut is a fruit of the soapnut tree generally found in tropical and sub-tropical climate areas in various parts of the world including Asia, America and Europe. Two main varieties (*Sapindus mukorossi* and *Sapindus trifoliatus*) are widely available in India, Nepal, Bangladesh, Pakistan and many other countries. The authors carried out a comprehensive study on the uses of various parts of the soapnut tree. Soapnut is widely used in mining/petroleum industry as dust suppressing agent. It is very useful in enhanced oil recovery in petroleum industry [9, 10] without causing any environmental impact.

The displacement of oil by water is unstable, because the oil viscosity is higher than the water viscosity. It is well known that use of polymer increases the viscosity of the injected water and reduces permeability of the porous media, allowing for an increase in the vertical and areal sweep efficiencies, and consequently, higher oil recovery [11, 12].

In the present paper, an indigenous method has been reported for preparation of powdered soapnut extract, which is non-hazardous with a considerable storage/shelf life and readily soluble in water. Investigation has also been made to characterize the extracted soapnut shell powder and its application in surfactant flooding for enhanced recovery of oil after conventional water flooding. The incremental effects of alkali and polymer on surfactant flooding have also been discussed.

EXPERIMENTAL

Extraction and Purification of Surfactant from Soapnut

The ground soapnut shell powder has shown considerable potential for use as natural surfactant in enhanced oil recovery. After removing seed from fruit, the soapnut fruit pericarp shells *S. mukorossi* were dried in an oven at 50 °C for 30 h. Soapnut fruit pericarp shells were crushed to a fine powder in a grinder for surfactant materials extraction. The powdered material was refluxed with ethanol for 6–8 h. It yielded a brown syrupy mass and after drying, a gummy sample appeared. Another part of the powdered sample was also refluxed with ethyl acetoacetate (EAA) and ethanol mixture (1:1) for 6–8 h and this yielded a dark brown syrup. After drying, this also gave a gummy sample. The gummy samples were triturated with diethyl ether and petroleum ether until a light yellowish white paste was formed. This was followed by vacuum evaporation and drying the extract at 50–60 °C, which gave a light yellowish white powder (Figures 1 and 2). For preliminary tests, aqueous solutions of 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, 0.8, and 1.0% ethanol and EAA + ethanol extract (gummy sample) were prepared in distilled water. Similarly, 0.00313, 0.00625, 0.0125, 0.025, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0, 2.0, 4.0, and 5.0% solutions were prepared by exact dilution by using both the light yellowish white powders (pure form).

Guar gum is used as a natural polymer for the flooding experiments. Reagent grade sodium hydroxide (96% purity) from SD Fine-Chem Ltd. was used as alkali. The crude oil used in the flooding experiments was collected from Ahmedabad Oil Field (India). It was degassed and dehydrated, with a viscosity of 50.12 mPa.s at 45 °C, and a total acid number of 0.038 mg KOH/g.

Fig. 1: *Ethyl Alcohol Extract of Soapnut (Pure Form).*

Fig. 2: *EAA + Ethyl Alcohol Extract of Soapnut (Pure Form).*

Measurement of Physicochemical Properties

The SEM analysis of the extracted soapnut powder was carried out using SEM-EDX technique to study the characterization of the samples in terms of their topography, crystallography and elemental composition of surfactant materials. For SEM analysis, the sample was coated with gold and palladium to prevent charging of the sample [13].

Infrared spectra of the pretreated and treated soapnut extracts were recorded between 350 and 4000 cm^{-1} using KBr-pellet techniques on a Brucker scientific IR-spectrophotometer M500. The spectra were interpreted using Ganz and Kalkreuth method [14].

Surface tension measurements were carried out using an auto tentiometer (Model: 6801ES with platinum ring) under atmospheric pressure by the ring method [15] with an accuracy of ± 0.1 mN/m. All measurements were carried out at a temperature of 298 K.

Flooding Apparatus and Method

The experimental set-up (Figure 3) for sand pack flooding tests consists of four components: a sand pack holder, a displacement pump (Teledyne Isco), cylinders for holding crude oil and chemical slug and fraction collectors. The sand pack holder was first tightly packed with sand using brine solution. The sand pack was then completely saturated with brine solution, and absolute permeability was measured by injecting brine solution at constant pressure of 25 psig. It was next flooded with oil at an injection pressure of 800 psig to irreducible water saturation. The sand pack was rested for one day at this stage. It was then water-flooded with 200 psig injection pressure and continued to flood until water cut reached above 95%. Substantial amount of oil was recovered during this water/brine flooding. The remaining oil was recovered by different chemical methods, viz., surfactant flooding and alkaline-surfactant-polymer flooding at 200 psig followed by chase water flooding. The recovered fluids were collected by switching the fraction collector at regular interval. The effective permeability to oil (K_o) and effective permeability to water (K_w) were measured at irreducible water saturation (S_{wi}) and residual oil saturation (S_{or}) respectively using Darcy's law equation.

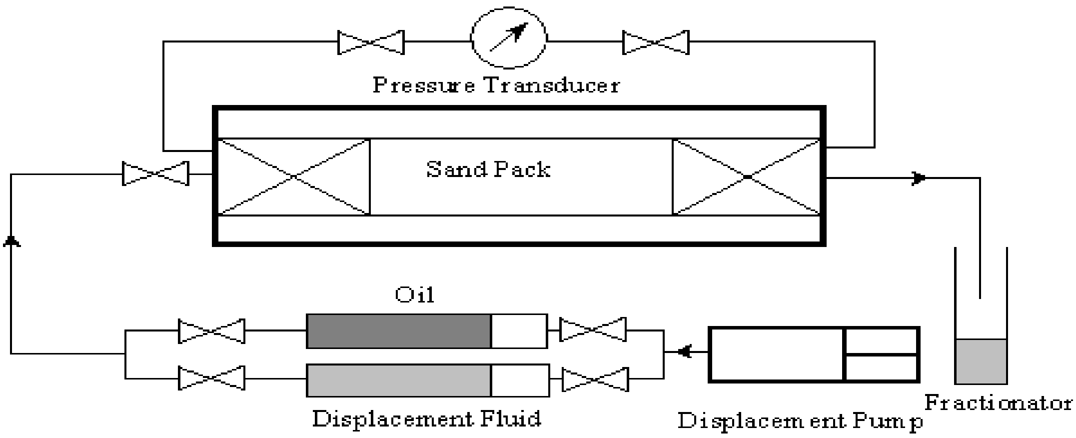

Fig. 3: *Schematic Diagram of Crude Oil Flooding System.*

RESULTS AND DISCUSSION

Characterization of Extracted Surfactant

SEM Analysis

SEM is considered as a rapid, inexpensive, and basically non-destructive approach to surface analysis [16]. The main objective of SEM analysis is to gather information on sample topography and or elemental composition of surfactant materials. For SEM the sample was coated with gold and palladium to prevent charging of the sample [13]. The SEM analyses of soapnut samples are shown in Figures 4–6. Though the sample appears to be powdery in nature, the SEM study reveals that this has got a polymer-type texture. The compositional analysis shows that it contains 50.3% carbon, 41.5% oxygen, 7.1% hydrogen and 1.1% other trace elements.

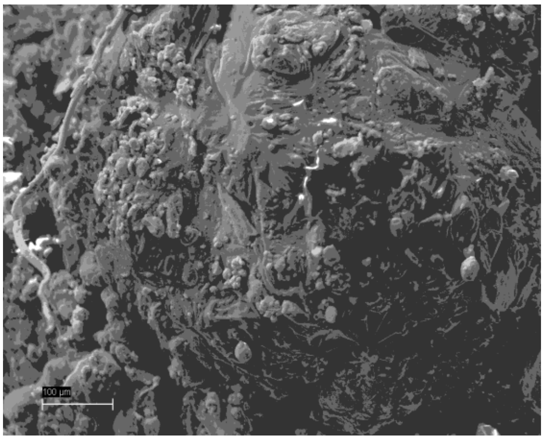

Fig. 4: *SEM of Soapnut Powder (Outer Surface).*

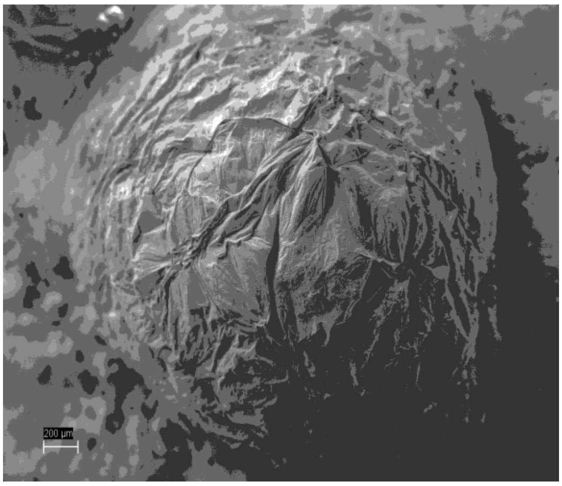

Fig. 5: *SEM of Ethyl Alcohol Extract of Soapnut (Powder).*

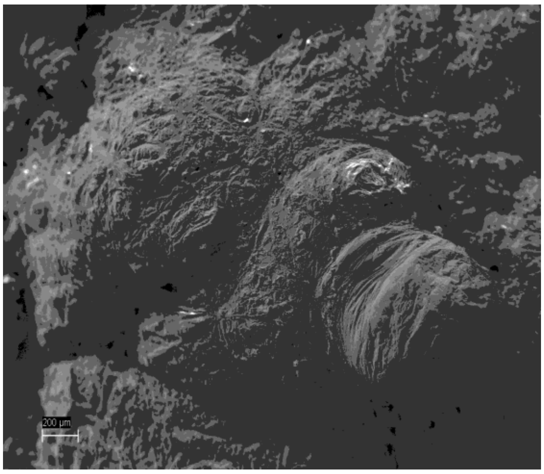

Fig. 6: *SEM of EAA + Ethyl Alcohol Extract of Soapnut (Powder).*

FTIR Spectroscopic Analysis of the Various Samples of Soapnut Extract

FTIR spectroscopic analysis of various samples of soapnut extract has been carried out in a Buck scientific IR-spectrophotometer M500. FTIR spectrum of hot water extract of soapnut reveals (Figure 7) the presence of alcoholic –OH (3392 cm^{-1}, broad). That the –OH broad peak is mainly due to alcoholic –OH is confirmed by the presence of an intense peak (1050 cm^{-1}), due to primary C–O of a carbinol. Intense band at 2931.41 cm^{-1} is due to aliphatic $–CH_2$ stretching. Presence of such an intense aliphatic band points towards aliphatic nature of the surfactant. Ketonic impurities (ν_{co} = 1728 cm^{-1} and 1693 cm^{-1}) are present. Methyl groups are also present (1412 and 1385 cm^{-1} peaks, –CH-deformation bands of $–CH_3$). However, some weak aromatic –CH peaks have also been observed (921–793cm^{-1}). FTIR spectra (Figures 8 and 9) of ethyl alcohol and EAA + ethyl alcohol extract are much sharper than water extract of soapnut. Similar types of IR peaks are observed, but the intensities are more and the peaks are well resolved. The asymmetric $–CH_2$ peaks are sharp and intense in both the spectra (Figures 8 and 9). Unlike the broader –OH peak in case of the spectrum of hot water extract of soapnut the –OH peaks are sharper. These results point towards the better purity of the soapnut extract in the present cases. Sharper peaks are obtained in case of pure form (Figures 10 and 11).

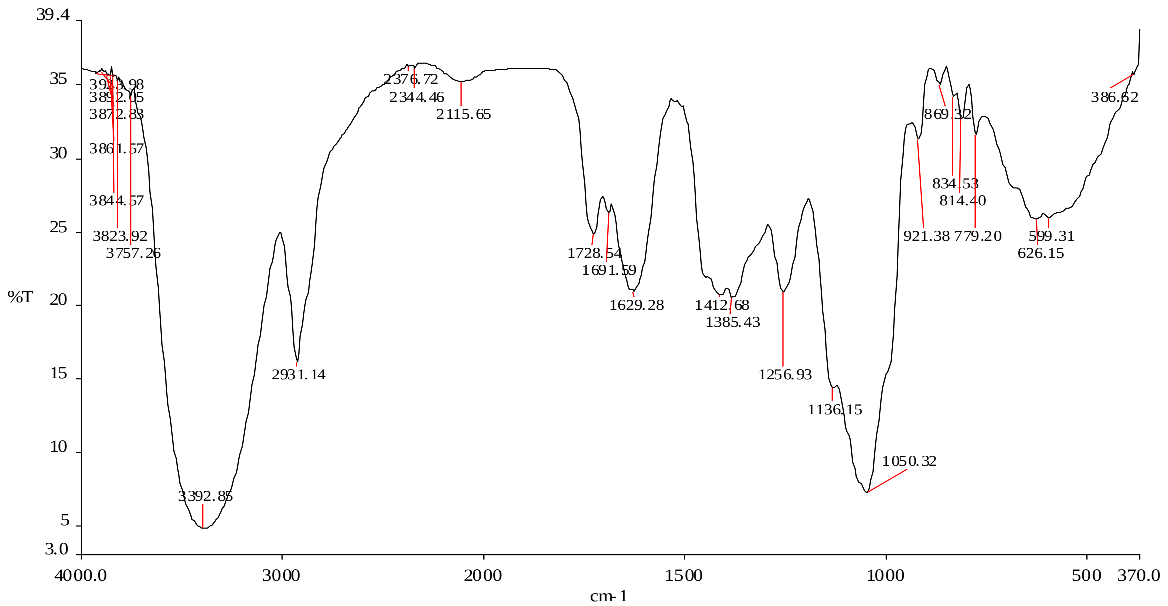

Fig. 7: *FTIR of Water Extract of Soapnut Powder.*

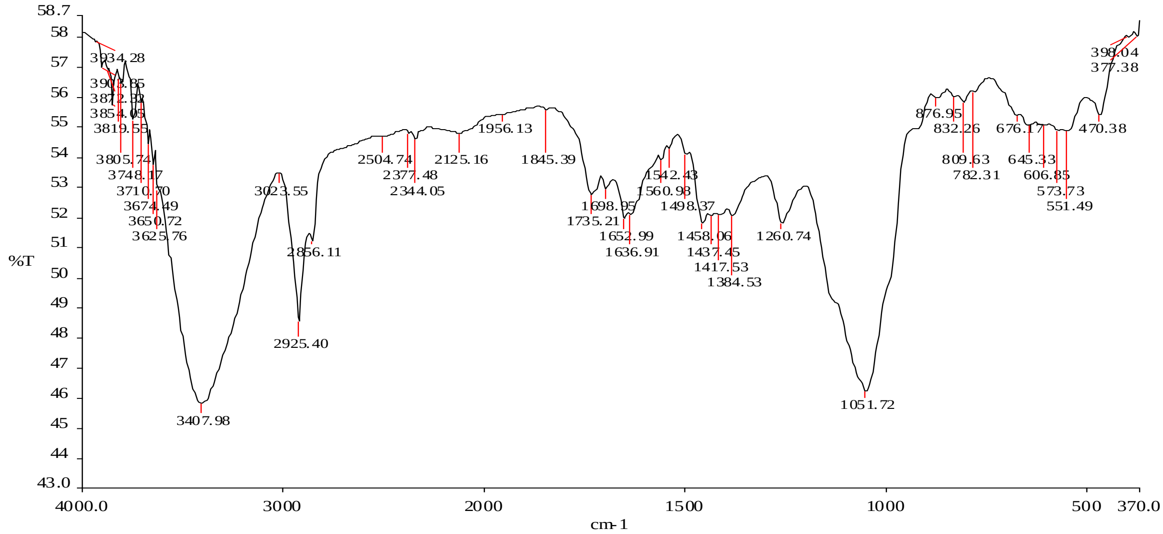

Fig. 8: *FTIR of Ethyl Alcohol Extract of Soapnut (Gummy Form).*

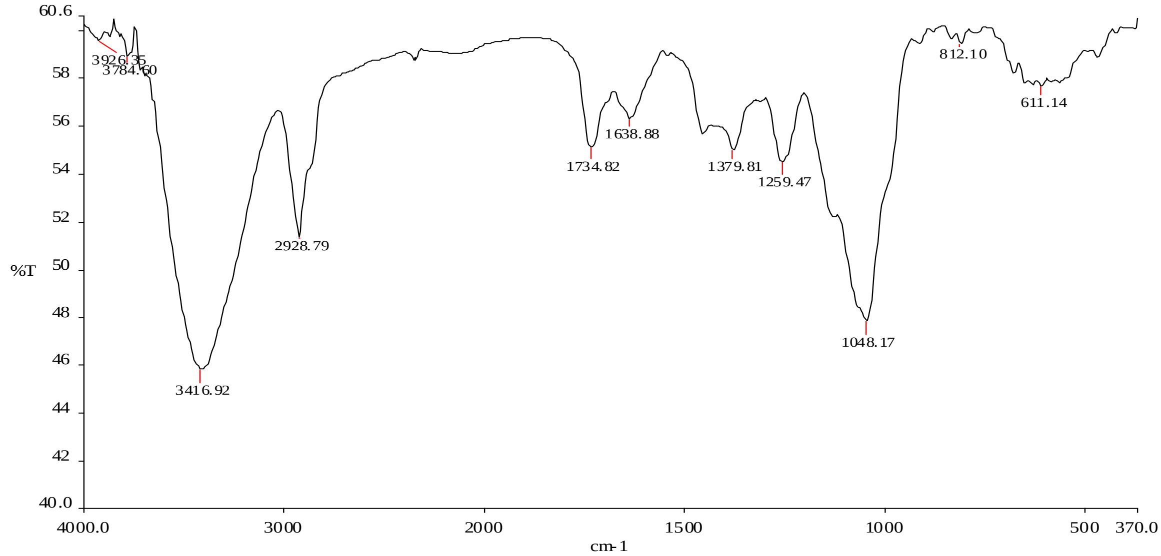

Fig. 9: *FTIR of EAA + Ethyl Alcohol Extract of Soapnut (Gummy form).*

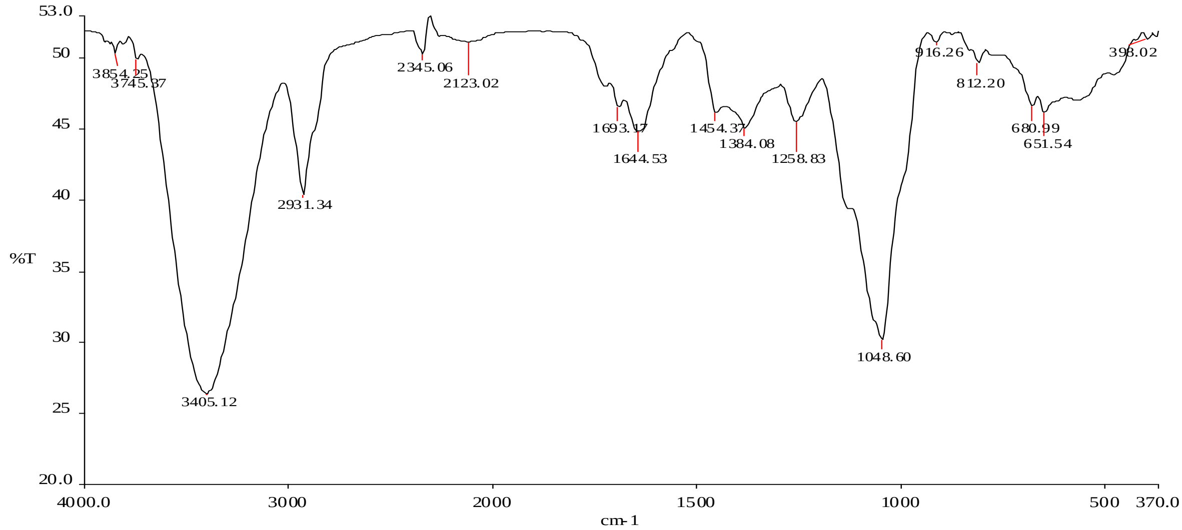

Fig. 10: *FTIR of Pure Form of Ethyl Alcohol Extract of Soapnut.*

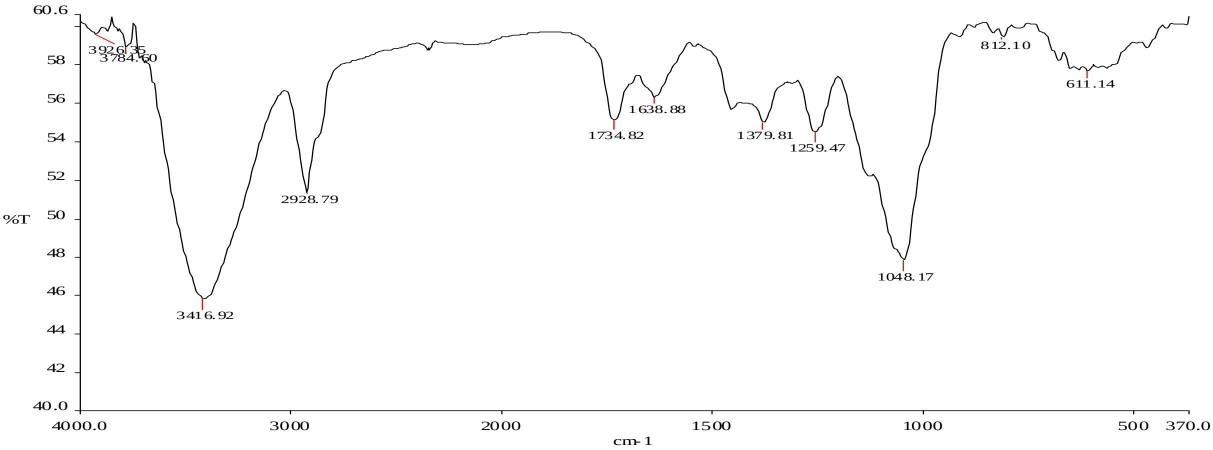

Fig. 11: *FTIR of Pure Form of EAA + Ethyl Alcohol Soapnut Extract.*

Surface Tension of Extracted Surfactant

The variation of surface tension of ethyl alcohol extract and EAA + ethyl alcohol extract of gummy sample as well as pure yellowish powder as a function of percentage of their concentrations are shown in Figures 12 and 13. In both cases, the surface tension decreases with increase in concentration of soapnut powder. These figures also show the critical concentrations corresponding to micelle formation (CMC), which is an important parameter of surfactant solutions.

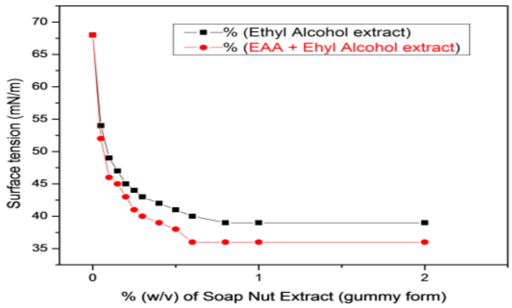

Fig. 12: *Surface Tension Measurements of Soapnut Extract (Gummy Form).*

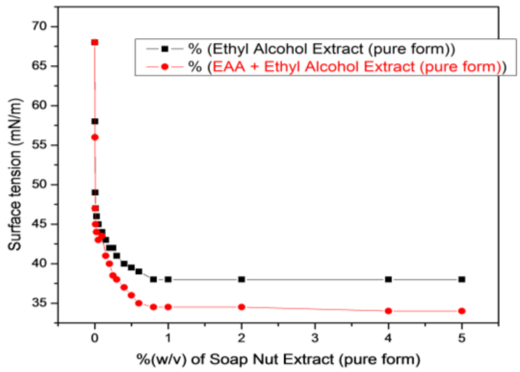

Fig. 13: *Surface Tension Measurements of Soapnut Extract (Pure Form).*

Flooding Test

The efficiencies of the extracted surfactant from the soapnut for its use in enhanced oil recovery were tested by a series of sandpack flooding experiments. The critical concentrations of the surfactant slug for injection were chosen above CMC. Some other experiments were also performed using polymer as mobility controller after the injection of surfactant slug. It has also been found that use of alkali also enhanced the oil recovery as it is well known that alkali also enhances the recovery of oil by reducing the interfacial area and changing the rock wettability [17, 18]. Figure 14 shows the oil recovery and water cut during water flooding and subsequent injection of 0.5 PV of surfactant slugs. Since in the present work, experiments were carried out in sand pack with higher porosity (~ 38%), the water flood recovers almost 50% of the original oil in place. During water flooding, as the water-cut reaches above 95%, it was subsequently flooded with different chemical slugs followed by chase water. The incremental recoveries along with other important parameters are shown in Table 1. It may be found that the incremental recoveries after water flooding are higher for EAA-Ethyl extract compared to Ethyl extract because of lower surface tension of the former.

The synergistic effects of surfactant, polymer and alkali result in incremental enhanced recovery of oil over surfactant flooding. To compare, same volumes (0.5 PV) of slugs having different composition were injected. Figure 15 shows the oil recovery and water cut when the system is flooded with surfactant (S) slug, followed by polymer buffer (guar gum) as mobility controller. It may be seen from the figures that the incremental recoveries of oil over water flooding are around ~ 19% when 0.3 PV surfactant slug and 0.2 PV polymer was used as slug. In this case also (EAA + ethyl alcohol) extract gives better recovery for the same reason as discussed earlier. Figure 16 shows that the incremental recovery is ~ 24% when the system was flooded with 0.3 PV alkali-surfactant-polymer slug using 0.7% NaOH, 0.5% soapnut extract and 2000 ppm guar gum followed by 0.2 PV polymer (guar gum) buffer solutions after water flooding. So, use of alkali increases the recovery by reducing the interfacial tension and *in situ* formation of surfactant reacting with the acidic components of crude oil [19]. The details of four systems along with their corresponding oil recoveries are given in Table 1.

CONCLUSIONS

In the present study, an attempt has been made to examine the applicability of natural materials for enhanced oil recovery. SEM study shows that this has got a polymer-type texture and quite probable that when it dissolves in water it remains in the form of flakes. FTIR analysis reveals the presence of alcoholic –OH and an intense aliphatic band points towards aliphatic nature of the surfactant. A detailed investigation has been made on surface tension of surfactant obtained from extracted soap nut shell. Six sets of flooding experiments were performed using chemical slugs of different compositions. It has been found that the extracted surfactant from soapnut enhanced the oil recovery after water flooding significantly. Use of alkali and polymer along with the surfactant used has beneficial effects on the incremental recovery. The surfactant used in this study are environmentally sustainable materials and show great potential to be used in future enhanced oil recovery operations.

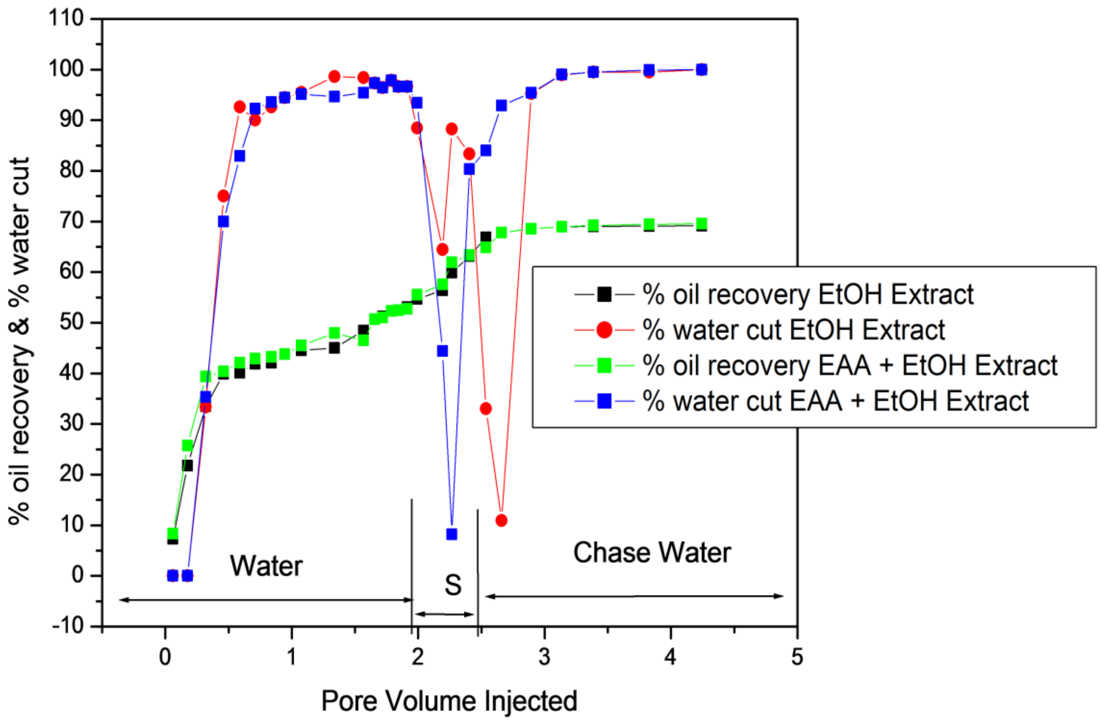

Fig. 14: *Production Performance on Soap Nut Extracts Flooding.*

Table 1: *Recovery of Oil by Chemical Flooding for Four Different Systems.*

Sand pack samples	**Porosity (%)**	**Permeability, k (Darcy)**			**Design of chemical slug for flooding**	**Recovery of oil after water flooding at 95% water cut (% OOIP)**	**Additional recovery (% OOIP)**	**Saturation, % PV**		
		k_w ($S_w = 1$)	**k_o (S_{wi})**	**k_w (S_{or})**				**S_{wi}**	**S_{oi}**	**S_{or}**
Sample-1	37.72	4.912	0.236	0.229	0.5 PV 0.5% Surfactant (ethyl alcohol extract) + Chase water	53.04	16.15	25.93	74.07	20.98
Sample-2	38.89	3.112	0.254	0.245	0.5 PV 0.5% Surfactant (EAA + EtOH extract) + Chase water	52.74	16.85	19.05	80.95	18.81
Sample-3	37.72	3.114	0.256	0.247	0.3 PV Surfactant (ethyl alcohol extract) + 0.2 PV 2000 ppm Polymer + Chase water	51.80	18.60	21.34	77.45	23.08
Sample-4	38.89	2.811	0.249	0.247	0.3 PV surfactant (EAA + ethyl alcohol extract) + 0.2 PV 2000 ppm polymer + Chase water	51.65	19.11	24.85	72.19	20.98
Sample-5	38.89	3.212	0.254	0.245	0.3 PV [0.7% NaOH + 0.5% Soap Nut (ethyl alcohol extract) + 2000 ppm polymer] + 0.2 PV Polymer + Chase water	51.42	23.49	21.12	79.96	19.95
Sample-6	39.05	3.084	0.261	0.253	0.3 PV [0.7% NaOH + 0.5% Soap Nut (EAA + ethyl alcohol extract) + 2000 ppm polymer] + 0.2 PV Polymer + Chase Water	52.79	24.10	21.02	78.98	20.57

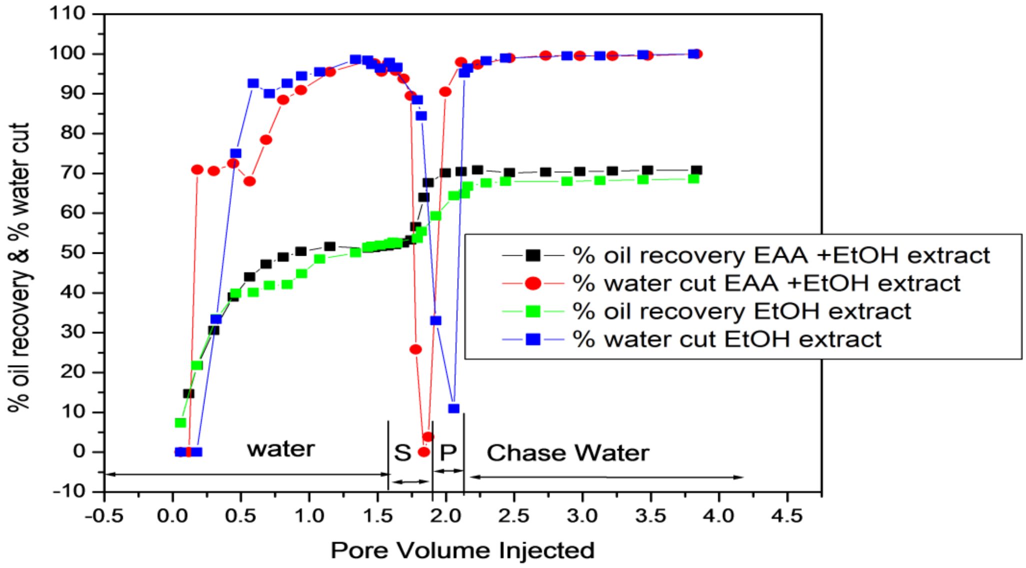

Fig. 15: *Production Performance of Surfactant-Polymer Flooding.*

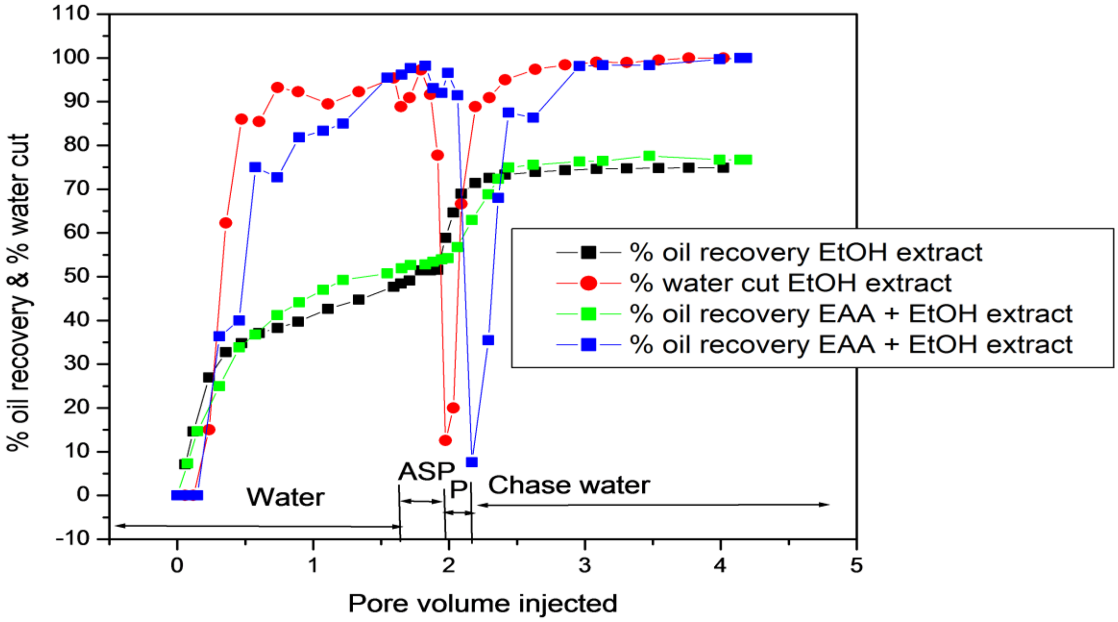

Fig. 16: *Production Performance on ASP Flooding.*

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NOMENCLATURE

ASP	Alkaline-surfactant-polymer
CMC	Critical micelle concentration
EAA	Ethyl acetoacetate
EOR	Enhanced oil recovery
OOIP	Original oil in place
P	Polymer
S	Surfactant
k	absolute permeability, Darcy
k_o	effective permeability to oil, Darcy
k_w	effective permeability to water , Darcy
S_{or}	residual oil saturation
S_{wi}	irreducible water saturation

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