Elution of 17α 25-Norhopanes and Triaromatic Steroids from Weathered Soils by Mixed Triton X-100/Na_2SiO_3 Surfactant Solution

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Abstract Sodium silicate(Na_2SiO_3) was used to improve the elution of super heavy oil from weathered soil on an ultrasound-enhanced elution system by the solution containing 0—6000 mg/L surfactant Triton X-100. The removal extent of three markers[$C_{26—34}$ 17α 25-norhopanes, $C_{26—28}$ triaromatic steroids(TAS), and $C_{27—29}$ methyl triaromatic steroids(MTAS)] was monitored. The average elution percentages of $C_{26—34}$ norhopanes, $C_{26—28}$ TAS, and $C_{27—29}$ MTAS by Triton X-100/Na_2SiO_3 solutions were increased by 11%—13%, 9%—11% and 8%—13% with increasing Triton X-100 concentrations from 150 mg/L to 6000 mg/L. All the concentrations of Triton X-100 improved the elution of TAS homologs containing fewer carbon atoms, whereas high concentrations improved the elution of larger 17α 25-norhopane and MTAS species. Addition of Na_2SiO_3 produced a noticeable increase in elution, particularly for lower-weight species. Scanning electron microscope(SEM) images and energy spectroscopy data reveal that surfactant solution of 6000 mg/L Triton X-100 and 4000 mg/L Na_2SiO_3 produced the greatest improvement in the elution of super heavy oil aggregates encapsulating the soil surface and the emulsification of particle dispersions. That is to say mixed solutions of Triton X-100 and Na_2SiO_3 in combination with ultrasound are a potential means of removing super heavy oil from weathered soils.

Keywords Triton X-100 surfactant solution; Na_2SiO_3; 17α 25-Norhopane; Triaromatic steroid; Biomarker

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1 Introduction

A variety of hydrophobic organic compounds(HOCs) are found in soils contaminated with super heavy oil. Many of them undergo biodegradation only with difficulty, including 17α 25-norhopanes, triaromatic steroids, methyl triaromatic steroids and carbazoles[1—5]. These refractory compounds undergo a weathered process with time, which are then absorbed and sequestrated in soils[6]. Once surrounding environment changed obviously, they can persistent in releasing to soil environment and cause more harm to human health[7—9]. Numerous physical, chemical and biological remediation technologies have been developed in recent years to mitigate the harm caused by HOCs in petroleum-contaminated soil[2,10,11]. Among them, surfactant elution is increasingly attracting international attention in the field of soil remediation due to its high efficiency and short cycle time. Non-ionic surfactants such as Triton X-100 have the advantages of a small critical micelle concentration(cmc), which can greatly decrease interfacial tension at the boundaries between oil-water, oil-soil and water-soil phases[3,10,12]. In addition, the distribution effect of micelle increases the solubility of HOCs in water phase[10,12].

Our previous studies[3] have found that the application of ultrasound was helpful to the elution of polycyclic aromatic hydrocarbons(PAHs), such as $C_{26—28}$ triaromatic steroids(TAS) and $C_{27—29}$ methyl triaromatic steroids(MTAS). When 28-kHz ultrasound was applied for 1080 s at a power level of 80 W/L, an increase of 12%—13% in the average elution percent of $C_{26—28}$ TAS and that of $C_{27—29}$ MTAS were obtationed *via* a solution of Triton X-100[3,4]. In addition, earlier studies[12,13] have demonstrated that adding Na_2SiO_3 or other neutral electrolyte to non-ionic surfactant solutions improves the elution of petroleum pollutants from soils. Inorganic salts such as Na_2SiO_3 can reduce boundary tension and cmc for non-ionic surfactants, increasing the emulsification and solubilization of the surfactant. Inorganic salts can also undergo complexation reactions with Ca^{2+} and Mg^{2+} and increase the solution salinity and pH[13—15]. To date, there has been no report concerning the use of Na_2SiO_3 to promote the elution of super heavy oil and its biomarkers from weathered soil by Triton X-100 solution. Therefore we examined the impact of adding Na_2SiO_3 to the solution on eluting three biomarkers of super heavy oil($C_{26—34}$ 17α 25-norhopanes, $C_{26—28}$ TAS, and $C_{27—29}$ MTAS) from weathered soil by Triton X-100 surfactant solutions at various concentrations. We also quantitatively investigated the mineral and surface characteristics of the eluted soils.

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2 Experimental

2.1 Chemicals and Apparatus

Triton X-100 surfactant(chemically pure grade) was purchased from Sinopharm Chemical Reagent Co., Ltd.(Beijing, China); Na_2SiO_3, petroleum ether, and trichloromethane(all analytical reagent grade) were purchased from Beihua Fine Chemical Products Co., Ltd.(Beijing, China); dichloromethane(HPLC grade) was obtained from Fisher(US); 1,2,3,4-tetradeutero cholestane and 1,2,3,4,5,6,7,8-octadeutero cholestane(spectroscopically pure grade) were supplied by Sinopharm Chemical Reagent Co., Ltd.(Beijing, China).

The pH and organic content of the soil and cation exchange capacity(CEC) were measured *via* standard methods[16,17]. The super heavy oil in soils was extracted by CH_2Cl_2 and the concentration of it was then measured *via* Ultraviolet spectrophotometry at a wavelength of 254 nm (SPECORD200, Analytik Jena AG, Germany). The concentration of super heavy oil in the eluent was also measured by means of Ultraviolet spectrophotometry. Saturated and aromatic hydrocarbon biomarkers were first removed by a Soxhlet extractor to obtain non-asphaltene compounds, then separated by neutral alumina and silica gel into saturated hydrocarbons, aromatic hydrocarbons, and colloids. The biomarkers were quantified by virtue of gas chromatography-mass spectrometry(GC-MS, HP6890-HP5973). The detailed analysis was described in our previous study[3] and related literature[6,18]. The soil particle sizes were measured with a laser particle size analyzer(Malvern 2000, Malvern Instruments Ltd., UK). The surface morphology of the soil particles was analyzed by dint of environmental scanning electron microscopy(SEM, Quanta 200FEG, FEI Company, USA).

2.2 Preparation of Contaminated Soil

Clean soil was collected from a surface layer 0—25 cm deep in an open zone of Haidian District, Beijing, China. After the removal of surface weeds, the samples were air-dried for 7 d and the debris was removed *via* a 20 mm-mesh sieve. The organic matter content of the clean soil was 3% with a CEC of 182 mmol/kg and a pH of 6.49. The fraction of particles less than 200 μm in size was almost 100% and the fraction of those less than 100 μm in size was 96%. Super heavy oil with a viscosity of 8.8×10^5 m·Pa·s at 55 ºC and a density of 1.005 g/cm was collected from the Liaohe Oil Field in China. The soil was prepared in our laboratory according to the method of ref.[19]. A 300 g of sample of super heavy oil was heated and dissolved in chloroform. The solution was stirred to which 2700 g of clean soil was added with continued heating to ensure complete evaporation of the chloroform. The prepared soil was kept in a ventilated cabinet for *ca*. 16 h, aged in a 50 ºC oven for 72 h, then stored in beakers at 5 ºC. As measured, the initial heavy oil concentration in weathered soil was 87.52 g/kg .

2.3 Test Procedure

The ultrasound-enhanced elution system used in this study included a reactor, a gravity separator, and an automatic controller. The diagram of this device was described in the previous literature[3]. The reactor consisted of a cylindrical steel container with a bottom diameter of 100 mm and an effective volume of 3 L. The container was equipped with an ultrasound generator(model HF100W-28/2MC, 28 kHz, maximum power 100 W), a stirrer and a temperature control device. Each experimental trial consisted of two parts, one was the surfactant solution contained only Triton X-100 at concentrations of 0—6000 mg/L and the other was Triton X-100(also at various concentrations up to 6000 mg/L) combined with 4000 mg/L Na_2SiO_3. The elution procedure involved mixing 100 g of contaminated soil with 1000 mL of surfactant solution and placing the mixture in the reactor. The elution parameters were optimized in a preliminary study and included a temperature of 70 ºC, an ultrasonic frequency of 28 kHz, a sonication time of 18 min, a stirring speed of 180 r/min, and an elution time of 30 min. Three samples were treated in parallel for each surfactant concentration level. At the conclusion of each trial, the contents in the reactor were discharged into the gravity separator and allowed to settle for 24 h to obtain complete separation of the liquid, solid and oil phases. The eluent, super heavy oil layer and eluted soil were individually collected from the gravity separator for analysis.

3 Results and Discussion

3.1 Elution of Super Heavy Oil by Mixed Triton X-100/Na_2SiO_3

In the absence of surfactant, ultrasound-enhanced elution removed 72%(mass fraction) of the super heavy oil in the contaminated soil. The use of Triton X-100 solution at concentrations ranging from 150 mg/L to 6000 mg/L improved the elution by 2%—13%(Fig.1). Increasing the concentration of Triton X-100 increased the quantity, hydrophobicity and capacity of the resulting micelle and decreased the oil-water interfacial tension[3,10]. In addition, the dispersive effects of the surfactant increased the solubility of HOCs in the water phase[10,20]. These factors also promoted the desorption of oil adsorbed on the soil surface. Earlier study[21] has shown that when the concentration of surfactant is greater than the cmc, the solubilization of HOCs increases as a linear function of surfactant concentration, which is in agreement with our results.

The addition of 4000 mg/L Na_2SiO_3 to the surfactant solution made elution percentage increased by 11%—16%[Fig.1(A) and (B)] for three reasons. First, adding Na_2SiO_3 prevented the surfactant from adsorption and sedimentation on the soil phase[12], which in turn promoted the movement of the oil from the soil to the water. Second, high ionic concentrations enabled the superficial micelle layer to organize more compactly *via* the reduction of repulsive interactions among directional ionic groups, reducing the ionic interfacial tension and the cmc so as to result in a more micellar surfactant[10]. Third, Na_2SiO_3 is a basic salt that can react with organic acids in the oil[22] and cause a reduction in the oil-water interfacial tension[23]. This is supported by our experiments, in which the pH of the solution decreased from 12 to 10 during elution.

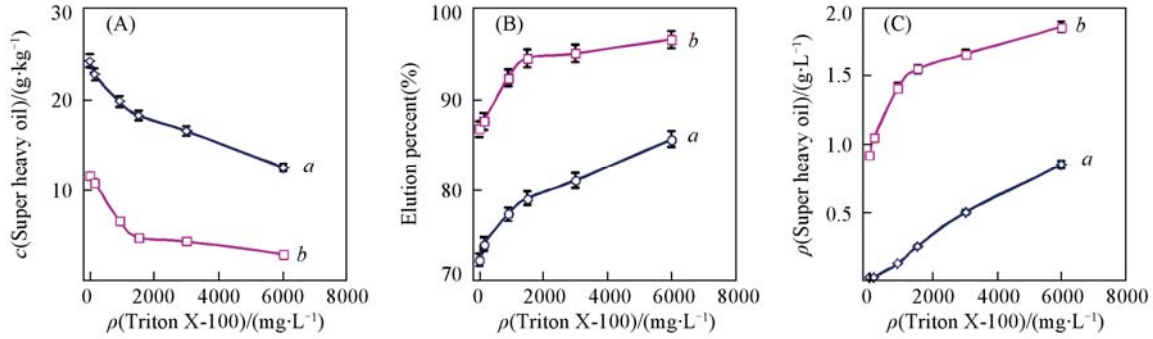

Fig.1 Content of super heavy oil in eluted soil(A), elution percent of super heavy oil(B) and content of super heavy oil in Triton X-100 solution(C)

a. Triton X-100; *b*. Triton X-100 + Na_2SiO_3.

3.2 Elution of Biomarkers by Only Triton X-100 with Various Concentrations

The $C_{26—34}$ 17α 25-norhopanes are typical alkane biomarkers in oil-contaminated soils, accounting for 4% of the oil quantity. The primary species are C_{29} 17α 25-norhopane and C_{28} 17α 25-norhopane, together comprising 1% of the total oil quantity. The typical aromatic hydrocarbon biomarkers in weathered soils are $C_{26—28}$ TAS and $C_{27—29}$ MTAS series, both accounting for 1% of the aromatic hydrocarbons in the oil quantity. The most predominant species are (20*R*)-C_{27} TAS(0.3%) and C_{29} 4, 23, 24-MTAS(0.6%, mass fraction).

As the Triton X-100 concentration was increased from 150 mg/L to 6000 mg/L, the average elution percent of $C_{26—34}$ species increased by 3%—15%. The fraction of (22*S*)-C_{26} 17α 25-norhopane removed was 71%—84% in the presence of surfactant, an increase of 3%—16%. Approximately 77%—93% of the larger molecular compound (22*R*)-C_{34} 17α 25-norhopane was eluted, an increase of 2%—22%[Fig.2(A) and (B)]. Species containing fewer C atoms were more easily eluted at low surfactant concentrations, while high concentrations of Triton X-100 solution improved the elution of molecules containing a greater number of C atoms. This might be attributed to the weak polarity of the norhopane species. When the surfactant concentration was greater than the cmc, a hydrophobic environment was formed in the interior of micelle[14]. At low concentrations of surfactant, a variety of spherical and rod-like micelles with small inner volumes are present. These smaller micelle are more conducive to the dissolution of smaller hydrocarbon species. At high concentrations the micelle are present as vesicles with large inner volumes, improving their ability to dissolve larger hydrocarbons[12,24].

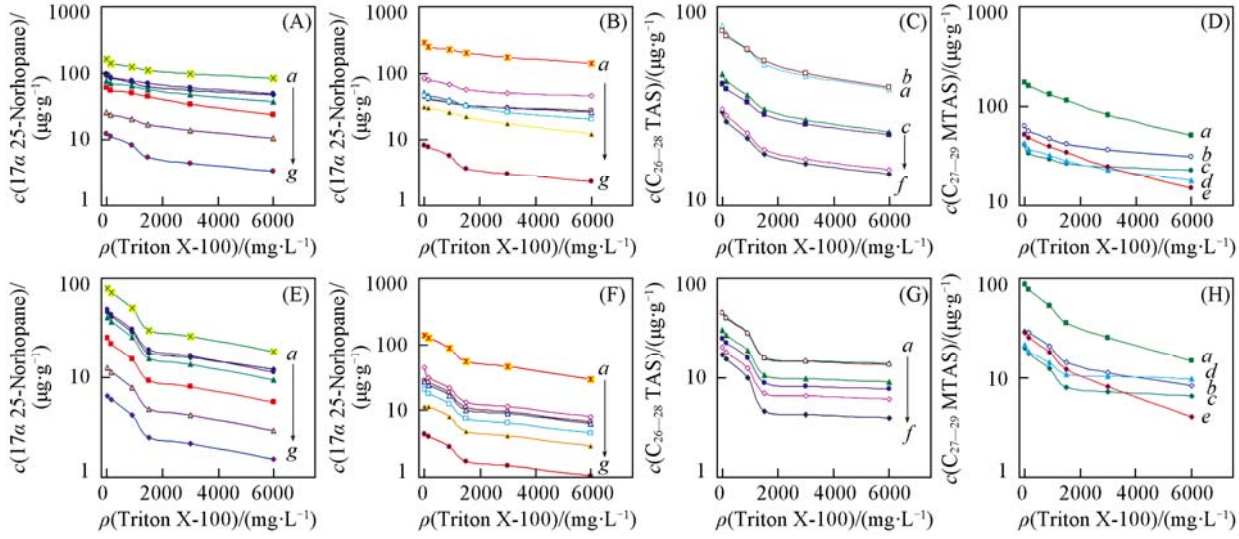

Fig.2 Concentrations of residual $C_{26—34}$ 17α 25-norhopanes, $C_{26—28}$ TAS and $C_{27—29}$ MTAS in soils after elution with Triton X-100 or Triton X-100/Na_2SiO_3 solution

(A) C_{28} 17α 25-Norhopane and *S*-$C_{26—34}$ 17α 25-norhopanes, Triton X-100 solution; (B) C_{29} 17α 25-norhopane and *R*-$C_{26—34}$ 17α 25-norhopanes, Triton X-100 solution; (C) $C_{26—28}$ TAS, Triton X-100 solution; (D) $C_{27—29}$ MTAS, Triton X-100 solution; (E) C_{28} 17α 25-norhopane and *S*-$C_{26—34}$ 17α 25-norhopanes, Triton X-100/Na_2SiO_3 solution; (F) C_{29}17α 25-norhopane and *R*-$C_{26—34}$ 17α 25-norhopanes, Triton X-100/Na_2SiO_3 solution; (G) $C_{26—28}$ TAS, Triton X-100/Na_2SiO_3 solution; (H) $C_{27—29}$ MTAS, Triton X-100/Na_2SiO_3 solution. (A) and (E) *a*. C_{28}; *b*. (22*S*)-C_{26}; *c*. (22*S*)-C_{30}; *d*. (22*S*)-C_{31}; *e*. (22*S*)-C_{32}; *f*. (22*S*)-C_{33}; *g*. (22*S*)-C_{34}. (B) and (F) *a*. C_{29}; *b*. (22*R*)-C_{26}; *c*. (22*R*)-C_{30}; *d*. (22*R*)-C_{31}; *e*. (22*R*)-C_{32}; *f*. (22*R*)-C_{33}; *g*. (22*R*)-C_{34}. (C) and (G) *a*. (20*R*)-C_{27}; *b*. (20*R*)-C_{28}; *c*. (20*S*)-C_{27}; *d*. (20*S*)-C_{28}; *e*. (20*R*)-C_{26}; *f*. (20*S*)-C_{26}. (D) and (H) *a*. C_{29} 4,23,24-MTAS; *b*. C_{27} 4-MTAS; *c*. C_{27} 3-MTAS; *d*. C_{29} 3M-24E; *e*. C_{29} 4M-24E.

The average elution percent of $C_{26—28}$ TAS was increased by 2%—12% with increasing surfactant concentration. A total of 76%—87% of (20*S*)-C_{26} TAS(the smallest homolog) was eluted, an increase of 3%—14% over elution without surfactant. Approximately 74%—85% of (20*R*)-C_{28} TAS(the largest TAS species) was eluted with an increase of 2%—13%[Fig.2(C)],

indicating that the elution of smaller homologs was improved at all the concentrations(>1% more than larger homologs). Possible reasons for this interesting result are that the polarity and hydrophilicity of the aromatic $C_{26—28}$ TAS species are higher than those of cyclanes[1,3]. Han *et al.*[12] reported that aromatic compounds were easier to solubilize in the outer regions of surfactant micelle. For aromatics with similar composition and structure, species containing fewer C atoms were more easily adsorbed and dissolved near the exterior of the micelle[24].

The average elution percent of $C_{27—29}$ MTAS was increased by 3%—17% as the Triton X-100 concentration was increased from 150 mg/L to 6000 mg/L. Approximately 74%—82% of the smaller C_{27} 3-MTAS was removed, an increase of 6%—14%, while 74%—92% of the larger C_{29} 4,23,24-MTAS was eluted, an increase of 3%—20% [Fig.2(D)]. In the same manner, as the $C_{26—34}$ norhopanes, MTAS species containing fewer C atoms were more easily eluted by Triton X-100 with low concentrations, whereas the more concentrated solutions improved the elution of molecules containing a grea- ter number of C atoms. This interesting result might be due to the hydrophobicity of MTAS. MTAS is the substitution of methyl and ethyl for 1—3 hydorgens on the aromatic rings of TAS. A greater number of substituents result in a larger $\lg k_{ow}$ (*n*-octanol/water partition coefficient), larger molecular weight and greater hydrophobicity for MTAS[25]. According to the principle of similarity and solubility, MTAS species containing a greater number of C atoms are therefore more easily eluted by Triton X-100 with low concentrations.

3.3 Elution of Biomarkers by Mixed Triton X-100/Na_2SiO_3 Solution

The average elution percent of $C_{26—34}$ norhopanes by Triton X-100/Na_2SiO_3 solutions was increased by 11%—13% with increasing Triton X-100 concentration from 150 mg/L to 6000 mg/L. Elution percent of (22*S*)-C_{26} 17α 25-norhopane increased by 12%—15% while elution of (22*R*)-C_{34} 17α 25-norhopane increased by 4%—11%[Fig.2(E) and (F)]. Low-concentration solutions of Triton X-100/Na_2SiO_3 displayed large improvements in norhopane elution.

The average elution percent of $C_{26—28}$ TAS by Triton X-100/Na_2SiO_3 solution was increased by 9%—11% as the surfactant concentration was increased from 150 mg/L to 6000 mg/L. Compared to that by solutions only employing Triton X-100 alone, the elution percent of (20*S*)-C_{26} TAS by Triton X-100/Na_2SiO_3 was increased by 10%—12% and the elution percent of (20*R*)-C_{28} TAS by Triton X-100/Na_2SiO_3 was increased by 9%—10%[Fig.2(G)]. Low concentration solutions of Triton X-100 with added Na_2SiO_3 displayed large improvements in the elution of species containing fewer C atoms.

The average elution percent of $C_{27—29}$ MTAS by Triton X-100/Na_2SiO_3 solutions was increased by 8%—13% with increasing Triton X-100 concentration from 150 mg/L to 6000 mg/L. The elution percent of C_{27} 3-MTAS was increased by 13% and the elution of C_{29} 4,23,24-MTAS was improved by 6%—14% when the mixed solution was employed[Fig.2(H)]. Low concentrations of Triton X-100 with added Na_2SiO_3 improved the elution of species containing fewer C atoms. Overall, addition of Na_2SiO_3 improved the elution of biomarkers containing fewer C atoms at low Triton X-100 concentrations. Using Triton X-100 surfactant alone is difficult to reduce the interfacial forces between oil and water to ultra-low levels[26]. Addition of an inorganic salt[12] aids in the replacement, detachment, and dispersion of hydrophobic hydrocarbons[27]. Adding inorganic salts also reduces the cmc of the surfactant[26] and increases micelle capacity, facilitating solubilization of smaller hydrocarbons in the micellar interior. Adding Na_2SiO_3 may increase the negative charges of the soil surface[28] and the surface of the micelle[26], reducing the adsorption losses of surfactant on the soil surface. This results in an increase in the surfactant of solution and micelle concentration and promotes the desorption of small hydrocarbons attached to the soil matrix.

3.4 Microscopic Characteristics of Soil Surface

The soil eluted by Triton X-100 alone was mainly composed of large oil aggregates attached to the surface of the soil particles[Fig.3(A) and(B)]. With the addition of Na_2SiO_3, many

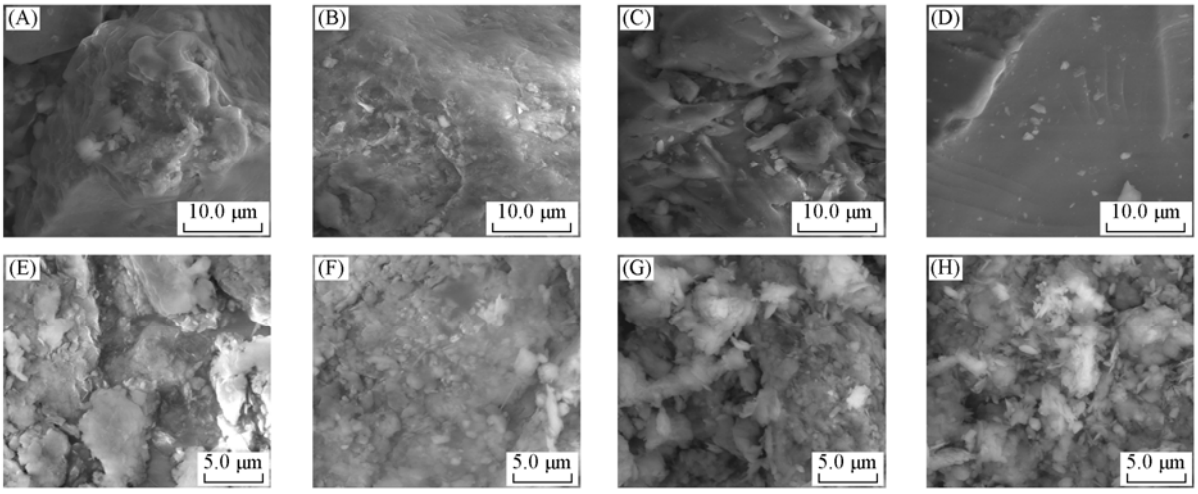

Fig.3 SEM images of eluted soil surface[(A)—(D)] and suspended particles[(E)—(H)]

(A) 1500 mg/L Triton X-100; (B) 6000 mg/L Triton X-100; (C) 1500 mg/L Triton X-100 and 4000 mg/L Na_2SiO_3; (D) 6000 mg/L Triton X-100 and 4000 mg/L Na_2SiO_3; (E) 1500 mg/L Triton X-100; (F) 6000 mg/L Triton X-100; (G) 1500 mg/L Triton X-100 and 4000 mg/L Na_2SiO_3; (H) 6000 mg/L Triton X-100 and 4000 mg/L Na_2SiO_3.

of these encapsulated aggregates were detached. The bare surface area of the soil particles increased from 30% to 90% with increasing surfactant concentration from 1500 mg/L to 6000 mg/L[Fig.3(C) and(D)]. The solids suspended in a 1500 mg/L surfactant solution consisted of compact aggregates 5—15 μm in size, while in a 6000 mg/L solution the suspended solids were more compact and were primarily composed of aggregates >30 μm in size[Fig.3(E) and(F)]. The reason for this might be that surfactant micelle promote HOC aggregation[29]. The Ca^{2+} and Mg^{2+} ions in soil are more easily associated with non-ionic surfactant micelle[30], which facilitates the formation of large aggregates.

Na_2SiO_3 reduced the diameter of the suspended aggregates to 3—8 μm and to 1—5 μm for 1500 mg/L and 6000 mg/L Triton X-100. These aggregates were also less compact[Fig.3(G) and (H)], and the changes were greater at higher concentrations. Possible reasons for this are that Na_2SiO_3 acts as a dispersant for HOCs, and that the addition of Na_2SiO_3 loosens the suspended aggregates, producing small-diameter particles with strong dispersion. Higher surfactant concentrations produced stronger dispersion and smaller capacity, with poorer aggregation[31—36]. In addition, the increased negative potential caused by addition of Na_2SiO_3[37] increased the repulsion among the suspended aggregates.

4 Conclusions

Our research shows that Triton X-100 in heavy-oil contaminated soil remediation improved the elution of TAS homologs containing fewer C atoms. High concentrations of Triton X-100 were helpful in eluting larger species of both 17α 25-norhopane and MTAS. Na_2SiO_3 can greatly increase the elution rate of oil adsorbed on the soil surface. Mixed solutions of Triton X-100 and Na_2SiO_3 in combination with ultrasound are a potential means of removing super heavy oil from weathered soils. Our studies only focus on the impacts of Na_2SiO_3 on the elution of 17α 25-norhopane, TAS, and MTAS by Triton X-100, the mechanisms of Triton X-100/Na_2SiO_3 for elution these biomarker should be studied further.

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