



# Impact of ultrasonication time on elution of super heavy oil and its biomarkers from aging soils using a Triton X-100 micellar solution

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## ABSTRACT

An ultrasound-enhanced elution system with Triton X-100 solution was used to remediate aging soils contaminated with super heavy oil. We used GC/MS, SEM, and X-ray diffraction (XRD) to analyze the effect of ultrasonic time (0–1800 s) on the elution of super heavy oil and its three characteristic biomarkers ( $C_{26-34}$   $17\alpha$  25-norhopanes,  $C_{26-28}$  triaromatic steroid [TAS], and  $C_{27-29}$  methyl triaromatic steroid [MTAS]). The oil and biomarkers remaining in the treated soils followed similar second-order functions with increasing ultrasonication times. Biomarker elution was closely related to carbon numbers in the marker. For  $C_{26-34}$   $17\alpha$  25-norhopanes, the smaller molecules were more readily eluted during 0–360 s ultrasound. This trend was reversed upon application of ultrasound during 1080–1800 s, with improved elution of larger molecules and elution followed a similar second-order function. For  $C_{26-28}$  TAS, smaller molecules were more readily eluted but the elution of larger molecules followed a similar second-order function. For  $C_{27-29}$  MTAS, elution of larger molecules was close to that of  $C_{26-34}$   $17\alpha$  25-norhopanes. Results of SEM and XRD indicated that the mineral and chemical compositions of soils eluted at ultrasonication times of 1080–1800 s closely resembled clean soils.

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## 1. Introduction

Super heavy oil is primarily composed of hydrophobic organic compounds (HOCs). During the processes of oil drilling, extraction, and transportation, super heavy oil enters the soil environment, causing serious alterations in the soil physical and chemical properties [1]. Such toxic HOCs-contaminated soil is increasingly arousing worldwide concerns, due to the great harm it poses to the ambient environment and human health [2]. Numerous physical, chemical, and biological technologies, including soil vapor extraction, ex situ chemical leaching, and bioremediation, have been developed to eliminate HOCs from contaminated soils [3]. However, poor bioavailability and the presence of persistent organic compounds make it difficult to effectively treat polluted soils [4].

Recent literature has indicated elution technology using non-ionic surfactant solution of Triton X-100 as a feasible and cost-effective method of HOCs-contaminated soil remediation [5]. Triton X-100 has the advantages of a small critical micelle concentration, not forming soaps with  $Ca^{2+}$  or  $Mg^{2+}$  [6,7], greatly decreasing liquid–liquid boundary tension, such as oil–water phases, and liquid–solid boundary tension, such as oil–soil phases and water–soil phases [5–7]. In addition, distributional effects of micelles can greatly increase solubility of HOCs in water phase and

typically being effective in solubilizing hydrocarbons [8]. Besides, studies have suggested that power ultrasound can cause cavitation, heating, and intense agitation of a liquid medium or suspension, and activates chemical processes and enhances heat and mass transfer processes [9]. Ultrasonic vibrations penetrate into different regions of a multiphase system and reach the areas of the interface (small cracks, closed pores), while a leaching chemical reagent or solvent can penetrate through formed fractures into the pores of particles under the action of capillary forces enhanced by ultrasonic capillary effect [9]. Therefore, ultrasound is of undoubted interest as a promising method of influence in the processes of the separation of heterogeneous mixtures. Earlier studies have suggested that the application of ultrasound could significantly increase the efficacy of surfactants in eluting PAHs [10,11], DDT and PCBs [12], diesel fuel [13], and tar sand or oil products [14,15]. However, there have been no reports concerning the effects of ultrasonication time on the remediation of aging soils contaminated with super heavy oil and its biomarkers.

Therefore, we examined the impact of the ultrasonication time (0–1800 s) on the elution of super heavy oil and its three associated biomarkers,  $C_{26-34}$   $17\alpha$  25-norhopanes,  $C_{26-28}$  triaromatic steroid (TAS), and  $C_{27-29}$  methyl triaromatic steroid (MTAS), from the aging soils contaminated with super heavy oil (AOCS) using a Triton X-100 micellar solution. The mineral and chemical compositions of the eluted soils and the surface characteristics of the AOCS, eluted soils, and suspended solids were also investigated.

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## 2. Materials and methods

### 2.1. Preparation of the AOCS

Sandy clean soil was collected from the surface layer (0–25 cm depth) in an open zone of the Haidian District, Beijing, P.R.C. after surface weed removal. Samples were air-dried for 1 week and debris was removed using a 20 mm-mesh sieve. The organic matter content of the clean soils was 2.7%, with a cation exchange capacity of 182 mmol kg<sup>-1</sup> and a pH of 6.49. The fraction of particles <200 μm in size was 99.5% and the fraction <100 μm in size was 96%.

Super heavy oil was collected from the Liaohe oil field in China with a viscosity of 8.8 × 10<sup>5</sup> m Pa s and a density of 1.020 g cm<sup>-3</sup> at 55 °C. The oil contained 42% bitumen, 14% colloids, 28% saturated hydrocarbons, and 16% aromatic hydrocarbons.

The AOCS was prepared by mixing clean soil and super heavy oil in the laboratory, according to Ururm et al. [16]. A 3-kg sample of super heavy oil was heated, dissolved in chloroform, stirred, and 27 kg of clean soil was added with continued heating to ensure complete evaporation of the chloroform. The contaminated soil was stored in a ventilated cabinet for ~16 h and then aged in a 50 °C oven for 72 h. The prepared AOCS was stored in beakers at 5 °C.

### 2.2. Test procedures

The ultrasound-enhanced elution system used in this study included a reactor, gravity separator, and automatic controller. The reactor consisted of a cylindrical steel container with a bottom diameter of 100 mm and an effective volume of 3 L, equipped with an ultrasound generator, stirrer, and temperature control device. Elution involved mixing 100 g of AOCS with 100 mL of 1.5 g L<sup>-1</sup> Triton X-100 solution at a mass and volume ratio of 1:10 and placing the mixture in the reactor. The elution parameters were optimized in a previous study [5] and included a temperature of 70 °C, ultrasonic frequency of 28 kHz, power density of 80 WL<sup>-1</sup>, stirring speed of 180 rpm, and elution time of 1800 s. The ultrasonication time was adjusted to 0, 360, 720, 1080, 1440, or 1800 s.

Three samples were treated in parallel for each ultrasonication time. At the conclusion of each trial, the reactor contents 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, oil layer, and eluted soil layer were individually collected from the gravity separator for analysis.

### 2.3. Analytical methods

The super heavy oil concentration in the eluent was measured using UV spectrophotometry at a wavelength of 254 nm (SPECORD200, Germany, Analytik Jena AG). The super heavy oil concentration in soil was measured using UV spectrophotometry at a wavelength of 254 nm according to the previous [17]. Saturated and aromatic hydrocarbon biomarkers were first extracted using a Soxhlet extractor to obtain non-bitumen compounds, then separated by neutral alumina and silica gel into saturated hydrocarbons, aromatic hydrocarbons, and colloids.

The saturated and aromatic hydrocarbons were quantified using gas chromatography/mass spectroscopy (GC/MS) by sampling 1 μL of a methylene chloride extract. Analysis was performed using a helium flow rate of 1 mL min<sup>-1</sup> and an MS scan range of 50–600 amu. The temperature program of the GC/MS consisted of holding at 50 °C for 2 min, ramping to 170 °C at a rate of 6 °C min<sup>-1</sup>, holding at 170 °C for 3 min, ramping to a final temperature of 300 °C at a rate of 2 °C min<sup>-1</sup>, and holding at 300 °C for 20 min.

Biomarker concentrations in the AOCS and eluted soils were determined by comparison to two internal standards, 1,2,3,4-

tetradetero cholestane and 1,2,3,4,5,6,7,8-octadetero cholestane [18,19]. Soil particle sizes were measured using a laser particle size analyzer (Malvern 2000, Malvern Instruments Ltd., UK). The surface morphology and energy spectra of the soil particles were analyzed using environmental scanning electron microscopy (SEM, Quanta 200FEG, FEI Company, USA). The mineral composition of the soils was analyzed using X-ray diffraction (XRD) (DMAX-2400, Rigaku Company, Japan).

### 2.4. Chemicals

Triton X-100 (chemically pure grade) and other solvents used (analytical reagent grade), 1,2,3,4-tetradetero cholestane, and 1,2,3,4,5,6,7,8-octadetero cholestane (spectroscopically pure grade) were supplied by Sinopharm Chemical (Beijing, China). Molecular formula of Triton X-100 in our study is C<sub>8</sub>H<sub>17</sub>C<sub>6</sub>H<sub>4</sub>O(OCH<sub>2</sub>CH<sub>2</sub>)<sub>9.5</sub>H with a molecular weight at 625, CMC of 0.31 mM, and Hydrophile Lipophile Balance of 13.5, respectively.

## 3. Results

### 3.1. Elution of super heavy oil

The concentrations of super heavy oil in the AOCS, eluted soils, and the Triton X-100 micellar solution are depicted in Fig. 1. The elution efficiency of Triton X-100 increased from 66.4% to 88.7% as the ultrasonication time increased from 360 to 1800 s. The relationship between the amount of super heavy oil that was dissolved or dispersed and the ultrasonication time (Fig. 1b) followed a second-order function [20]:

$$\frac{T}{S_0 - S_t} = 0.1508T - 0.2080, \quad R^2 = 0.9896 \quad (1)$$

where  $T$  is the time (s) and  $S_t$  is the amount of oil (mg L<sup>-1</sup>) dissolved or dispersed at time  $t$ . The residual oil in the eluted soils decreased with increasing ultrasonication time as a second-order function (Fig. 1b):

$$\frac{T}{C_0 - C_t} = -0.0405T - 0.0750, \quad R^2 = 0.9956 \quad (2)$$

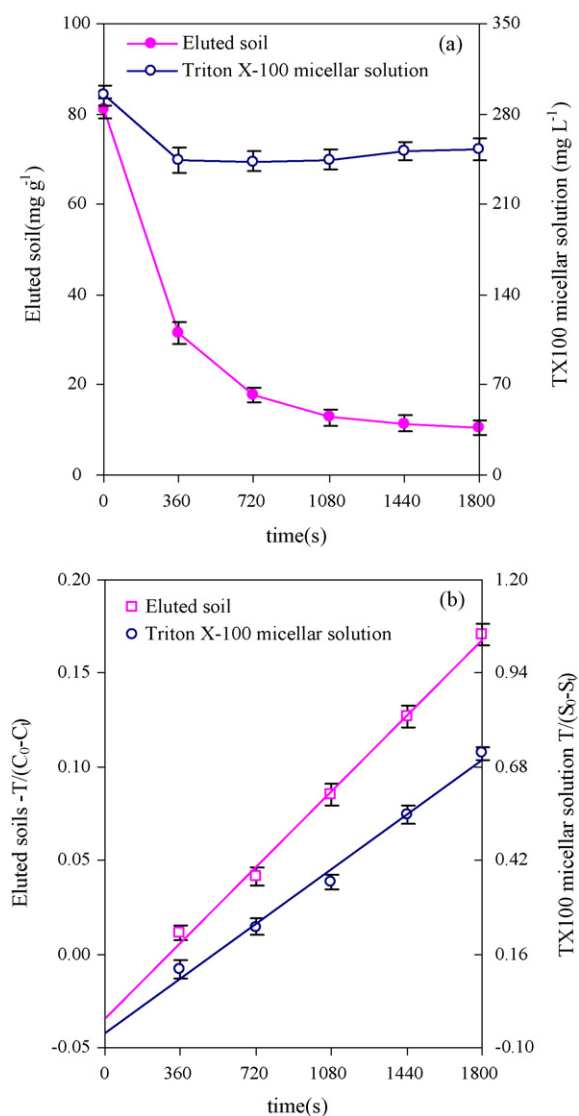
where  $C_0$  is the initial oil concentration (mg kg<sup>-1</sup>) in the AOCS,  $C_t$  is the oil concentration (mg kg<sup>-1</sup>) in soil eluted for time  $t$ , and  $T$  is the ultrasonication time (s).

The amount of oil eluted from the ACOS by the Triton X-100 micellar solution accounted for 23.9% of the total oil removed without ultrasound. However, this ratio decreased from 3.9% to 3.1% with increasing ultrasonication times from 360 to 1800 s (Fig. 1a). Furthermore, an 85–95% oil layer accumulated at the water–soil interface during the elution process.

### 3.2. Elution of 17α 25-norhopane

Most alkane biomarkers in the AOCS were C<sub>26–34</sub> 17α 25-norhopanes. These comprised 3.9% of the super heavy oil, with its main peaks at C<sub>29</sub> 17α 25-norhopane and C<sub>28</sub> 17α 25-norhopane, individually accounting for 1.0% and 0.6%, respectively (Fig. 2a and b). As the ultrasonication time increased from 0 to 360, 1080, or 1800 s, the average elution of C<sub>26–34</sub> 17α 25-norhopanes increased from 13.3% to 55.7%, 80.8%, or 87.3%, respectively; the elution of the species ((22S)-C<sub>26</sub> 17α 25-norhopane) with the lowest carbon numbers increased from 15.1% to 57.6%, 77.6%, or 82.6%, respectively; and elution of (22R)-C<sub>34</sub> 17α 25-norhopane (which had the greatest carbon numbers) increased from 10.9% to 31.8%, 82.5%, or 94.1%, respectively (Fig. 2a and b).

The elution trends of C<sub>26–34</sub> 17α 25-norhopanes compounds with respect to ultrasonication time were closely related to car-



**Fig. 1.** Concentrations of super heavy oil in eluted soils and Triton X-100 micellar solution. (a) Concentrations curve; (b) function curve.

bon numbers and followed a similar second-order function. Species with fewer carbon atoms were more easily eluted by Triton X-100 for ultrasonication times of 0–360 s. This trend was reversed upon application of ultrasonication for 1080–1800 s, with improved elution of molecules containing a greater carbon numbers (Fig. 3a and b).

### 3.3. Elution of TAS

A typical aromatic hydrocarbon biomarker in the AOCS was C<sub>26–28</sub> TAS, which accounted for 1.1% of the super heavy oil. (20R)-C<sub>27</sub> TAS was the dominant C<sub>26–28</sub> TAS, accounting for 0.3% of the super heavy oil (Fig. 2c). As the ultrasonication time was increased from 0 to 1800 s, the average elution of TAS increased from 14.3% to 85.7%; the elution of (20S)-C<sub>26</sub> TAS (which contains the fewest C atoms) increased from 16.1% to 89.8%; and the elution of (20R)-C<sub>28</sub> TAS (which contains the most C atoms) increased from 12.9% to 83.8% (Fig. 2c). Thus, species containing fewer C atoms were more easily eluted by Triton X-100 at ultrasonication times of 0–1800 s. This elution process followed a similar second-order function, with the correlation coefficient increasing with a increasing carbon numbers (Fig. 3c).

### 3.4. Elution of MTAS

The aromatic hydrocarbon biomarker C<sub>27–29</sub> MTAS accounted for 1.2% of the super heavy oil, with the dominant C<sub>27–29</sub> MTAS homolog, 4,23,24-trimethyl triaromatic steroid (C<sub>29</sub> 4,23,24-MTAS), accounting for 0.6% (Fig. 2d). As the ultrasonication time was increased from 0 to 1800 s, the average elution rate of MTAS increased from 12.0% to 87.4%; the elution rate of C<sub>27</sub> 3-MTAS (which contains the fewest C atoms) increased from 12.1% to 77.2%; and the elution rate of C<sub>29</sub> 4,23,24-MTAS (which contains the most C atoms) increased from 12.5% to 94.1% (Figs. 2d and 3d). Thus, the elution trends of MTAS species with respect to ultrasonication time were closely related to carbon numbers. The greater carbon numbers, the larger was the improvement in elution with ultrasound. The elution of C<sub>27–29</sub> MTAS containing more C atoms followed a similar trend as 17 $\alpha$  25-norhopane, and the elution of MTAS containing fewer C atoms followed a similar trend as TAS (Figs. 2 and 3).

### 3.5. Surface characteristics of clean soils, AOCS, and eluted soils

Fig. 4a–c contains a series of SEM images depicting the soil particle surfaces and solid particles suspended in the Triton X-100 solution. Soil surfaces were composed of a variety of clay, silt, and sand particles. The AOCS was mainly composed of soil aggregates with a particle size of  $\sim 60 \mu\text{m}$ , which was very different from clean soils (Fig. 4a–c). Following treatment with ultrasound for 360 s, most of the residual super heavy oil present in the soils had detached from the surface, and 40% of the soil surface area was in the form of “bare patches”. This figure reached almost 80% when the ultrasonication time was increased to 1080 s (Fig. 4a–c).

### 3.6. Morphology of suspended solids in the Triton X-100 micellar solution

Without ultrasound, the suspended solids were mainly composed of aggregates  $>30 \mu\text{m}$  in size. Although there were some small particles of  $\sim 1\text{--}3 \mu\text{m}$ , almost all of these were bound to large aggregates and they rarely existed in the free state (Fig. 4d–f). Furthermore, although the number of clay particles located in the surface soils increased, there was almost no difference in the morphology or size of suspended particles between samples treated without or with ultrasound for 360 s (Fig. 4d–f). When the ultrasonication time was increased to 1080 s, the largest diameter of suspended aggregates decreased to  $5 \mu\text{m}$ , and numerous small particles of  $1\text{--}3 \mu\text{m}$  were observed in the Triton X-100 micellar solution.

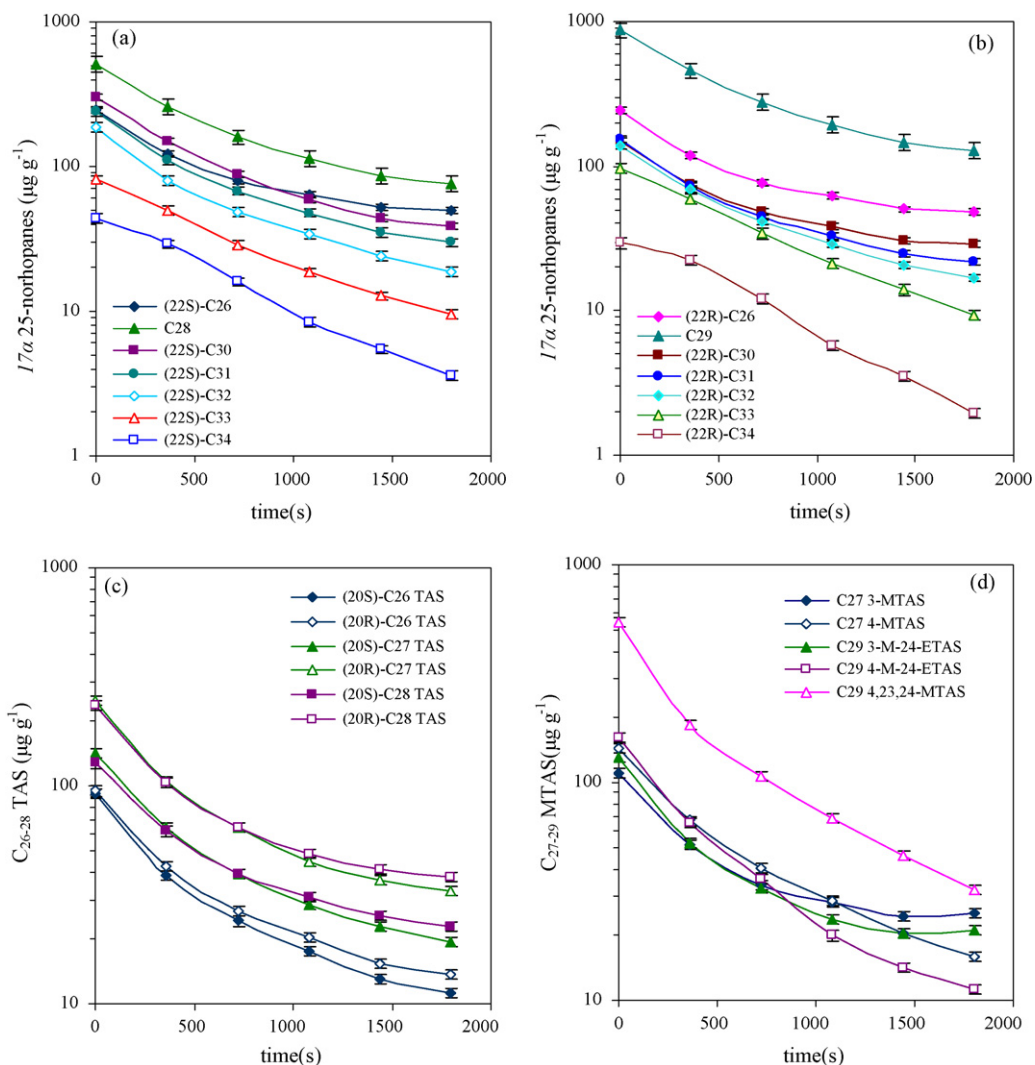
### 3.7. Mineral and elemental compositions of clean, AOCS, and eluted soils

X-ray diffraction revealed that the primary minerals present in the clean and eluted soils were quartz (SiO<sub>2</sub>), feldspar (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>), muscovite (KAl<sub>2</sub>(Al-Si<sub>3</sub>O<sub>10</sub>)(OH)<sub>2</sub>), and chlorite {(Mg, Al, Fe)<sub>6</sub>[(Si, Al)<sub>4</sub>O<sub>10</sub>](OH)<sub>8</sub>} (Fig. 5). The relative abundance of the last two minerals and Ca and Mg in the eluted soils decreased with increasing ultrasonication time (Fig. 6).

## 4. Discussion

### 4.1. Elution of super heavy oil

The amount of super heavy oil that was dissolved or dispersed by a Triton X-100 micellar solution acted as a second-order function with increasing ultrasonication times (Fig. 1 and Eq. (1)). Interestingly, although the amount of residual oil in the eluted soil



**Fig. 2.** Concentrations of  $17\alpha$  25-norhopanes, TAS, and MTAS in the AOCS and eluted soils. (a) (22S)-C<sub>26–34</sub>  $17\alpha$  25-norhopanes, and C<sub>28</sub>  $17\alpha$  25-norhopane; (b) (22R)-C<sub>26–34</sub>  $17\alpha$  25-norhopanes and C<sub>29</sub>  $17\alpha$  25-norhopane; (c) C<sub>26–28</sub> TAS; (d) C<sub>27–29</sub> MTAS.

displayed a second-order decrease with respect to sonication time (Fig. 1a and Eq. (2)), this only accounted for 24% of the total oil removed, even in the absence of ultrasound. Furthermore, this ratio decreased with increasing sonication time (Fig. 1a and b), because a heavy oil film layer (>90% heavy oil) accumulated at the water–soil interface after gravity separation for 24 h. This layer is distinct from that formed during elution of a soil with a high concentration of light oil, which forms an oil film on the water surface [21,22]. The high density of the heavy oil (1.020 g cm<sup>-1</sup>, greater than that of water) and the oil concentration (93.58 g kg<sup>-1</sup>) in the polluted soil in the present study resulted in multi-layer adsorption on the soil particle surface [2]. Increasing the ultrasonication time increased the number of shock waves and enhanced the cavitation processes, overcoming the interfacial forces between the soil particles and the surfactant [23,24]. This enabled the Triton X-100 micelles to easily infiltrate the soil particle surface [25] and promoted detachment of the oil film absorbed in the outer soil layer. The oil films coagulated during the gravity sedimentation process into the layer observed at the water–soil interface.

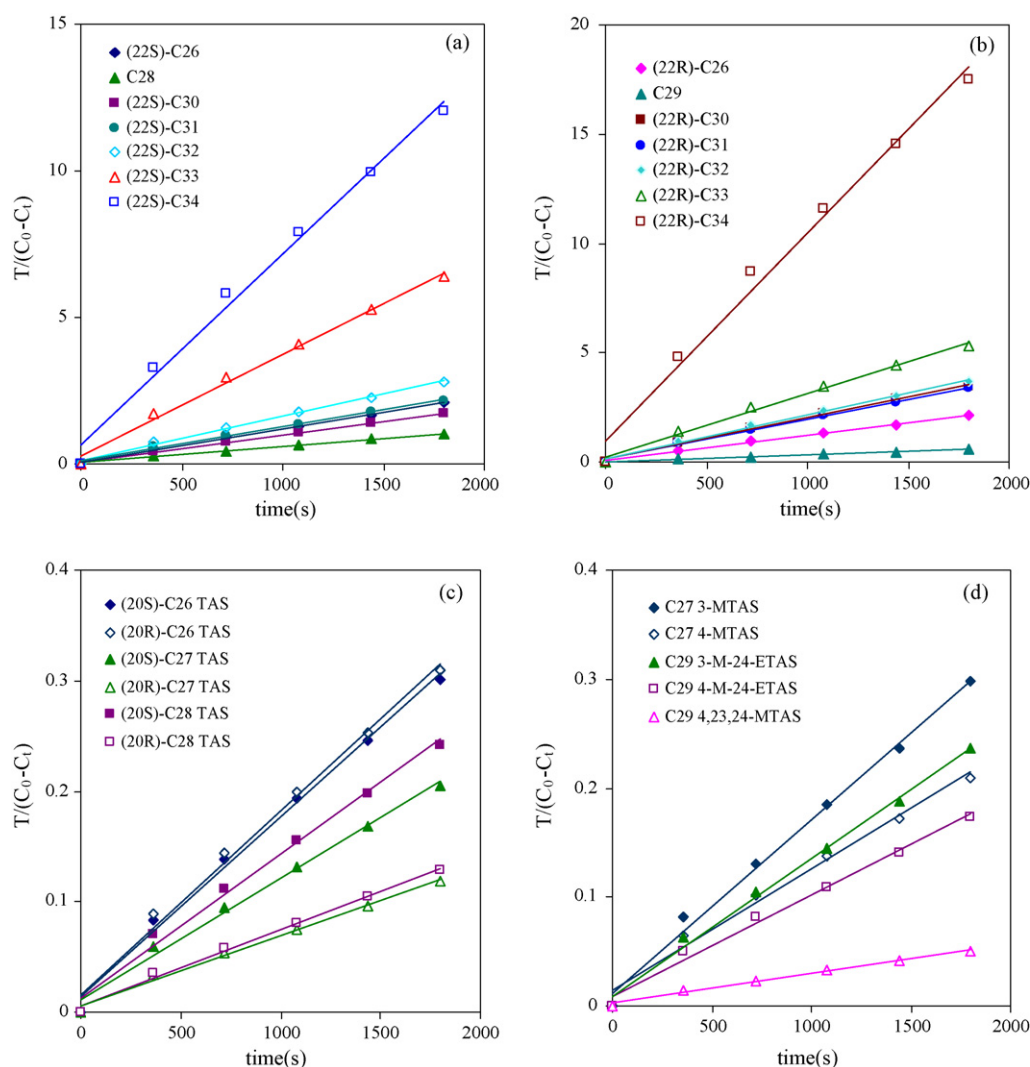
#### 4.2. Elution of $17\alpha$ 25-norhopane

The elution of  $17\alpha$  25-norhopane, a weak polarity HOC, was closely related to carbon numbers in the marker (Figs. 2a, b and 3a,

b). The large quantity of micelles present in the Triton X-100 solution ( $\sim 10\times$  its critical micelle concentration) enabled the formation of a similar hydrocarbon hydrophobic environment in vesicles in the absence of ultrasound. This improves the solubility of weak polarity HOCs [24], as it is much easier for shorter-chain hydrocarbons of weak polarity to enter the interior of a micelle and be eluted [26].

Ultrasound use possibly reduces the hydration of the polyoxyethylene chains in the Triton X-100 micellar solution and increases the number of micelles. As the ultrasonication time increases, the hydration decreases and the number of micelles increases, resulting in a greater number of weak polarity HOCs dissolved in micelles [23]. However, long-time ultrasound may also cause substantial damage to the Triton X-100 micelles and hydrocarbon aggregates, reducing their internal capacity. Therefore, long-time ultrasound is not favorable to the dissolution and aggregation of hydrocarbon molecules containing many C atoms or of greater polarity than the outer portion of the micelles [16,27]. However, long-time ultrasound may benefit hydrocarbons by forming a stable emulsifying dispersed system as a type of oil-packing water. The more C atoms in a hydrocarbon species, the more stable the formed system [2,27,28].

Ultrasound-enhanced elution of  $17\alpha$  25-norhopanes followed a similar second-order function as that of super heavy oil in the



**Fig. 3.** Elution trend of 17α 25-norhopanes, TAS, and MTAS in the AOCS and eluted soils. (a) (22S)-C<sub>26–34</sub> 17α 25-norhopanes, and C<sub>28</sub> 17α 25-norhopane; (b) (22R)-C<sub>26–34</sub> 17α 25-norhopanes and C<sub>29</sub> 17α 25-norhopane; (c) C<sub>26–28</sub> TAS; (d) C<sub>27–29</sub> MTAS.

AOCS (Fig. 3a and b). Thus, dissolution and aggregation are the proposed mechanisms for its elution at short ultrasonication times (0–360 s), when species with fewer carbon atoms were more easily eluted. However, emulsifying dispersion was the main eluting mechanism at long times (1080–1800 s), when species with more carbon atoms were easier to elute.

#### 4.3. Elution of TAS

In the elution of TAS, species containing fewer C atoms were more easily eluted and the elution followed a similar second-order function (Figs. 2c and 3c). C<sub>26–28</sub> TAS belongs to the group of aromatic HOCs, which have a stronger polarity and hydrophilia than cyclanes [29]. Aromatic hydrocarbons are easily dissolved in surfactant micelles without ultrasound [22]. Furthermore, aromatic hydrocarbons containing fewer C atoms are more easily adsorbed and dissolved in the outer portion of the surfactant micelle [26].

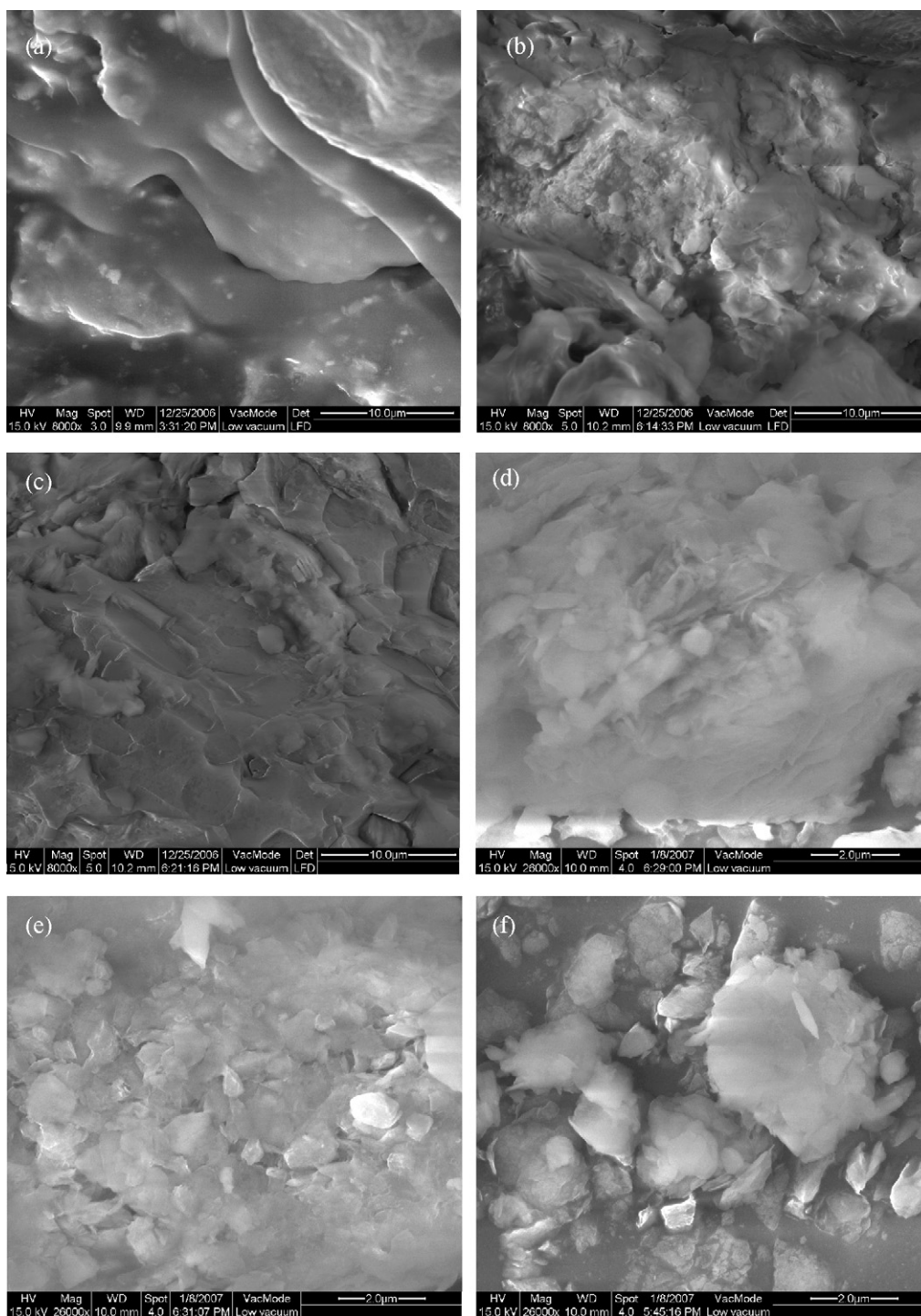
Long-time ultrasound can damage micellar vesicles, reducing their internal capacity but increasing their external capacity. This is favorable to the dissolution of aromatic hydrocarbons in the outer micellar portion [16,27]. Aromatic hydrocarbons are also easily combined with bitumen in the AOCS by hydrogen bonding. Compared to alkane hydrogen, the combination of aromatic hydrocarbon with hydrogen bond is stronger and easier to be pack-

aged by bitumen, making them easier to be curled and removed with bitumen by ultrasound [30]. Curled aromatic hydrocarbons and bitumen can form tar spherical granules by emulsifying the dispersion and dissolution of the surfactant. They are then stably dispersed into the Triton X-100 surfactant micellar solution, which serves as a type of oil-packing water. This system is increasingly stable with an increasing carbon numbers in the hydrocarbon species [26,28].

Elution of C<sub>26–28</sub> TAS followed a similar second-order function as super heavy oil in the AOCS (Fig. 3c). Thus, the main elution mechanism for C<sub>26–28</sub> TAS is formation of an emulsifying solution as a type of water-packing oil.

#### 4.4. Elution of MTAS

The elution of MTAS was closely related to carbon numbers in the marker. MTAS followed a similar trend as 17α 25-norhopane for species with more C atoms (Figs. 2d and 3d). This result was both interesting and surprising. MTAS is a product of 1–3 hydrogen atoms in an aromatic ring substituted by methyl or ethyl. Substitution by methyl increases the  $\log K_{ow}$  (n-octanol-water partition coefficient) of aromatics; the greater the number of substituents, the larger the  $\lg K_{ow}$  and the stronger the hydrophobicity [26]. Thus, it is easier to elute MTAS products with more substituents,



**Fig. 4.** SEM image depicting the surfaces of soil and solid particles suspended in Triton X-100 solution. AOCs (a), eluted soil surface at 360 s (b) or 1800 s (c), suspended solid particles at 0 s (d), 360 s (e), or 1080 s (f).

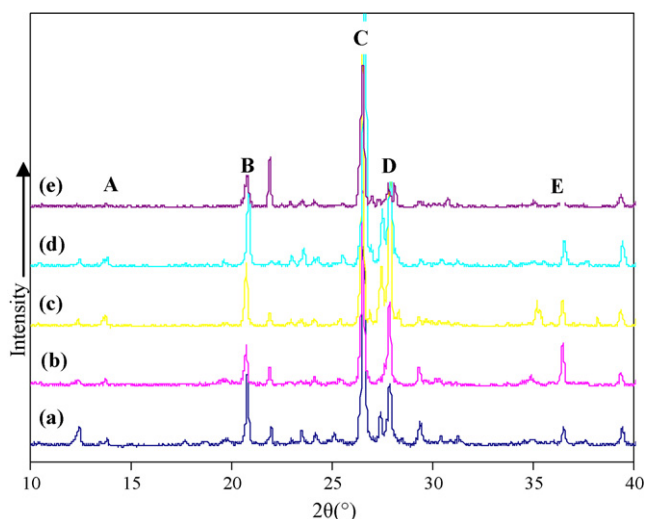
and the elution trend is similar to the highly hydrophobic 17 $\alpha$ -25-norhopane.

#### 4.5. Surface characteristics of soil-suspended solids

The differences between the AOCs and clean soils (Fig. 4) in our study agree with those of previous studies [31]. This may be because the heavy oil first adsorbed to the surface of smaller particles such as clay and silt, then aggregated into larger granules with a higher oil concentration. Following sonication, 40% of the soil surface area was in the form of “bare patches,” which per-

centage increased with increasing ultrasonication time (Fig. 4). These observations demonstrate that long-time ultrasonication is helpful in eluting super heavy oil and its biomarkers from the AOCs.

Without ultrasound, most of suspended solids in the Triton X-100 solution were bound to large aggregates and rarely existed in the free state (Fig. 4). This is because the surfactant micelles (or vesicles) assisted the HOCs in coagulating and forming aggregates [32]. Furthermore, the Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in the soil minerals enabled non-ionic surfactant micelles (or vesicles) to easily form larger aggregates [6,7].

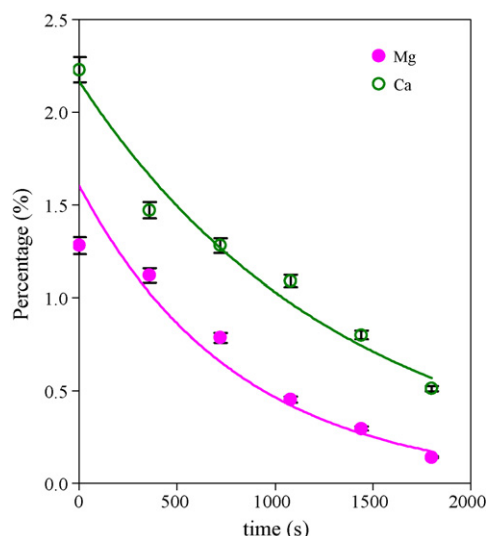


**Fig. 5.** XRD plots for clean and eluted soils. Eluted soil at 0 s (a), 360 s (b), 720 s (c), 1080 s (d), or 1800 s (e). A: Chlorite ( $\text{Mg,Al,Fe}_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$ ); B: Quartz; C: Quartz and  $\text{KMg}_3\text{Si}_3\text{AlO}_{10}\text{F}_2$ ; D: Muscovite; E: Feldspar.

There was almost no difference in the morphology or size of suspended particles between samples treated without or with ultrasonication for 360 s (Fig. 4). When this time was increased to 1800 s, the largest diameter of the suspended aggregates decreased to 5  $\mu\text{m}$ , and numerous small particles (1–3  $\mu\text{m}$ ) were observed (Fig. 4). This is because the dispersion ability of the ultrasound was directly related to the aggregate diameter. An increased ultrasonication time produced strong dispersion and smaller diameter aggregates, as well as a more stable colloid system [33]. Longer ultrasonication times increased the negative potential on the suspended aggregate surfaces [34], creating a greater repulsive force between the particles. All of these consequences resulted in the uneasy aggregation of the suspended particles.

#### 4.6. Minerals and elemental composition

The relative abundance of muscovite, chlorite, and Ca and Mg in the eluted soils decreased with increasing ultrasonication time (Figs. 5 and 6), consistent with the SEM results of small-size particles (Fig. 4). Ca and Mg is the main constituent of chlorite and



**Fig. 6.** Energy spectra of Ca and Mg in soil particle surfaces.

muscovite [7,35], and its prevalence decreases upon dispersion and suspension of clay minerals. In addition, Triton X-100 easily undergoes association reactions with the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in feldspar and muscovite [36]. Increased ultrasonication time also improves  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ion dispersion in the Triton X-100 solution [6], reducing the relative abundance of Ca and Mg.

## 5. Conclusions

The concentration of residual super heavy oil in treated soils and TX100 solution decreased as a similar second-order function with increasing ultrasonication time. The elution trends of  $\text{C}_{26-34}$   $17\alpha$  25-norhopanes,  $\text{C}_{26-28}$  TAS, and  $\text{C}_{27-29}$  MTAS compounds were closely related to carbon numbers.  $\text{C}_{26-34}$   $17\alpha$  25-norhopanes compounds containing fewer C atoms were most easily eluted at 0–360 s of ultrasound, while compounds with more C atoms were most easily eluted at 1080–1800 s of ultrasound. Both elution processes followed similar second-order functions.  $\text{C}_{26-28}$  TAS containing fewer carbon atoms was easily eluted but larger species was eluted as a similar second-order function with increasing time. For  $\text{C}_{27-29}$  MTAS, elution of larger molecules was close to that of  $\text{C}_{26-34}$   $17\alpha$  25-norhopanes.

The mineral and elemental compositions, and the functional groups, and therefore represents a potentially useful method for enhancing the removal of super heavy oil from contaminated soil.

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