



Impact of ultrasonic time on hot water elution of severely biodegraded heavy oil from weathered soils

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ARTICLE INFO

Article history:

Received 30 December 2009

Received in revised form 11 February 2010

Accepted 25 February 2010

Available online 3 March 2010

Keywords:

Ultrasonic irradiation time

Weathered soils

Thermal water elution

Severely biodegraded heavy oil

Biomarker

ABSTRACT

An ultrasound-enhanced elution system employing water at a temperature of 70 °C was used to remedy weathered soils contaminated with severely biodegraded heavy oil (SBHO). The effect of varying the ultrasonic irradiation time from 0 to 1800 s on the elution of SBHO and three characteristic biomarkers (C_{26-34} 17 α 25-norhopanes, C_{26-28} TAS, and C_{27-29} MTAS) was analyzed using GC/MS, scanning electron microscopy (SEM), and X-ray diffraction (XRD). Elution of the three biomarkers was closely related to the carbon number of the marker. C_{26-34} 17 α 25-norhopanes and C_{26-28} TAS species with higher carbon numbers and C_{27-29} MTAS species with lower carbon numbers were more readily eluted using sonication times of 1080–1800 s, while smaller TAS homologs were more readily eluted after sonication times of 0–360 s. SEM images of samples treated for longer periods revealed larger “bare patches” on the soil surface. The results of XRD and energy spectroscopy experiments indicated that ultrasound irradiation for 1080 s negatively affected the deposition of $CaCO_3$, but overall improved the mineral and chemical compositions of treated soils and removal of SBHO.

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1. Introduction

Severely biodegraded heavy oil (SBHO) is an important energy source whose worldwide production accounts for 17% of total petroleum production [1]. Approximately 8 million tons of petroleum reportedly enter the soil every year during oil drilling, silo operation, extraction, and accidents such as blowouts and leakage. Heavy oil pollution from a single oil well can affect an area of 0.5–20 m², and the area covered with oil during a blowout can be 3000–4000 m². In the Arshan oil field located in the Inner Mongolia Autonomous Region of China, the average amount of heavy oil entering the soil annually is over 2 tons per well, impacting 150–200 m² of grassland vegetation. The SBHO concentration in the 0–20 cm surface layer of the soil can reach 10–50% in the Daqing and Liao oil fields in China, resulting in the blockage of soil pores, changes to soil physical and chemical properties, and serious degeneration of the soil ecosystem, leading to a biomass reduction of 15–30% for reeds, corn, and sunflowers planted near these oil fields [2–5].

The principal toxic components of petroleum are alkanes and aromatic hydrocarbons. In SBHO, the residual hydrocarbons are typically C_{26-34} 17 α 25-norhopane, C_{26-28} triaromatic steroids

(TAS), and C_{27-29} methyl triaromatic steroids (MTAS) [6]. These compounds share a common characteristic of being strongly resistant to biodegradation, and they are subject to microbial attack only after severe degradation [7]. Exposure at the surface results in oxidation to other compounds with higher toxicity than linear chain alkanes and PAHs such as phenanthrene and pyrene [4,6,8].

The technologies of soil vapor extraction, biological remediation, and ex-situ elution have been developed in recent years to recover petroleum-contaminated soils [6,9]. Among these methods, soil vapor extraction is effective in removing compounds with high vapor pressure such as low-weight hydrocarbons. However, the technique is less appropriate for less volatile organic compounds such as PAHs, and cannot effectively remove super heavy oil pollutants containing high concentrations of bituminous material and resin [5]. Biological remediation is effective for compounds that are easily biodegraded, but provides no significant remediation for hydrophobic organic compounds (HOCs) such as PAHs, bitumens, and resin [10]. For these soils, ex-situ elution technology has the obvious advantages of high efficiency and short treatment time [11].

Despite the marginal benefit, stirring has been used to improve the effectiveness of traditional hot water elution methods [12]. Earlier studies suggested that the application of ultrasound could greatly increase the efficacy of surfactants in eluting PAHs and diesel fuel [6,13,14]. When 20 kHz ultrasound was applied for 1800 s, Kamalavathany [15] obtained a 65% increase in the aver-

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age elution of 12 PAHs. Mason et al. [14] obtained a 70% increase in the amount of DDT and PCBs removed when ultrasound was applied for 1200 s. Feng and Aldrich [12] reported that treatment with 300 s ultrasound improved the elution of diesel fuel from soils. However, there have been no reported investigations concerning the remediation of SBHO-polluted soils using hot water elution.

Thus, this work primarily examines the impact of sonication time (from 0 to 1800 s) on the remediation of weathered soils polluted with SBHO and three associated biomarkers (C_{26-34} 17α 25-norhopanes, C_{26-28} TAS, and C_{20-29} MTAS) using hot water elution. This paper also focuses on the mineral and chemical composition of the eluted soils and the surface characteristics of weathered soils, eluted soils, and SBHO aggregates.

2. Materials and methods

2.1. Preparation of weathered soil

Weathered soil was prepared by mixing clean sandy soil and SBHO in the laboratory. Clean sandy soil was collected from a surface layer of 0–25 cm depth in an open zone of the Haidian District, Beijing, P.R.C. following removal of weeds. The samples were air-dried for one week and debris was removed using a 20 mm-mesh sieve. The organic matter content of the clean soil was 2.7% with a cation exchange capacity (CEC) of 182 mmol kg^{-1} and a pH of 6.49. The fraction of particles smaller than $200 \mu\text{m}$ was 99.5% and the fraction smaller than $100 \mu\text{m}$ was 96%.

SBHO with a viscosity of $5.8 \times 10^5 \text{ mPa s}$ and a density of 0.995 g cm^{-3} at 60°C was collected from the Liaohe oil field in China. The weathered soil was prepared according to the method of Urum et al. [16]. A 1.5 kg sample of SBHO was heated and dissolved in chloroform. The solution was stirred and 13.5 kg of clean soil was added with continued heating to ensure complete evaporation of the chloroform. The prepared soil was stored in a ventilated cabinet for approximately 16 h and then placed in a 50°C oven for 72 h. The soil samples were stored in beakers at 5°C .

2.2. Test procedures

Our ultrasound-enhanced elution system consisted of a reactor, a gravity separator, and an automatic controller (Fig. 1). The reactor was a cylindrical steel container with a bottom diameter of 100 mm and an effective volume of 3 L, equipped with an ultrasound gen-

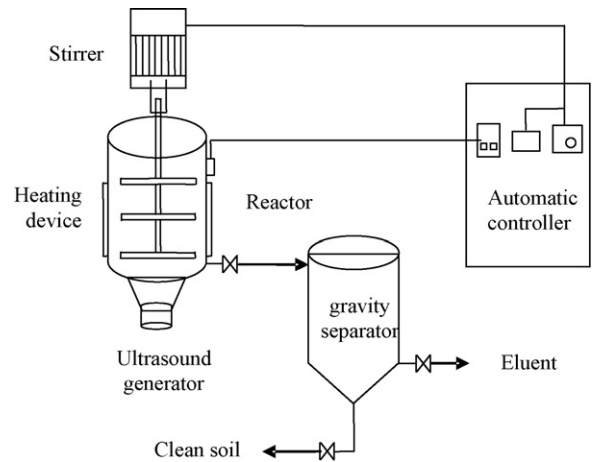


Fig. 1. Schematic of the ultrasound-enhanced elution system.

erator, a stirrer, and a temperature control device. Elution involved placing a mixture of 100 g soil and 1000 mL de-ionized water in the reactor. The elution parameters were optimized in a previous study [5,6] and included a temperature of 70°C , an ultrasonic frequency of 28 kHz, a power density of 80 W L^{-1} , a stirring speed of 180 rpm, and an elution time of 1800 s. Triplicate samples were irradiated for 0, 360, 720, 1080, 1440, or 1800 s. At the conclusion of each trial, the contents of the reactor were discharged into the gravity separator and allowed to settle for 24 h. The mixture was then centrifuged at 1400 rpm to obtain complete separation of the liquid, solid, and oil phases. The eluent, the SBHO accumulation layer, and eluted soils were individually collected from the gravity separator for analysis.

2.3. Analytical methods

The concentrations of oil in the eluent were measured using UV spectrophotometry at a wavelength of 254 nm (SPECORD 200, Germany, Analytik Jena AG). The concentrations of oil in soil samples were also measured according to the literature [17]. SBHO fractions consisting of saturated hydrocarbons, aromatic hydrocarbons, resins, and heptane asphalt were gravimetrically analyzed. The non-asphalt components were extracted using a Soxhlet extrac-

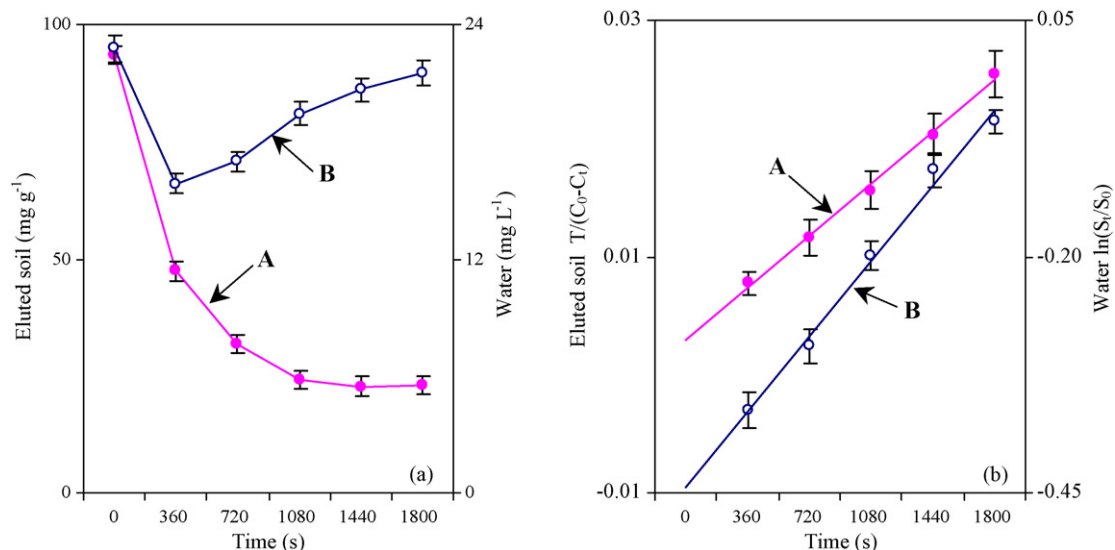


Fig. 2. Concentrations of SBHO in eluted soils and hot water (a: concentration curve; b: function describing concentration; A: eluted soils; B: hot water).

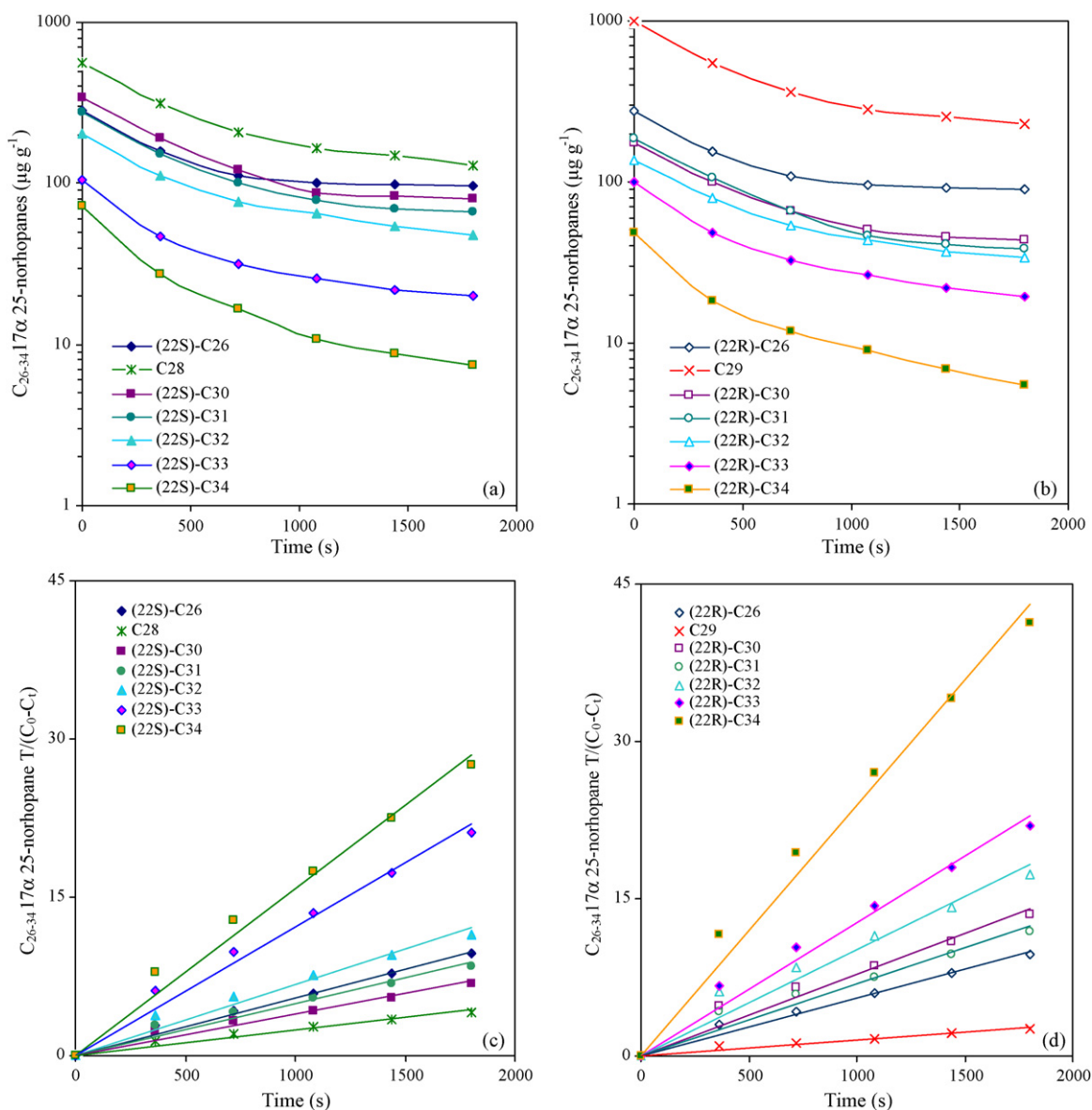


Fig. 3. Concentration curves for $C_{26-34} 17\alpha, 25\text{-norhopanes}$ in eluted soils (a: concentration curves for 22S and $C_{28} 17\alpha, 25\text{-norhopane}$; b: concentration curves for 22R and $C_{29} 17\alpha, 25\text{-norhopane}$; c: functions describing concentrations of 22S and $C_{28} 17\alpha, 25\text{-norhopane}$; d: functions describing concentrations of 22R and $C_{29} 17\alpha, 25\text{-norhopane}$).

tor, separated using neutral alumina and silica gel into saturated hydrocarbons, aromatic hydrocarbons, and resins, and quantified by injecting $1 \mu\text{L}$ of a methylene chloride extract into a GC–MS (HP6890–HP5973). The analysis was performed using a helium flow rate of 1 mL min^{-1} and a 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^{-1} , holding at 170°C for 3 min, ramping to the final temperature of 300°C at a rate of 2°C min^{-1} , and holding at 300°C for 20 min. The compounds 1,2,3,4-tetradeutero cholestane and 1,2,3,4,5,6,7,8-octadeutero cholestane were selected as internal standards. The concentrations of the biomarkers in the soil samples were determined by comparison to these two compounds [7,18]. The 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

Petroleum ether, *n*-heptane, chloroform, toluene, aluminum oxide, absolute alcohol, and trichloromethane (analytical grade), 1,2,3,4-tetradeutero cholestane, and 1,2,3,4,5,6,7,8-octadeutero cholestane (spectroscopic grade) were supplied by Sinopharm Chemical (Beijing, China).

2.5. Regression analysis

All data analyses were performed using SPSS for Windows (Version 13.0) produced by SPSS Inc.

3. Results

3.1. Elution of SBHO

The fraction of SBHO removed from the soil increased from 49.4% to 75.5% as the ultrasonic irradiation time was increased from 360 to 1800 s (Fig. 2a). The amount of SBHO dissolved or dispersed in

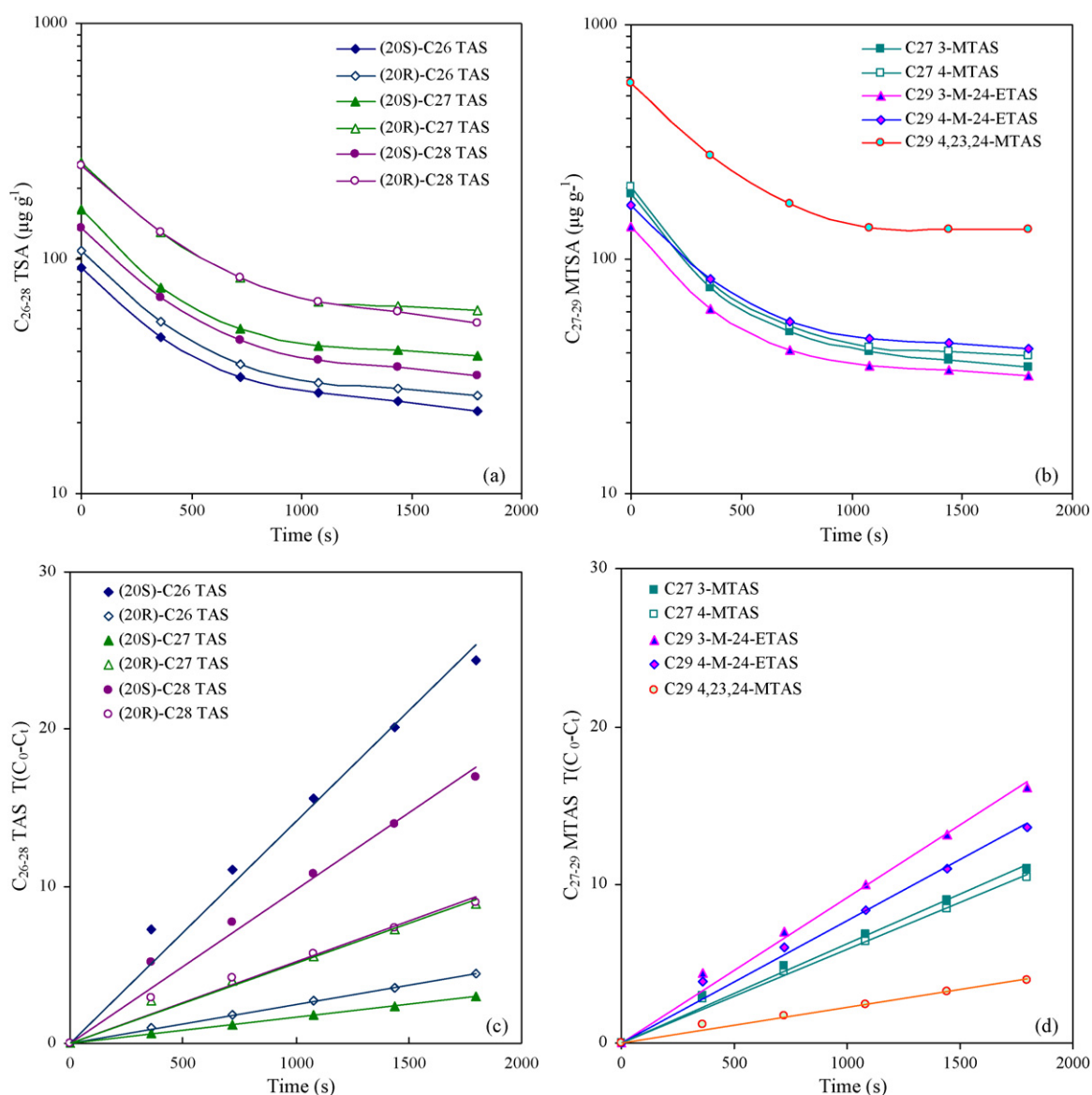


Fig. 4. Concentrations of C_{26-28} TAS and C_{20-29} MTAS in eluted soils (a: concentration curve for TAS; b: concentration curve for MTAS; c: function describing concentration of TAS; d: function describing concentration of MTAS).

the hot water increased as a first-order function with increasing ultrasonic irradiation time (Fig. 2b) according to the equation:

$$\ln\left(\frac{S_t}{S_0}\right) = 0.0799T - 0.5239, \quad R^2 = 0.9916 \quad (1)$$

in which S_0 is the amount (in mg L^{-1}) of SBHO dissolved or dispersed into the water after no ultrasonic irradiation, S_t is the amount (in mg L^{-1}) of the SBHO dissolved or dispersed into the water after irradiation for T seconds, and T is the ultrasonic irradiation time in s.

The amount of SBHO remaining in the eluted soils decreased with increasing irradiation time as a second-order function (Fig. 2a):

$$\frac{T}{C_0 - C_t} = 0.0044T - 0.0015, \quad R^2 = 0.9955 \quad (2)$$

in which C_0 is the initial SBHO soil concentration in mg kg^{-1} , C_t is the SBHO concentration in mg kg^{-1} in the soil after ultrasonic irradiation for time T , and T is the ultrasonic irradiation time in s.

It is interesting that although the amount of SBHO dispersed and dissolved in the hot water increased with increasing sonica-

tion time, this amount only accounted for 3.4% of the total SBHO removed after sonication for 360 s. This ratio decreased to a minimum of 2.5% after sonication for 720 s, then again began to increase with increasing sonication time to 2.7% after sonication for 1800 s (Fig. 2a and b). After gravity separation for 24 h, a layer of SBHO accumulated at the water–soil interface containing 70–80% of the eluted oil.

3.2. Elution of alkane biomarkers

The C_{26-34} 17α 25-norhopanes are typical alkane biomarkers found in SBHO-polluted soils. They comprise 3.9% of the SBHO with the C_{29} and C_{28} members of the series individually accounting for 1.0% and 0.6% of the SBHO. As the ultrasonic irradiation time was increased from 360 to 1800 s, the average elution of C_{26-34} increased from 44.6% to 75.4% (Fig. 3a and b). The elution of the species with the lowest carbon number ((22S)- C_{26}) increased from 44.2% to 66.1%, whereas the elution of ((22R)- C_{34} 17α 25-norhopane (the compound with the highest carbon number) increased from 63.1% to 88.9% (Fig. 3a and b).

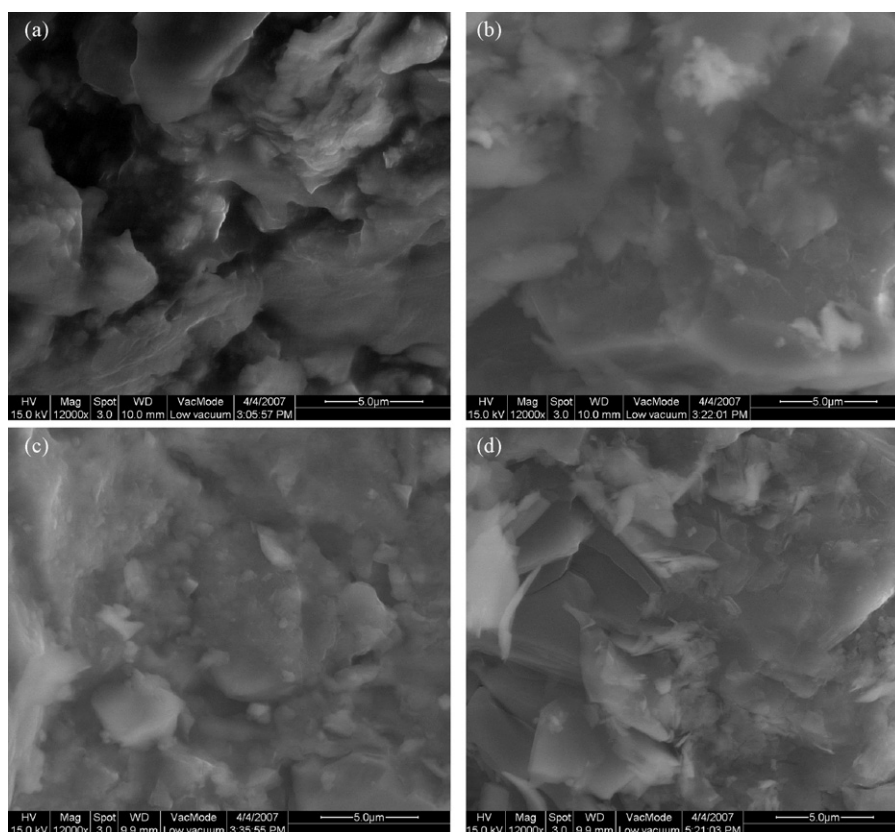


Fig. 5. SEM images depicting the surfaces of eluted soil particles (a: without ultrasound; b: 360 s; c: 1080 s; d: 1800 s).

The elution of the C_{26-34} 17α 25-norhopanes followed a second-order function with respect to sonication time. Larger correlation coefficients were observed for markers with higher carbon numbers (Fig. 3c and d). The impact of sonication time on the elution of C_{26-34} 17α 25-norhopanes is closely related to the carbon number, with higher carbon number species eluting more readily at long sonication times.

3.3. Elution of aromatic biomarkers

The typical aromatic hydrocarbon biomarkers found in SBHO are C_{26-28} TAS and C_{27-29} MTAS, individually accounting for 1.1% and 1.2% of the SBHO. The most abundant homologs are (20R)- C_{27} TAS and C_{29} 4,23,24-MTAS, accounting for 0.3% and 0.6% of the SBHO. As the ultrasonic irradiation time was increased from 360 to 1800 s, the average elution of C_{26-28} TAS increased from 51.0% to 77.1%; elution of (20S)- C_{26} TAS increased from 52.0% to 76.8% and elution of (20R)- C_{28} TAS increased from 49.1% to 78.1% (Fig. 4a). The elution of C_{26-28} TAS followed a second-order function with respect to sonication time, and larger correlation coefficients were obtained for species containing greater numbers of carbon atoms (Fig. 4c). The effectiveness of C_{26-28} TAS removal was closely related to the carbon number of the marker. At short sonication times, species containing fewer carbon atoms were more readily eluted, while longer irradiation times, the elution of molecules with higher carbon numbers was improved.

As the irradiation time was increased from 360 to 1800 s, the average elution of C_{27-29} MTAS increased from 56.8% to 78.3%, with the elution of 3- C_{27} MTAS increasing from 61.5% to 81.6% and the elution of 4,23,24- C_{29} MTAS increasing from 52.1% to 77.0% (Fig. 4c). The elution trends of MTAS species with respect to sonication time followed a second-order function (Fig. 4d). Species containing fewer carbon atoms were more easily eluted at long

sonication times, while species containing a greater number of carbon atoms displayed second-order behavior in terms of the amount eluted with respect to sonication time.

3.4. Surface characteristics of eluted soils

Fig. 5 is an SEM image depicting the surface of eluted soil particles. Soils eluted without ultrasound presented mainly as aggregates, and the soil surface was composed of a variety of clay particles and silt. Following treatment with ultrasound at 360 s, a fraction of the initially dispersed clay particles were curled. After ultrasonic irradiation for 1080 s, the eluted soils were composed of dispersed large particles encapsulated by SBHO, clay particles, and silt. Most of the particles were curled at the surface and 70% of the soil particle surface area was in the form of “bare patches”. This figure reached almost 85% when the ultrasonic irradiation time was increased to 1800 s.

3.5. Mineral and elemental composition of clean soils, SBHO, and eluted soils

Analysis of X-ray diffraction and energy spectroscopy experiments revealed that the primary minerals present in the clean and eluted soils were quartz (SiO_2), feldspar ($CaAl_2Si_2O_8$), muscovite ($KAl_2(Al-Si_3O_{10})(OH)_2$), and chlorite ($(Mg, Al, Fe)_6[(Si, Al)_4O_{10}](OH)_8$) (Fig. 6). The carbon content and the relative abundance of the last three minerals in the eluted soils decreased with increasing ultrasonic irradiation time, while the Si and O content followed the reverse trend (Fig. 6 and Table 1). In addition, the relative abundance of $CaCO_3$ and Ca after sonication for 360 s was higher than in the absence of ultrasound, but decreased noticeably with increasing sonication time from 360 to 1800 s (Fig. 6 and Table 1).

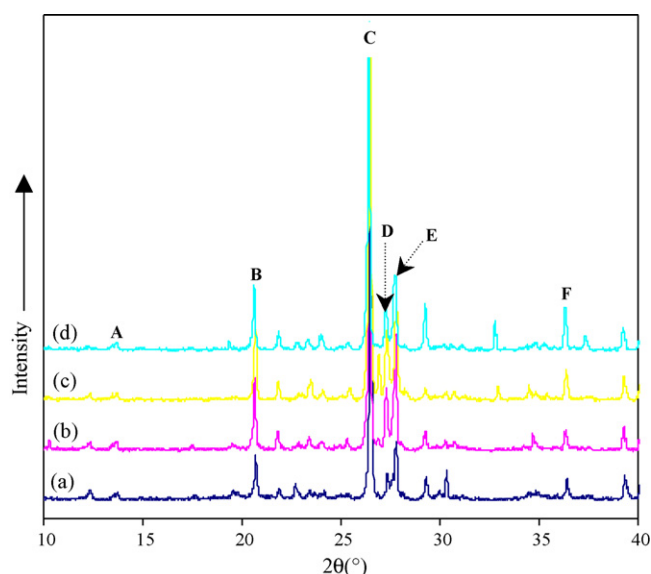


Fig. 6. XRD plots for clean and eluted soil (a: without ultrasound; b: 360 s; c: 1080 s; d: 1800 s; A: chlorite (Mg,Al,Fe)₆[(Si,Al)₄O₁₀](OH)₈; B: quartz; C: quartz and KMg₃Si₃AlO₁₀F₂; D: feldspar; E: muscovite; F: feldspar).

4. Discussion

4.1. Elution of SBHO

The results described in Fig. 2b and Eq. (1) indicate that the amount of SBHO that is dissolved or dispersed in hot water increases as a first-order function with increasing ultrasonic irradiation time. Possible reasons for this include interactions among various HOCs and competition between them for the same absorption site in soils [19], adsorption of HOCs by soils and dissolution of HOCs by the water phase [20], ultrasonic desorption to HOCs that are then re-adsorbed by soils, and ultrasonic dispersion to desorbed HOCs. Increasing sonication time causes continuous disruption of suspended aggregates [21]. Furthermore, cavitation due to ultrasound may also produce a “smashing” effect on the bulk soil aggregate, loosening the SBHO adsorbed to the soil surface [22]. The above effects result in increased dispersion into the hot water with increasing sonication time.

Interestingly, although the amount of residual SBHO in eluted soil displays a second-order decrease with respect to irradiation time (illustrated in Fig. 2a and Eq. (2)), this only accounted for 2.5–3.4% of the total SBHO removed. After gravity separation for 24 h, a layer of SBHO accumulated at the water–soil interface. This is different from the elution of soils containing high concentrations of light oils, in which an oil film is formed at the water surface [14]. The density of SBHO (0.995 g cm⁻³) is close to that of water, and bonding to clay particles may sufficiently increase its density to enable it to sink in water.

The high concentration of oil in the test samples (94.4 g SBHO kg⁻¹) resulted in multi-layer adsorption on the

surface of the soil particles [2,22]. Increasing the sonication time increased the number of shock waves and enhanced the production of high-speed microjets, overcoming the interfacial forces between the soil particles and the surfactant [12,23,24] and improving the elution of multi-layer adsorbed SBHO. Wang et al. [25] reported that increasing the sonication time obviously decreased the viscosity of SBHO and promoted the detachment of SBHO absorbed in the outer soil layer. During the gravity sedimentation process, this curled SBHO coagulated into the layer observed at the water–soil interface.

4.2. Elution of alkane biomarkers

The results illustrated in Fig. 3a and b indicate that elution of C_{26–34} 17 α 25-norhopanes in our ultrasound-enhanced system is closely related to the carbon number of the marker. Both C_{26–34} 17 α 25-norhopanes and the SBHO followed a second-order elution function (Figs. 2b, 3c and d). There are three possible reasons for this phenomenon. First, 17 α 25-norhopane is a relatively polar HOC. Species of lower carbon number are strongly hydrophobic and possess low solubility in water [18]. Second, it is much easier for smaller hydrocarbons to enter micropores and narrow channels in the soil surface and be immobilized [4,26]. Third, long-term ultrasound may stabilize dispersed hydrocarbons and enable them to form emulsions [22,27]. Increased numbers of carbon atoms in the hydrocarbon species lead to more stable emulsion systems and more effective elution [9].

4.3. Elution of aromatic biomarkers

Elution of C_{26–28} TAS was closely related to carbon number. Species containing fewer carbon atoms were more readily eluted at short sonication times, while longer sonication times improved the elution of larger species. Interestingly, elution of C_{26–28} TAS also followed a second-order function (Figs. 2b and 4c). C_{26–28} TAS is a PAH with three benzene rings and greater polarity than 17 α 25-norhopane. It combines more easily with asphalts through hydrogen bonding, resulting in curling [5,28,29]. Application of ultrasound enabled the curled material to readily disperse in the water. These dispersed particles were more stable when they contained smaller TAS species [27,30], which resulted in TAS homologs with smaller carbon numbers being easier to elute.

Elution of C_{27–29} MTAS was also dependent on the carbon number of the marker, with species containing fewer carbon atoms being more readily eluted at long sonication times (Fig. 4b). As in the cases of SBHO and C_{26–28} TAS, elution of C_{26–28} TAS followed a second-order function (Figs. 2b and 4d). A possible reason for this is that the aromatic rings of MTAS contain 1–3 methyl or ethyl side chains. Increased substitution leads to larger IgKow and greater hydrophobicity [30], increasing the difficulty of elution. Although the hydrophobicity of MTAS is increased by substitution, it still not as hydrophobic as cyclic saturated hydrocarbons, and eventually formed dispersions with water.

4.4. Surface characteristics of soils

Eluted soils appeared mainly as aggregates (Fig. 5), which agrees with previous descriptions [31]. This may be due to the presence of small clay particles and silt in the weathered soil. These small particles bonded to each other and then attached to the surface of soil particles to form aggregates. Stirring without ultrasound produces limited decomposition of these aggregates [22]. Ultrasound treatment for 360 s initiated curling of the soil particles; after treatment for 1080–1800 s 70–80% of the soil surface area existed as “bare patches” (Fig. 5). These observations demonstrate that the elution mechanism of SBHO and biomarkers in weathered soils is curling.

Table 1
Energy spectra of soil particle surfaces (at%).

Element	CS	0 s	360 s	1080 s	1800 s
CK	31.6	69.8	55.8	34.8	32.1
OK	44.6	21.3	32.2	44.7	46.5
MgK	1.0	0.3	0.8	0.2	0.5
AlK	4.4	2.1	2.6	1.0	2.4
SiK	15.1	5.1	6.4	18.4	17.0
CaK	0.9	0.3	0.6	0.2	0.1
FeK	1.5	0.5	0.9	0.3	0.4

Extended periods of sonication time are helpful in decomposing and curling TAS and MTAS immobilized in soil micropores, ducts, and crystals.

4.5. Minerals and elemental composition

The relative abundance of feldspar, muscovite, and chlorite in the eluted soils decreased with increasing ultrasonic irradiation time (Fig. 6), because all of them are major constituents of clay particles.

It is interesting that the relative abundance of CaCO_3 and Ca first increased (360 s) then decreased (1080–1800 s) (Fig. 6 and Table 1). Possible reasons for this include cavitation-induced decomposition and dispersion of clay particles leading to dissolution of soil Ca^{2+} in the water, and association of Ca^{2+} with CO_3^{2-} in water to form CaCO_3 [3,5,32]. Ultrasound treatment for 360 s had a weak dispersion effect on suspended CaCO_3 , and small deposits of calcite were observed on the surface of the eluted soil particles. Ultrasound exposure for longer periods produced a stronger dispersion effect on the suspended CaCO_3 and prevented deposition of CaCO_3 on the surface of the soil particles.

5. Conclusions

- (1) The concentration of residual SBHO and three biomarkers in treated soils decreased in a second-order manner, while the increase in SBHO dissolved and dispersed in the eluent water was first-order with respect to increased ultrasound time.
- (2) The elution trends of C_{26-34} 17α 25-norhopanes, C_{26-28} TAS, and C_{27-29} MTAS compounds were closely related to carbon number. 17α 25-norhopane species with higher carbon numbers eluted more easily after longer irradiation times. TAS species with higher carbon numbers eluted more easily after 1080–1800 s of ultrasound exposure, whereas TAS species containing fewer carbon atoms were easier to elute after 0–360 s ultrasound. Longer periods of ultrasound improved the elution of MTAS homologs containing fewer carbon atoms.
- (3) Ultrasonic irradiation for periods of more than 1080 s had a negative impact on deposition of CaCO_3 , but improved the elution of SBHO and its three biomarkers and the overall mineral and elemental composition of the soil. Ultrasound treatment therefore represents a potentially useful method for enhancing the removal of SBHO from weathered soils.

Acknowledgement

This study was funded by a grant from the National Natural Science Foundation of China (No. 40772146).

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