

Article

Oil-Based Drilling Cuttings from Shale Gas Wells Treated with CO₂ Switchable Hydrophilic Solvents: Priority Pollutant Migration and Produced Wastewater Assessment

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Abstract: The exploitation of shale gas resources brings in abundant hazardous oil-based drilling cuttings (ODBCs). Herein, N, N-Dimethylcyclohexylamine (DMCHA) acted as the CO₂ switchable hydrophilic solvents (SHSs), and the ODBC treated with DMCHA was studied, especially priority pollutant migration and produced wastewater assessment during the extraction process. The petroleum hydrocarbon content of ODBC decreased from 10.73 to 0.84 wt% after the DMCHA extraction was conducted at a DMCHA/ODBC liquid–solid ratio of 20:1, 35 °C, and 200 rpm for 30 min. Using the CO₂ switchability of SHSs, the petroleum hydrocarbon and DMCHA were recovered. There was wastewater, which was produced after recovering DMCHA, and the produced wastewater assessment showed that chemical oxygen demand, 5-day biochemical oxygen demand, total nitrogen, total organic carbon, and petroleum were 561.00, 238.00, 40.60, 309.00, and 0.27 mg/L, respectively. Meanwhile, phenols (0.0031 mg/L), naphthalene (0.0000129 mg/L), phenanthrene (0.000059 mg/L), anthracene (0.000058 mg/L), as well as heavy metal ions such as Cu (0.01 mg/L) could be detected in the produced wastewater. As a result, a priority pollutant migration mechanism from ODBC to the produced wastewater was proposed. This would be helpful for the better management policy making of the ODBC treated by using CO₂ SHSs and the produced wastewater.

Keywords: priority pollutants; wastewater; switchable hydrophilic solvents; oil-based drilling cuttings; shale gas



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1. Introduction

Shale gas, as one of the fossil fuels, is rich in shale reservoirs [1,2], which have been supplying clean, low-carbon, and highly efficient energy to humans [3]. It is well known that in order to create excellent borehole stability and reduce the formation damage of shale gas reservoirs, large amounts of oil-based drilling fluids must be applied in the drilling engineering of shale gas horizontal wells [2,4–6]. Generally, there would be huge oil-based drilling cuttings (ODBCs) generated during drilling operations of the horizontal wells worldwide [5,7–10]. For example, the shale gas resources in southwest China are mainly distributed in the Sichuan Basin; thereby, the shale gas industry has drawn increasing investments in this region over the last decade [11–14]. With the shale gas exploration and development, however, the treatment and management of the ODBC became a great issue and concern in the regions of Sichuan, China [15,16].

Because of the serious potential risks to human health and the ecological environment, ODBC containing harmful substances, such as heavy metals and organic matters,

have been classified as hazardous waste [17,18], so that the discharge of ODBC is strictly regulated in many countries around the world. It is reported that the total petroleum hydrocarbon, an important and obvious pollutant index, should be removed fully after the treatment of ODBC [17,18]. Traditional disposal methods, i.e., landfill and injection strata, cannot eliminate the petroleum hydrocarbon (e.g., diesel and mineral oil), thus the environmental risk still remains [18]. In recent years, several studies have reported some novel strategies such as pyrolysis [19–23], superheated steam extraction [24], pressurized hot water extraction [25], low-temperature thermal desorption [26], supercritical CO₂ extraction [27], supercritical water oxidation [28], solvent extraction [29], surfactant washing [30], and microemulsion cleaning [31–33] to remove the petroleum hydrocarbon of ODBC. In fact, the pressurized hot water extraction, superheated steam extraction, pyrolysis, and thermal desorption would afford high energy consumption. The treatment cost of ODBC with the supercritical CO₂ extraction and supercritical water oxidation was very costly. It is difficult to reuse the surfactant components for surfactant-enhanced washing. The use of microemulsion cleaning for the treatment of ODBC has been investigated, but its operations were complicated. Intriguingly, solvent extraction was favored to recover the petroleum hydrocarbon of ODBC because of its easy operations and simple processing equipment. Alkane, toluene, petroleum ether, as well as their mixtures, were efficient organic solvents for extraction, but such conventional solvents were highly toxic [34]. Thus, eco-friendly solvents as extractants of ODBC have attracted great attention.

To the best of our knowledge, the treatment of ODBC by using green hydrophobic deep eutectic solvents (DESS) has been reported [34]. However, the treatment process with DESS was complex because of its cumbersome workflow. Therefore, eco-friendly solvent extraction with simple workflow would be extremely advantageous. Fortunately, other green CO₂ switchable hydrophilic solvents (SHS), such as tertiary amine derivatives and amidine compounds, can change reversibly between hydrophilicity and hydrophobicity through the entry and removal of CO₂, which was discovered by Jessop et al. [35–39]. Soon afterward, some studies have shown that CO₂ SHS have great potential applications in extracting oil. For example, Phan et al. conceded that using CO₂ SHS, soy oil could be extracted successfully from crushed soybeans [36]. Holland et al. described that CO₂ SHS were efficient to extract bitumen of oil sands [40]. Samorì et al. confirmed that extraction of hydrocarbons using CO₂ SHS was possible from microalga *botryococcus braunii* [41]. Wang et al. studied the solubility of diesel oil in CO₂ SHS and demonstrated that CO₂ SHS could be applied to recover the diesel oil [42]. As a result of the reported studies [35–42], it is possible that an eco-friendly CO₂ switchable hydrophilic solvent extraction with simple workflow can be found for the treatment of ODBC, as illustrated in Figure 1. Furthermore, few reports focused on priority pollutant migration and produced wastewater assessment during the CO₂ SHS extraction process.

In this work, ODBC from deep shale gas wells treated with CO₂ SHS were studied, especially priority pollutant migration and produced wastewater assessment during the extraction process. The influence of operating parameters, such as SHS/ODBC liquid–solid ratio (volume versus mass), temperature, contact time and stirring speed on residual petroleum hydrocarbon content, and the petroleum hydrocarbon removal rate of the shale gas ODBC, were explored. The residual cuttings were studied by FT-IR, SEM, EDS, as well as contacted angles, and the recovered petroleum hydrocarbon and SHS from the switchable hydrophilic solvent extraction process were determined by FT-IR. In addition, an optimized dose of water was explored, and the quality of produced wastewater in the switchable hydrophilic solvent extraction process was evaluated. Finally, a possible priority pollutant migration mechanism during the treatment of ODBC by using SHS was proposed.

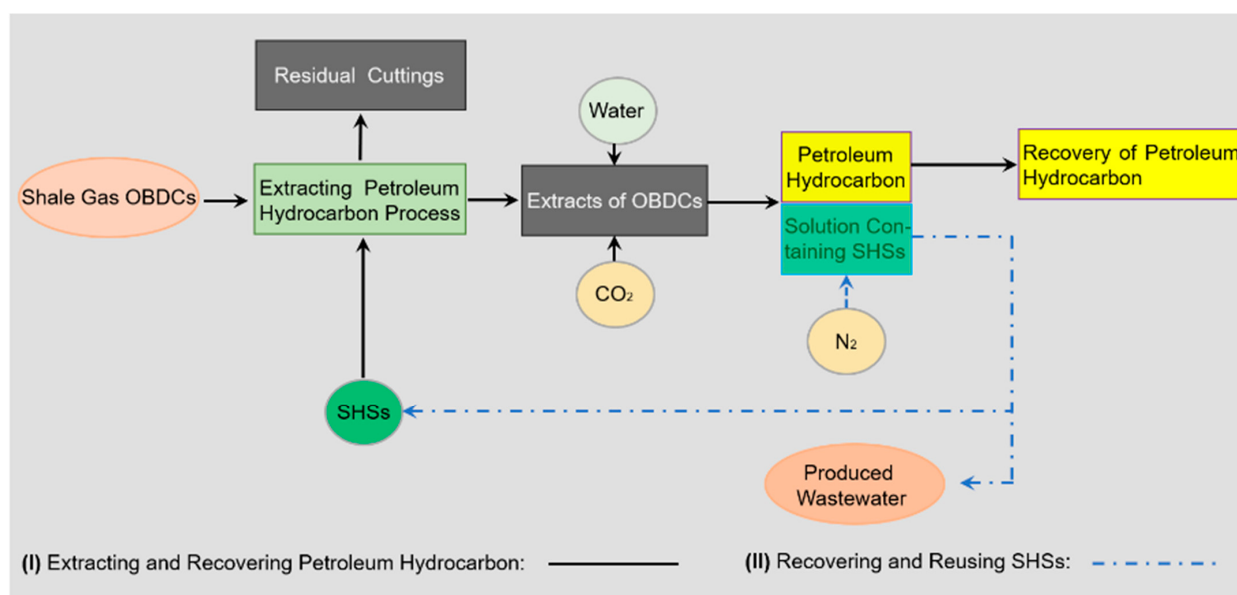


Figure 1. The treatment process of shale gas OBDs with CO₂ SHSs.

2. Materials and Methods

2.1. Materials

The sample of OBDs was obtained from a well site of shale gas blocks in the south of the Sichuan Basin (Sichuan, China). N, N-Dimethylcyclohexylamine (DMCHA, 98%), perchloroethylene (AR), and anhydrous sodium sulfate (AR) were purchased from Macklin Biochemical Co., Ltd., Shanghai, China. Deionized (DI) water (18.25 MΩ cm) used throughout was prepared with a UPH Automatic Water Purifier (Sichuan Ulupure Science and Technology Co., Ltd., Chengdu, China).

2.2. Extracting Petroleum Hydrocarbon from OBDs with CO₂ SHSs

2.2.1. Extracting Petroleum Hydrocarbon Procedure

Figure 1 depicts the treatment process of shale gas OBDs by using CO₂ SHSs, and DMCHA was a candidate of the CO₂ SHSs. As shown in Figure 1, shale gas OBDs were washed with DMCHA through the extracting petroleum hydrocarbon process under mechanical agitation. The DMCHA/OBDs liquid–solid ratio, temperature, contact time, and stirring speed varied 5:1~30:1, 25~50 °C, 10~60 min, and 100~350 rpm, respectively. Then, the residual cuttings were separated and extracts of OBDs were obtained by utilizing high-speed centrifugation at 1500 rpm for 10 min.

To optimize the dose of fresh water (DI water), the CO₂ response of DMCHA in DI water was investigated. The DMCHA/DI water liquid–liquid ratio (volume versus volume) varied from 1:1 to 1:3, and CO₂ was bubbled at a rate of 150 mL/min for 2 h. Conductivity changes were recorded every 1 h. Furthermore, to recover petroleum hydrocarbon, DI water was added in the obtained extracts of OBDs and bubbling CO₂ continued at a rate of 150 mL/min for 2 h, and then the amount of the DI water was optimized by the above studies. The petroleum hydrocarbon was separated by means of a liquid–liquid separation.

2.2.2. Recovering CO₂ SHSs Procedure

N₂ was bubbled into the solution containing the protonated DMCHA at 70 °C for 2 h, in which the ventilation rate was controlled at 150 mL/min. The DMCHA was recovered and reused after another liquid–liquid separation operation, but wastewater was produced in this treatment process.

2.3. Analytical Methods

The pH measurements were conducted on a SevenGo Duo Pro pH meter (METTLER TOLEDO, Zurich, Switzerland), and all of conductivity measurements were carried out with a DDS-307 conductometer (INESA and Scientific Instruments Co., Ltd., Shanghai, China). The petroleum hydrocarbon content was measured by using an Oil 460 Infrared Oil Content Analyzer (Huaxia Kechuang Instrument Technology Co., Ltd., Beijing, China). The chemical oxygen demand (COD), five-day biochemical oxygen demand (BOD₅), total organic carbon (TOC), phenols, polycyclic aromatic hydrocarbons, and total dissolved solids (TDS) were analyzed according to the APHA Standard Methods [43,44]. The ammonia nitrogen content and total nitrogen content were quantified with a UV7504 UV-Vis Spectrophotometer (Shanghai Jingmi Instrument Co., Ltd., Shanghai, China). Petroleum was detected by using a JLBG-126U infrared oil content analyzer (Jilin Jiguang Technology Co., Ltd., Jilin, China). The inorganic ions such as Cl^- , PO_4^{3-} , SO_4^{2-} , and NO_3^- were detected by using a ECO ion chromatography with an 863 Compact IC Autosampler (Metrohm AG, Herisau, Switzerland) after samples were filtered through a 0.22 μm filter. Trace analysis of metal elements such as Na, K, Ca, and Mg was conducted on a PinAAcle 900 atomic absorption spectrophotometer (PerkinElmer, Waltham, MA, USA). The other metal elements (e.g., Al, As, Ba, Co, Cr, Cu, Fe, Mn, Ni, etc.) were detected on an Optima 8300 Inductively Coupled Plasma Optical Emission Spectroscopy (PerkinElmer, Waltham, MA, USA).

2.4. Characterizations

Fourier transform infrared (FT-IR) spectrums were recorded using a Nicolet 170SX infrared spectrometer (Perkin Elmer Co., Madison, WI, USA), and the FT-IR measurements were conducted in the optical range of 400–4000 cm^{-1} by averaging 16 scans with a resolution of 4 cm^{-1} . The contacted angles of DI water on the surface of OBDCs before and after treatment by using CO_2 SHSs were recorded with an SDC-200 S Contact Angle Measuring Instrument (Shengding Precision Instruments Co., Ltd., Dongguan, China). The measurements of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed on a ZEISS Gmini 300 field emission scanning electron microscope (Carl Zeiss Jena, Jena, Germany), and an accelerating voltage of 10 kV was employed to obtain high resolution images.

3. Results and Discussion

3.1. Morphology and Composition of Shale Gas OBDCs

In general, there were 250–300 m^3 OBDCs produced from a single shale gas well in the south of the Sichuan Basin (Sichuan, China), and this production lasted approximately one month. Furthermore, the throughput of shale gas OBDCs would be enlarged in the scale of increasing deep regional shale gas development. Apparently, it can be seen from Figure 2a that deep regional shale gas OBDCs which smelt like oil were of semi-solid state. To efficiently manage and treat the shale gas OBDCs, their composition was studied, as shown in Figure 2b. Figure 2b shows that the shale gas OBDCs consisted of petroleum hydrocarbon, inorganic matter, moisture, and others, which is consistent with the previous studies. All studies reported that human health and environment suffered easily from the petroleum hydrocarbon of OBDCs. Thus, it is more important to deal with the shale gas OBDCs for deep regional shale gas development.

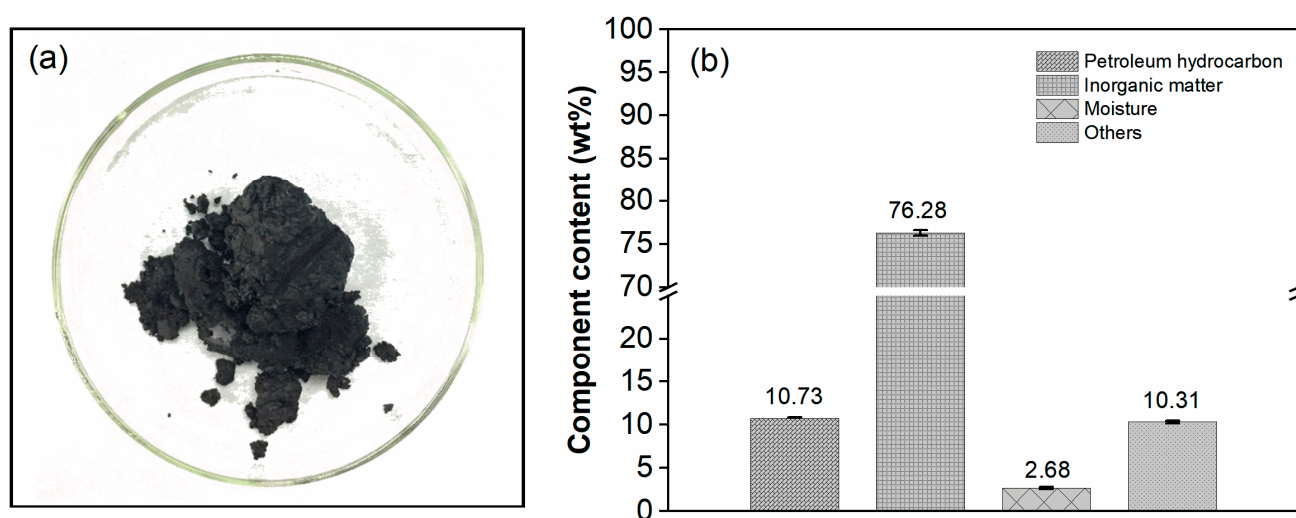


Figure 2. Morphology (a) and composition distribution (b) of ODBC produced from a deep shale gas well site in the southern Sichuan Basin, China.

3.2. Extracting Petroleum Hydrocarbon from shale gas ODBC by Using CO₂ SHSs

DMCHA, one of the CO₂ SHSs, has been used for extracting petroleum hydrocarbon of deep regional shale gas ODBC, and a sustainable treatment process of the shale gas ODBC with DMCHA is illustrated in Figure 1. Residual petroleum hydrocarbon content and petroleum hydrocarbon removal rate of the shale gas ODBC after treatment by using DMCHA were explored, as shown in Figure 3. It can be observed from Figure 3a that the residual petroleum hydrocarbon content decreased with the increasing liquid–solid ratio at 35 °C and 200 rpm for 30 min, but hardly changed after reaching the liquid–solid ratio of 20:1. This is because most of the petroleum hydrocarbon from shale gas ODBC can be dissolved by DMCHA but DMCHA could not perfectly drive the desorption of petroleum hydrocarbon on surfaces of drilling cuttings. Furthermore, the influence of contact time, temperature, and stirring speed on residual petroleum hydrocarbon content and petroleum hydrocarbon removal rate was studied, as shown in Figure 3b–d. Figure 3b shows that the residual petroleum hydrocarbon content changed with contact time increasing at the liquid–solid ratio of 20:1, 35 °C, and 200 rpm, suggesting that a contact time of 30 min is enough. Figure 3c exhibits the residual petroleum hydrocarbon content reduced with the increasing temperature at the liquid–solid ratio of 20:1 and 200 rpm for 30 min, which indicates that the temperature increasing would be beneficial for the desorption of petroleum hydrocarbon. However, the temperature influence became weak when the temperature exceeded 35 °C. What is more, a higher temperature might result in a worse DMCHA loss because of DMCHA volatilization, so extracting petroleum hydrocarbon from the ODBC with DMCHA at 35 °C would be better. Figure 3d shows the changes of the residual petroleum hydrocarbon content with stirring speed, which reveals 250 rpm was favorable. As result of Figure 3, under the optimal conditions (namely liquid–solid ratio of 20:1, 35 °C, 250 rpm, and 30 min contact time), the minimum of residual petroleum hydrocarbon content and the maxima of petroleum hydrocarbon removal rate were 0.84% and 92.17%, respectively. These results indicate that the petroleum hydrocarbon has been efficiently extracted from the ODBC.

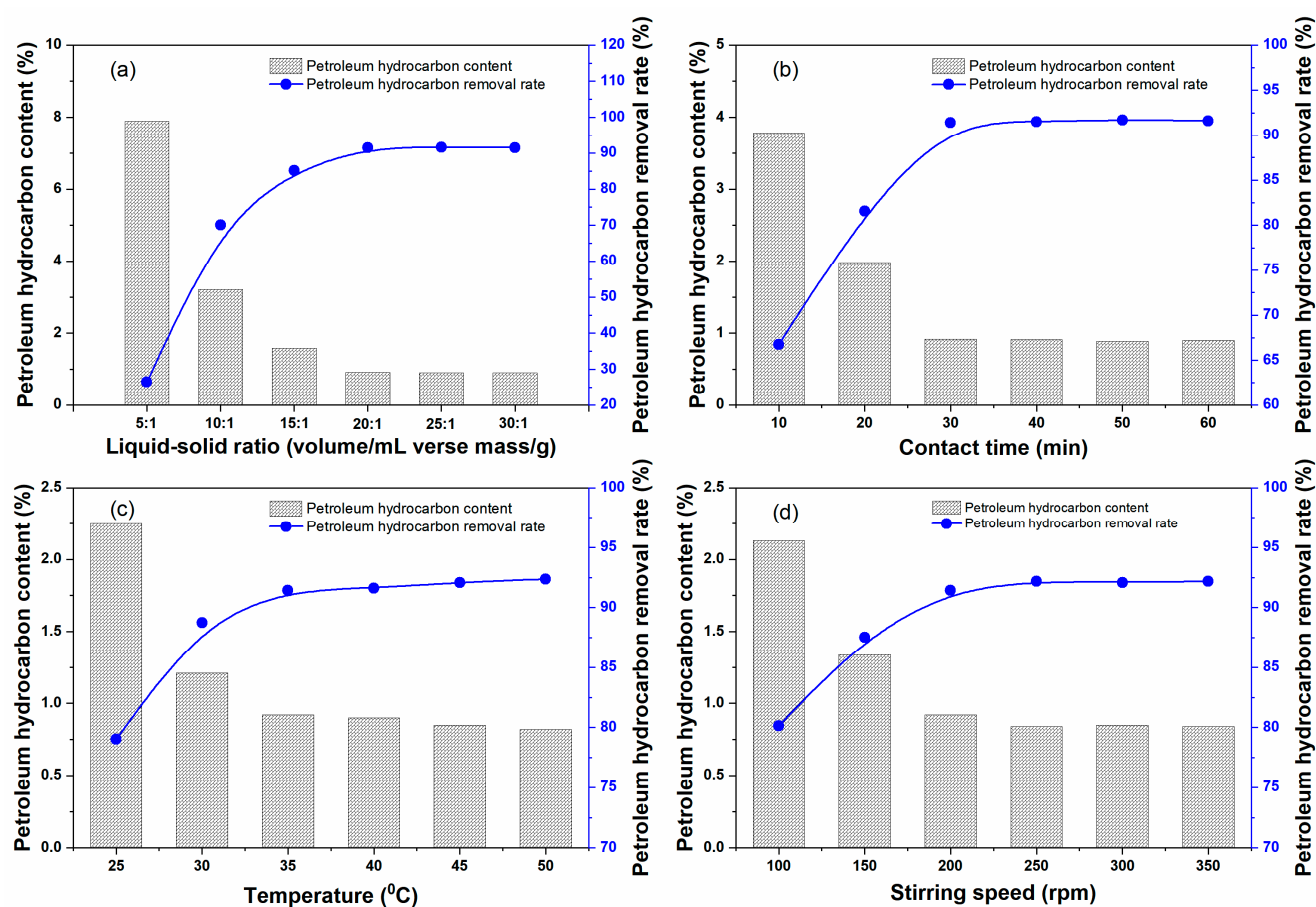


Figure 3. Influence of liquid–solid ratio (a), contact time (b), temperature (c), and stirring speed (d) on residual petroleum hydrocarbon content and petroleum hydrocarbon removal rate.

An optimized dose of fresh water was confirmed, as shown in Figure 4. Figure 4a shows that DMCHA was not insoluble in DI water at 25 °C, and a DMCHA-DI water interface could be observed clearly. After bubbling CO₂ at a rate of 150 L/min for 120 min, DMCHA was partly dissolved in DI water, but the DMCHA-DI water interface still existed for DMCHA and DI water mixtures with a 3:1 volume ratio. In contrast, the DMCHA-DI water interface which existed in DMCHA and DI water mixtures with a 1:1 and 1:3 volume ratio disappeared completely, and aqueous solutions formed (see Figure 4b). Moreover, Figure 4c exhibits that the conductivity of these mixtures increased when CO₂ was bubbled continuously within 120 min. The conductivity change is because DMCHA can enforce a reversible conversion from hydrophobic DMCHA to hydrophilic DMCHAH⁺ through bubbling CO₂. Therefore, to reduce water consumption and achieve an excellent separation of DMCHA with recovered petroleum hydrocarbon, the dose of water with DMCHA in a proportion of 1:1 (by volume) was favorable.

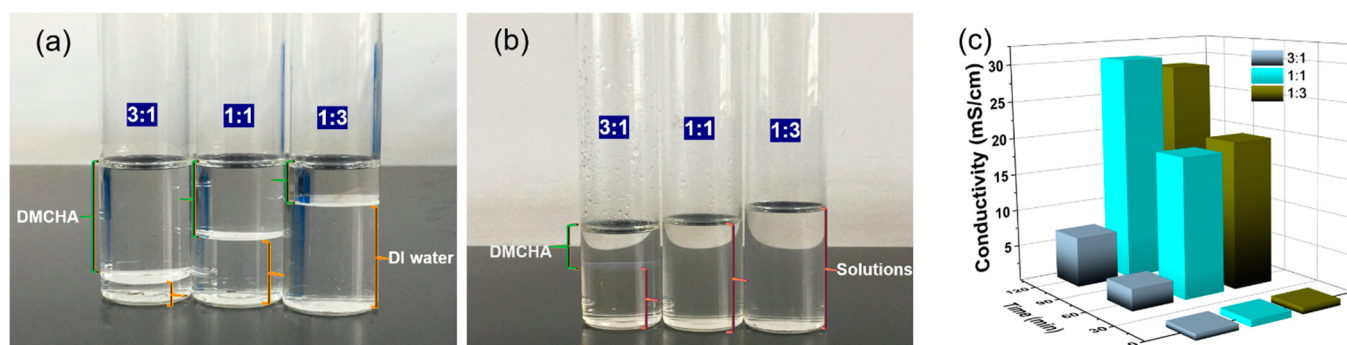


Figure 4. Digital photos of DMCHA and DI water mixtures with different volume ratios before (a) and after (b) bubbling CO₂ for 120 min, and conductivity of the mixtures at different times (c).

To reveal the potential values of recovered petroleum hydrocarbon and DMCHA, FT-IR measurements were conducted. The recovered petroleum hydrocarbon from the shale gas OBDCs was analyzed with FT-IR, as shown in Figure 5. In the spectrum of the initial diesel oil (i.e., base oil of oil-based drilling fluids), characteristic peaks such as 2930 (C–H stretching vibration of methyl groups), 2855 (C–H stretching vibration of methyne groups), 1453 (C–H symmetric deformation vibration of methyl or methyne groups), and 1373 cm^{−1} (deformation vibration of methyl groups) can be found. Importantly, the characteristic peak at 777 cm^{−1} belonged to the (–CH₂)_n ($n \geq 4$) rocking vibration. Moreover, similar characteristic peaks could be found in the spectrum of the recovered petroleum hydrocarbon. These indicate that the saturated long straight-chain alkanes were the main components of the initial diesel oil and the recovered petroleum hydrocarbon from OBDCs. Furthermore, Figure 5b shows the FT-IR spectrums of the initial and recovered DMCHA. In the spectrum of the initial DMCHA, characteristic peaks such as 2931 (C–H stretching vibration of methyl groups), 2770 (C–H stretching vibration of methyne groups), and 1448 cm^{−1} (C–H bending vibration of methyne groups) can be observed. Meanwhile, it is found that the C–N stretching vibration of tertiary amine compounds varied between 1350 and 1000 cm^{−1}. Obviously, the FT-IR spectrum of the recovered DMCHA was similar with that of the initial DMCHA, suggesting that the recovered DMCHA could be reused in the treatment process of shale gas OBDCs.

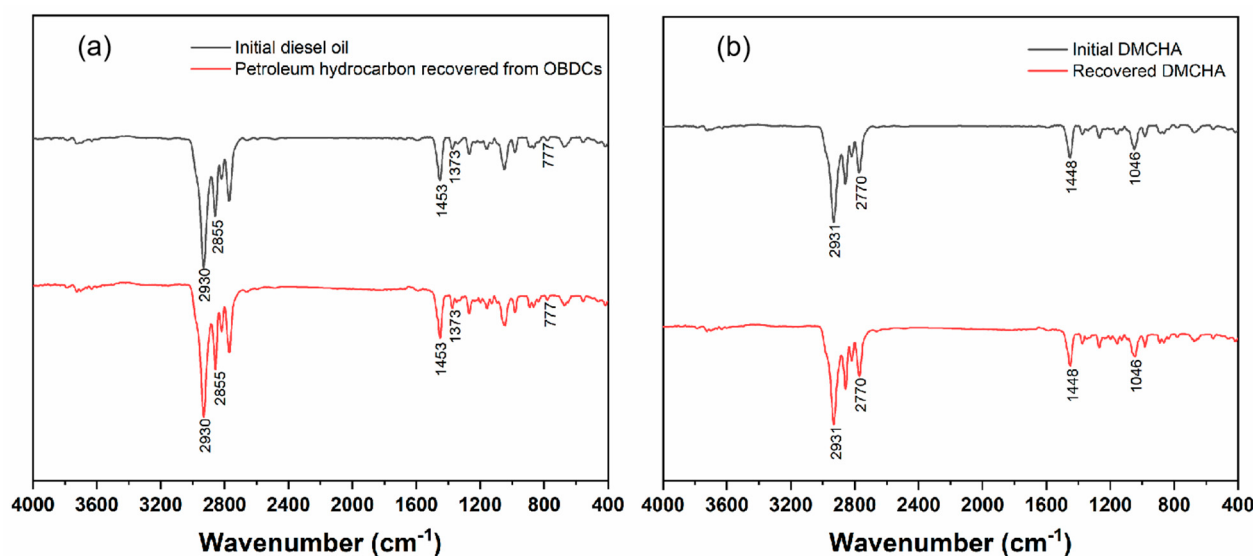


Figure 5. FT-IR spectrums of petroleum hydrocarbon from OBDCs (a) and recovered DMCHA (b).

3.3. Priority Pollutant Migration and Produced Wastewater Assessment

3.3.1. FT-IR Analysis

So far, the petroleum hydrocarbon is known to be a priority pollutant index. Priority pollutant migration of the shale gas OBDCs was studied by using FT-IR. Figure 6 shows the FT-IR spectrums of shale gas OBDCs before and after treatment using SHSs. It can be seen from Figure 6 that the absorption bands at 3433 cm^{-1} (O–H stretching vibrations of water), 2924 and 2855 cm^{-1} (–CH stretching vibrations of alkanes), 1636 cm^{-1} (C=C stretching vibrations of aromatic hydrocarbons), 1455 and 876 cm^{-1} (C–O asymmetric stretching vibrations and in-plane bending vibrations of carbonate ions resulting from CaCO_3 , respectively), 1086 and 466 cm^{-1} (Si–O stretching vibrations and O–Si–O bending vibrations of SiO_2), and 610 cm^{-1} (corresponding to a characteristic absorption peak of BaSO_4) existed in FT-IR spectrums of shale gas OBDCs before treatment and after treatment using SHSs. Compared with the absorption peak intensity of shale gas OBDCs before treatment, however, the absorption peak intensity of shale gas OBDCs after treatment by using SHSs decreased dramatically at 3443 , 2924 , 2855 , and 1636 cm^{-1} , suggesting that the moisture and petroleum hydrocarbon have been removed away from the shale gas OBDCs.

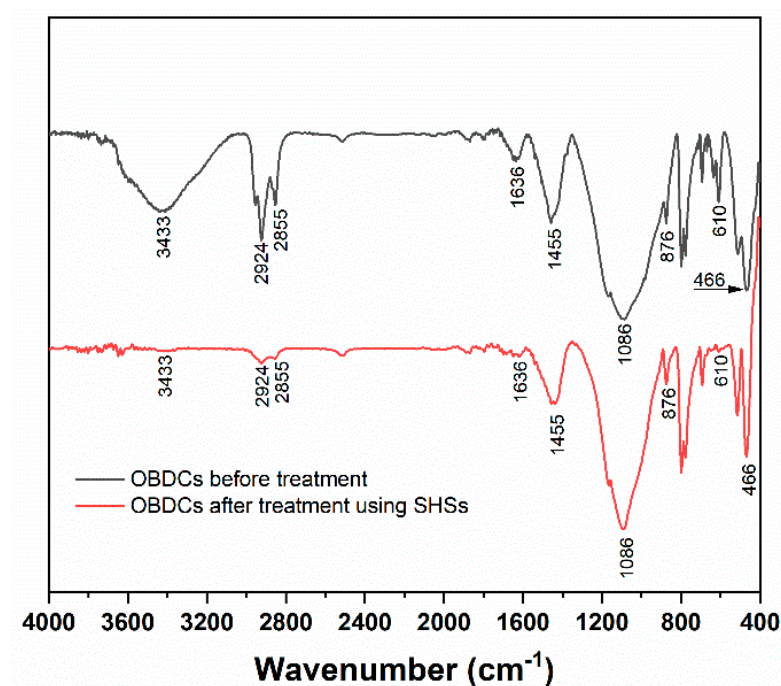


Figure 6. FT-IR spectrums of the shale gas OBDCs before and after treatment using SHSs.

3.3.2. Contacted Angle Analysis

To confirm petroleum hydrocarbon migration, contacted angle measurements were carried out (see Figure 7a). As shown in Figure 7b, the contacted angle value of initial shale gas OBDCs (115.8°) was higher than 90° , and that of shale gas OBDCs after treatment by using DMCHA (65.9°) was lower than 90° . As a result, these reveal that the surface wettability of shale gas OBDCs changed from a hydrophobic surface to hydrophilic surface because of removing abundant petroleum hydrocarbon.

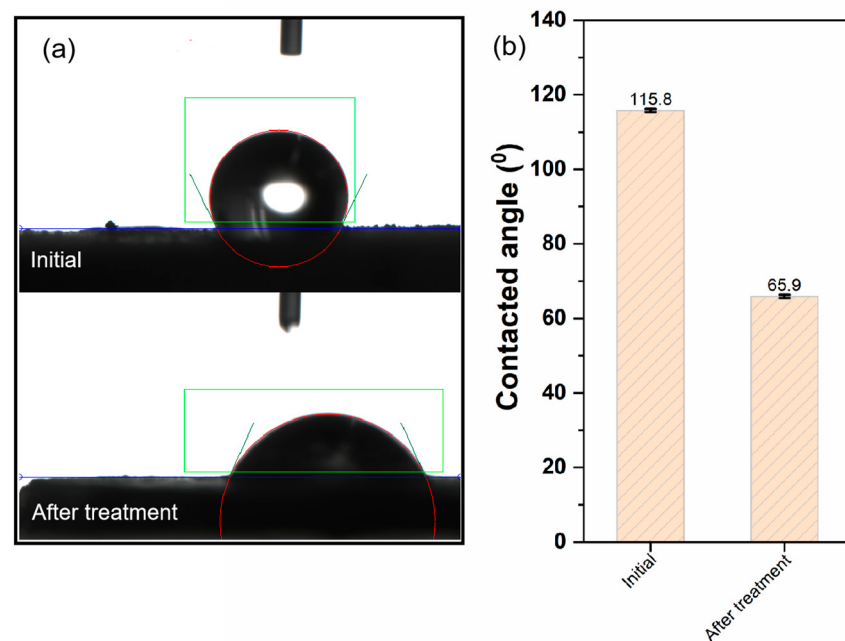


Figure 7. Contacted angle images (a) and values (b) of shale gas OBDCs before and after treatment by using DMCHA.

3.3.3. SEM Analysis

On the other hand, SEM measurements were conducted to study micromorphology changes of shale gas OBDCs before and after treatment by using DMCHA, as shown in Figure 8. Figure 8a,b show that initial shale gas OBDCs looked like compact agglomerations, and cutting particles cannot be found clearly because of covering by the petroleum hydrocarbon, even under a high magnification ($\times 10,000$). Compared with Figure 8a,b, Figure 8c exhibits that the micromorphology of shale gas OBDCs after treatment by using DMCHA had changed. The profile of cutting particles can be clearly observed within view of SEM observation (Figure 8c), because the agglomerations were destroyed. Moreover, it is seen from Figure 8d that surfaces of the cutting particles were rough at a high magnification ($\times 10,000$). Thus, all SEM results indicate that the petroleum hydrocarbon of shale gas OBDCs reduced significantly as well.

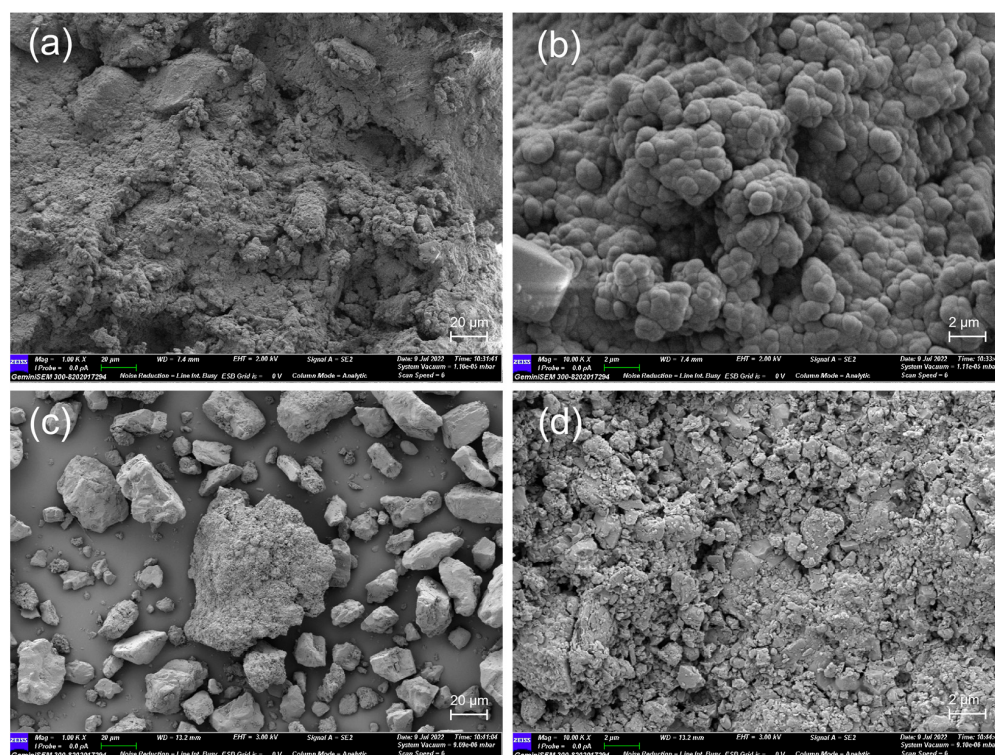


Figure 8. SEM images of shale gas OBDCs before ((a) $\times 1000$) and ((b), $\times 10,000$) and after ((c), $\times 1000$) and ((d) $\times 10,000$) treatment using SHSs.

3.3.4. EDS Analysis

In order to obtain insights into shale gas OBDCs before and after treatment by using DMCHA, EDS measurements were conducted. Figure 9 shows the EDS profile and elemental mappings involved in the surface of shale gas OBDCs before treatment. It is found from Figure 9 that elemental compositions of the initial shale gas OBDCs contained C, O, S, Cl, Na, K, Ca, Cr, Fe, Co, Ni, Cu, Zn, Sb, and Ba. In addition, the shale gas OBDCs after treatment by using DMCHA were comprised of 12 chemical elements such as C, O, N, S, Cl, Si, As, Na, Al, Ca, Sr, and Ba, as shown in Figure 10. It is not surprising, that there were real differences between the elemental compositions of Figures 9 and 10. This is because the shale gas OBDCs could take on different elemental compositions, depending on which horizontal layers they were in. Therefore, EDS analyses might ensure the elemental compositions of the shale gas OBDCs including heavy metals such as Cr, Co, Ni, Cu, Zn, Sb, and As, which is in agreement with preceding studies.

Based on the EDS map sum spectrums (Figure 11a,c), atomic percentages of shale gas OBDCs before and after treatment by using DMCHA were analyzed. As shown in Figure 11b,d, the C percentage of untreated shale gas OBDCs was higher than that of treated shale gas OBDCs with DMCHA, which should ascribe to the petroleum hydrocarbon of shale gas OBDCs decreasing. Fortunately, although shale gas OBDCs contained heavy metals, the percentage of heavy metals, for example Cr, Co, Ni, Cu, Zn, Sb, and As, was very low (see Figure 11b,d). These proofs suggest that the environmental risks of shale gas OBDCs have been weakened.

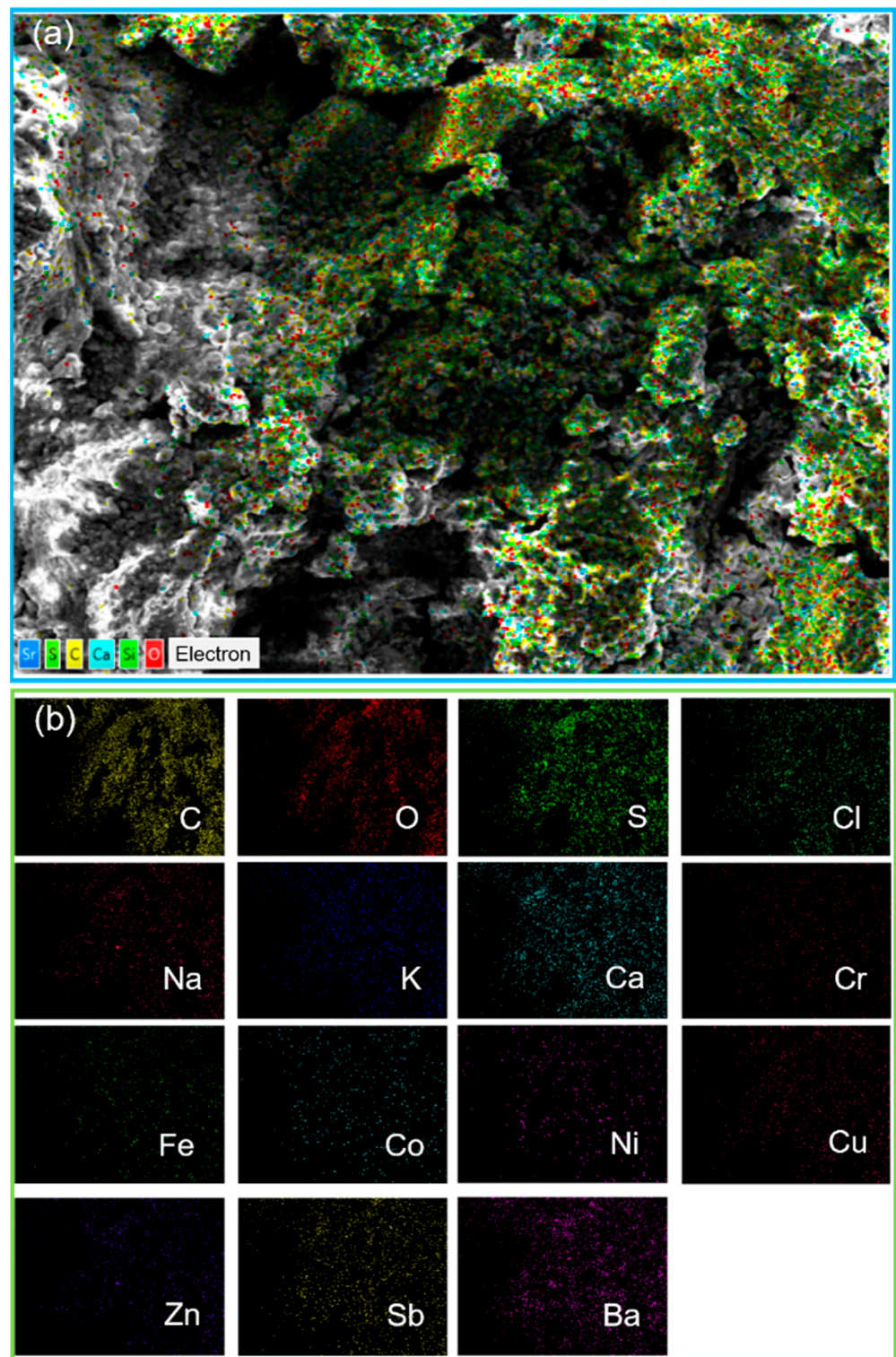


Figure 9. EDS profile (a) and elemental mappings (b) involved in the surface of shale gas OBDCs before treatment.

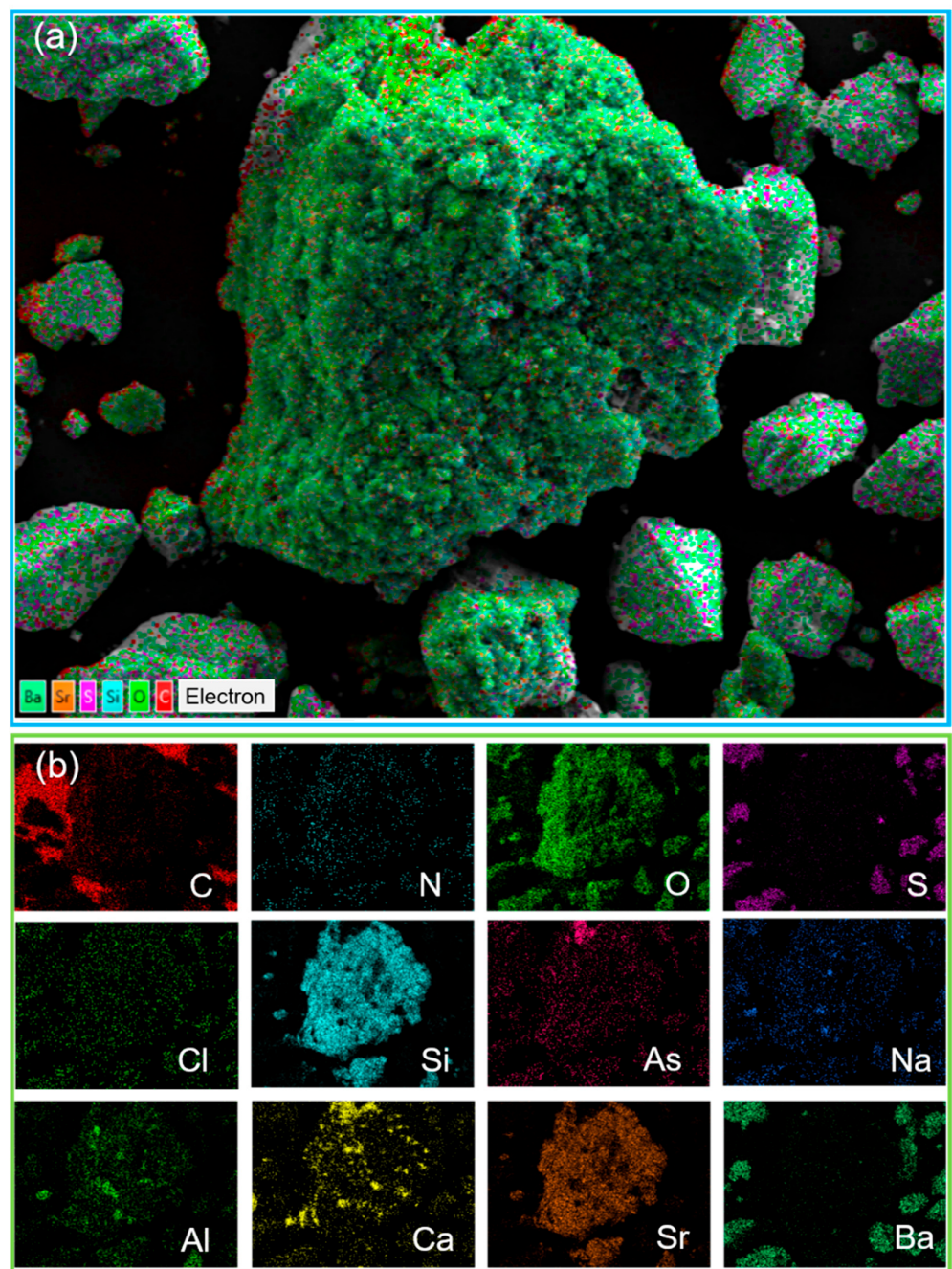


Figure 10. EDS profile (a) and elemental mappings (b) involved in the surface of shale gas OBDCs after treatment by using CO₂ SHSs.

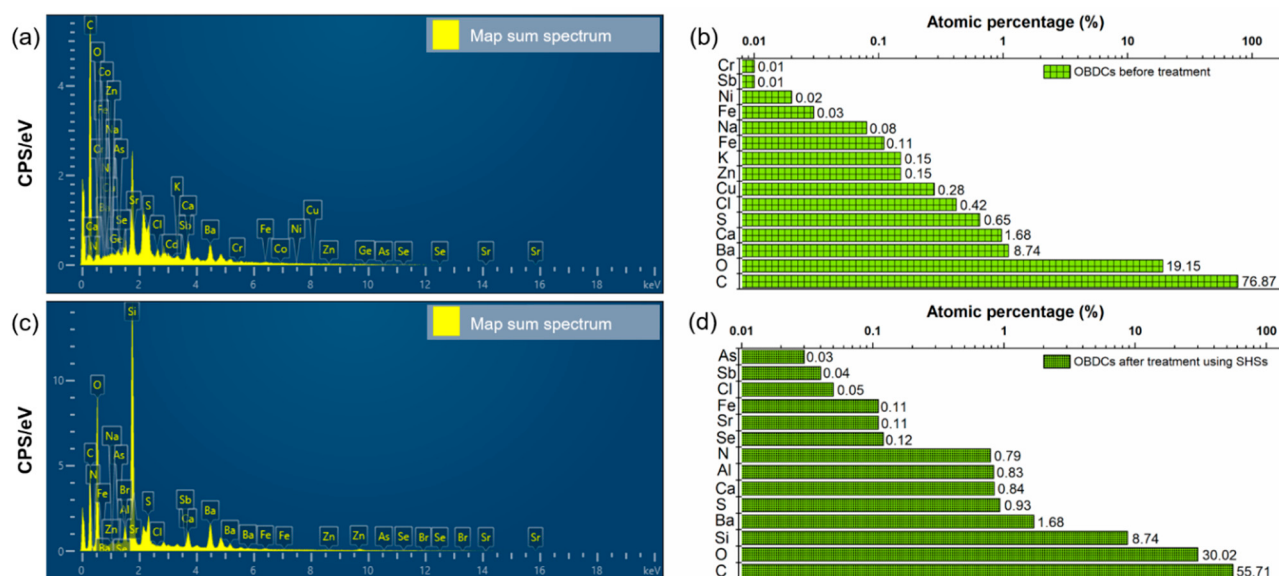


Figure 11. EDS elemental map sum spectra and atomic percentages of shale gas OBDCs before (a,b) and after (c,d) treatment by using SHSs.

3.3.5. Produced Wastewater Analysis

DI water was used throughout the treatment process of shale gas OBDCs with CO₂ SHSs. To evaluate water quality, DI water and produced water were measured and analyzed, as listed in Table 1. The conductivity of DI water (0.75 µS/cm) was lower than that of produced water (341.00 µS/cm), which indicates the influence of ionic substances during the extracting petroleum hydrocarbon process (See Figure 1). There was no petroleum in DI water, but unfortunately a little petroleum (0.27 mg/L) was detected in the produced water, resulting from the first liquid–liquid separation operation. The pH value DI water and produced water was 6.8 and 8.9, respectively. The pH of produced water was high due to the existence of residual DMCHA after the second liquid–liquid separation operation, making the produced water alkalic. Furthermore, COD, BOD₅, ammonia-N, TN, and TOC of DI water and produced water were studied in detail. For DI water, COD, BOD₅, and ammonia-N were not detected, and TN and TOC were 0.19 and 1.00 mg/L, respectively. Meanwhile, ammonia-N for produced water was still not detected, but COD, BOD₅, ammonia-N, TN, and TOC of produced water increased to 561.00, 238.00, 40.60, and 309.00 mg/L, respectively. This is because of the migration of organic matters from OBDCs and the residual DMCHA into the produced water.

Table 1. Water quality of DI water and produced water.

Samples	pH	Conductivity (µS/cm)	COD (mg/L)	BOD ₅ (mg/L)	Ammonia-N (mg/L)	Total Nitrogen (mg/L)	TOC (mg/L)	Petroleum (mg/L)
DI water	6.8	0.75	ND	ND	ND	0.19	1.00	ND
Produced water	8.9	341.00	561.00	238.00	ND	40.60	309.00	0.27

TDS of DI water and produced water is shown in Table 2. For DI water, TDS below the lower detection limit was not detected, but TDS of the produced water was 264 mg/L. This suggests that produced water includes many ionic substances. To discover information of ionic substances, metal elements and anions of DI water and produced water were investigated. Table 2 shows that DI water contained anions such as Cl[−] (5.36 mg/L), NO₃[−] (0.096 mg/L), and SO₄^{2−} (0.984 mg/L), but many metal elements were not detected because their concentrations might be below lower detection limit. By contrast, produced water not only included anions such as Cl[−], NO₃[−], and SO₄^{2−}, but also contained metal elements

such as K, Na, Ca, Ba, Cu, Fe, and Sr. The concentrations of Cl^- , NO_3^- , and SO_4^{2-} were 145, 0.802, and 9.830 mg/L, respectively. The dramatic increasing of Cl^- indicates that the main soluble salts of OBDCs were chlorides. Furthermore, the concentrations of K, Na, Ca, Ba, Cu, Fe, and Sr were 6.44, 12.60, 28.80, 0.28, 0.01, 0.01, and 0.16 mg/L, respectively. Importantly, it was found that heavy metals, i.e., Cu, could migrate into produced water due to the existence of moisture.

Table 2. Metal elements, anions, and TDS of DI water and produced water.

Samples	K (mg/L)	Na (mg/L)	Ca (mg/L)	Ba (mg/L)	Cu (mg/L)	Fe (mg/L)	Sr (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	TDS (mg/L)
DI water	ND	ND	ND	ND	ND	ND	ND	5.36	0.096	0.984	ND
Produced water	6.44	12.60	28.80	0.28	0.01	0.01	0.16	145	0.802	9.830	264

The release of organic pollutants, such as phenols and polycyclic aromatic hydrocarbons, was determined after the treatment of shale gas OBDCs by using CO_2 SHSs, as shown in Table 3. Table 3 shows that phenol, naphthalene, phenanthrene, and anthracene were not found in DI water, but there was phenol (0.0031 mg/L), naphthalene (0.0000129 mg/L), phenanthrene (0.000059 mg/L), and anthracene (0.000058 mg/L) in produced water. Thus, it is concluded that the phenol, naphthalene, phenanthrene, and anthracene could move from OBDCs to produced water after the treatment with CO_2 SHSs.

Table 3. The content of phenols and polycyclic aromatic hydrocarbons in DI water and produced water.

Samples	Phenol (mg/L)	Naphthalene (mg/L)	Phenanthrene (mg/L)	Anthracene (mg/L)
DI water	ND	ND	ND	ND
Produced water	0.0031	0.0000129	0.000059	0.000058

3.4. Priority Pollutant Migration Mechanism from OBDCs to Produced Wastewater

Based on the present results obtained from studies on the migration of priority pollutants and produced wastewater assessment, a possible priority pollutant migration mechanism during the treatment of OBDCs by using CO_2 SHSs is proposed in Figure 12. As shown in Figure 12, shale gas OBDCs, including petroleum hydrocarbon, inorganic matter, moisture, and others (see Figure 2), are hazardous solid wastes. As one of the CO_2 SHSs, DMCHA can efficiently extract petroleum hydrocarbon from shale gas OBDCs, so that the hazardous situation of residual cuttings reduced significantly because their petroleum hydrocarbon content was below 1% (see Figure 3). Meanwhile, the petroleum hydrocarbon was dissolved into DMCHA to form extracts of OBDCs, and salts were leached out of OBDCs as well because the moisture existed (See Table 2). To achieve an excellent separation of the petroleum hydrocarbon with DMCHA, DI water was introduced, and CO_2 was bubbled into the extracts of OBDCs. Because DMCHA was protonated to form hydrophilic DMCHAH^+ (See Figure 4), the petroleum hydrocarbon was recovered successfully after the first liquid–liquid separation operation (See Figure 5a). Unfortunately, there were few phenols and polycyclic aromatic hydrocarbons and little residual petroleum in the lower liquids located below the petroleum hydrocarbon layer. Furthermore, in order to recover DMCHA, N_2 was bubbled into the lower liquids at 70 °C. The hydrophilic DMCHAH^+ was converted to hydrophobic DMCHA. Most of the DMCHA could be recovered after the second liquid–liquid separation operation (See Figure 5b), but little residual DMCHA existed in the lower liquids located below the DMCHA layer (i.e., produced wastewater). As a result, the hazardous situation of the residual cuttings became weak because the petroleum hydrocarbon was removed from OBDCs. However, COD, BOD_5 , TN, TOC, petroleum, and TDS can be detected in the produced wastewater (see Tables 1 and 2),

and the release of phenol, naphthalene, phenanthrene, anthracene, and heavy metals (Cu) from OBDCs to the produced wastewater occurred (see Tables 2 and 3). Worst of all, the wastewater with high COD, BOD₅, TN, and TOC was produced after treatment of OBDCs by using CO₂ SHSs, which could ascribe to the priority pollutants such as the leachables of OBDCs and the residual DMCHA.

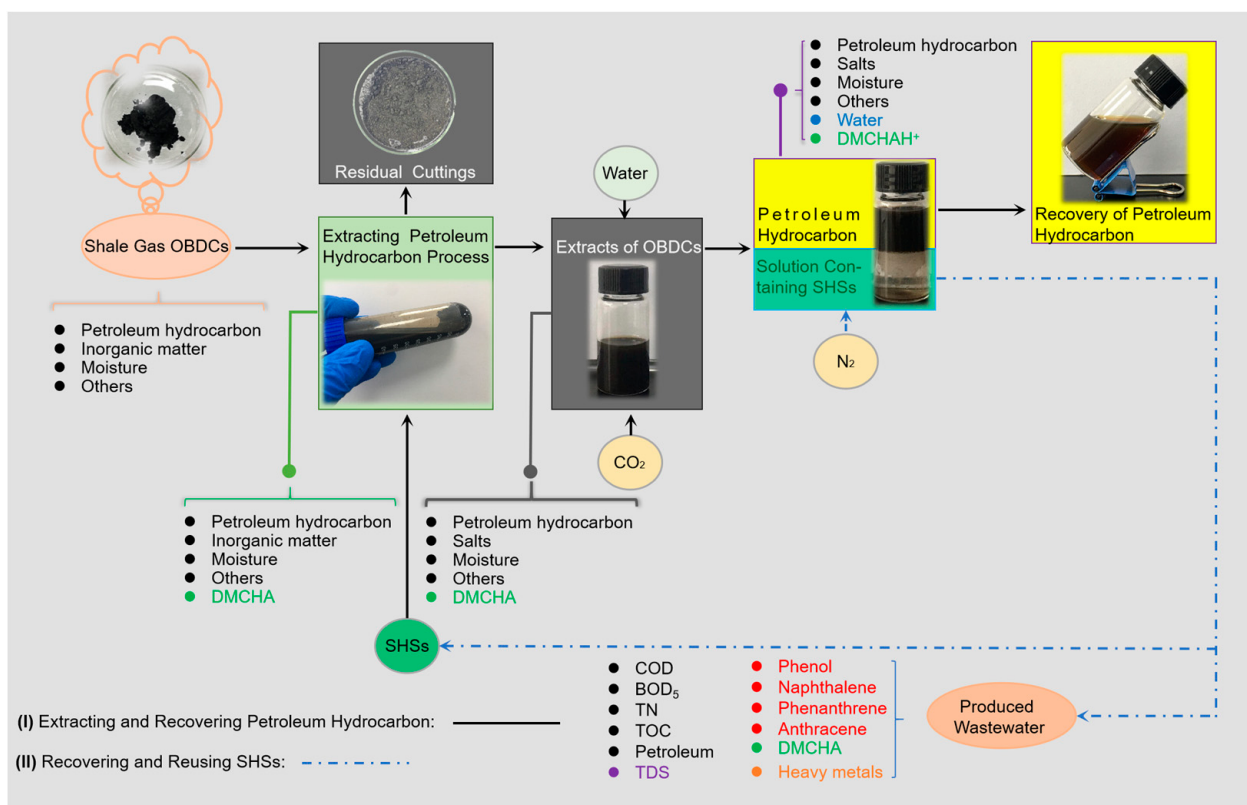


Figure 12. A possible priority pollutant migration mechanism during treatment of ODBC by using CO₂ SHSs.

4. Conclusions

In summary, DMCHA, as one of the CO₂ SHSs, was applied to deal with ODBC_s, and priority pollutant migration and produced wastewater assessment during the extraction process were analyzed in this study. When the DMCHA extraction process was controlled at DMCHA/OBDC_s liquid–solid ratio of 20:1, 35 °C, and 200 rpm for 30 min, the petroleum hydrocarbon content of OBDC_s decreased from 10.73 to 0.84 wt%. The petroleum hydrocarbon and DMCHA were recovered by using the CO₂ switchability of SHS_s. Unfortunately, wastewater was produced after recovering DMCHA. It was found that COD, BOD₅, total nitrogen, TOC, and petroleum were 561.00, 238.00, 40.60, 309.00, and 0.27 mg/L, respectively. Additionally, phenols (0.0031 mg/L), naphthalene (0.0000129 mg/L), phenanthrene (0.000059 mg/L), anthracene (0.000058 mg/L), as well as heavy metal ions such as Cu (0.01 mg/L) were discovered in the produced wastewater. According to the produced wastewater assessment, priority pollutant migration mechanism from ODBC_s to produced wastewater was elaborated. Although the environmental risks of shale gas OBDC_s have been weakened after DMCHA extraction, pollution of the produced wastewater should be taken care of in the future.

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