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RESEARCH PAPER

Scalable Production of Eco-friendly Modified SiO_2 as Demulsifier of Crude Oil

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ABSTRACT

The extracted crude typically contains water-in-oil (w/o) emulsions. In this regrd, a novel demulsifier was synthesized in this research through modifying silica with benzalkonium chloride (SBKC). This demulsifier serves as a low-cost and biodegradable solution for the treatment of w/o emulsions. The amphipathic demulsifier was characterized by various techniques such as scanning electron microscope (SEM) and X-ray diffraction (XRD). In addition, the effects of temperature, standing time, and optimal demulsifier dosage were systematically investigated. Silica was modified with varying contents of BKC. According to the bottle test results, SBKC-20 achieved complete water separation from crude oil in 50 minutes (compared to 75 minutes for pristine silica). The studies showed the considerable effect of temperature on demulsification efficiency, as SBKC-20 separated water in just 1 minute at 95°C. Interfacial tension (IFT), optical microscopy, and contact angle measurements were also employed to better understand the demulsification mechanism. The ability of SBKC-20 particles to penetrate the oil-water interface was confirmed by IFT and optical microscopy. For example, SBKC-20 decreased the IFT between water and crude oil from 18.6 to 6.9 $mN.m^{-1}$.

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INTRODUCTION

Oil and gas industry is one of the most critical global sectors [1]. Crude oil extracted from reservoirs typically contains water-in-oil (w/o) emulsions [2], posing significant challenges for petrochemical industries [3] such as equipment corrosion [4,5], transportation difficulties, and higher costs of oil refinery products [6,7]. The treatment of immiscible water/oil mixtures is both expensive [8] and challenging due to their high stability [5,10]. Crude oil naturally encompasses interface-active species such as asphaltenes, resins, and naphthenic acid [7,8], which stabilize w/o emulsions [12,13] by forming rigid, solid-like interfacial layers [14,15]. Therefore, the separation of water from oil is highly essential [16,17]. Numerous studies have demonstrated the decisive role of asphaltene in the formation of rigid films [9,1,11]. Thus, proper demulsification requires the destruction of the asphaltene interfacial layer [18].

Several physical, chemical, and biological techniques have been developed for crude oil demulsification [4,19] each operating via a distinct mechanism [20]. Chemical treatment is generally more effective [4] while offering lower costs [6,21]. Numerous studies have reported that surfactant-modified particles can dehydrate crude oil [1,6]. SiO_2 can enhance oil recovery by decreasing the interfacial tension and oil viscosity, while altering the wettability [22].

Huang et al. [3] modified SiO_2 with carbon nanotubes (CNTs) to treat water content of crude oil emulsions, achieving 87.4% efficiency after 30 minutes at the optimal demulsifier concentration. In a previous study by the authors [2], the

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synthesized GO-SiO_2 nanoparticles managed to completely separate water from crude oil. Yuan et al. [4] synthesized silicon dioxide/carbon sphere composite demulsifiers (SiO_2@CS) using a hydrothermal-calcination route and reported a demulsification performance of 89.5% under optimal conditions, with the ability to operate at different pH levels. Dhandhi et al. [6] revealed that partially hydrophobic silica nanoparticles could demulsify surfactant stabilized water in cyclohexane emulsions. Ye et al. [23] prepared oxidized carbon black Ox-CB@SiO_2 to break w/o emulsions and achieved the water removal efficiency of 93.5% after 3 hours at 75°C. Ge et al. [24] utilized mesoporous SiO_2/TiO_2 composite to demulsify surfactant stabilized water toluene emulsions and adsorb pollutants. Feng et al. [25] coated Fe_3O_4 nanoparticles with polydopamine and polyether to prepare an eco-friendly water-in-oil demulsifier. Their results showed a demulsification efficiency of 98% in addition to magnetic recyclability. Guo et al. [26] synthesized Fe_3O_4/CNNs as a green and reusable demulsifier using carbon nanosphere and Fe_3O_4. They reported the water separation efficiency of 92% for this demulsifier. Ahangar et al. [27] prepared the photocatalytically active Fe_3O_4@ SiO_2/TiO_2 nanocomposite to remove dyes from textile wastewater. Their UV-Vis results indicated a separation efficiency up to 100% at low dye concentrations.

Many of traditional treatment methods can, however, cause secondary pollution. Moreover, they fail to offer sufficient efficiency for industrial scaled up [28].

This research simultaneously addresses two important features: environmental compatibility and cost-effectiveness. Therefore, environmentally friendly industrial materials were employed. The manufacturing method of this demulsifier can also be industrialized. In this study, industrial silica powder was modified with various contents of benzalkonium chloride (as a commercial surfactant) to produce biodegradable and cost-effective demulsifiers. The particles were characterized by X-ray fluorescence (XRF), photoinduced light scattering (PLS), Brunauer–Emmett–Teller (BET), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), and X-ray diffraction (XRD) techniques. Bottle test was considered to evaluate the treatment performance of the demulsifiers and determine their optimal concentration. Standing time and temperature effects were also measured. Additionally, the potential demulsification mechanism was explored using contact angle (CA) measurements, interfacial tension (IFT) analysis, and optical microscopy.

EXPERIMENTAL

Materials

The crude oil samples were extracted from the oil fields of Iran. Table 1 lists the chemicals utilized in the experiments.

Preparation of water in crude oil emulsion

The water-in-crude oil emulsion included 30g of distilled water in 70g of crude oil. The mixture was then stirred at 1000 rpm for 30 minutes using a Heidolph MR Hei-Standard stirrer. The resulting emulsion maintained its stability for several weeks.

Extraction of asphaltene

Asphaltene was extracted in accordance with the IP-143 standard [29]. The extraction process involved dissolving asphaltene in n-heptane at a ratio of 1:40 (g/L), followed by centrifugation. The resulting black solid was then dried in an oven at 70°C for 24 hours to obtain pure, dry asphaltene.

Synthesis of SiO_2@BKC

In separate experiments, different contents of BKC (1, 2, 3, 4, and 5g) (Table 2) were added to mixtures containing 10g of SiO_2 and 100g of distilled water. The mixtures were then stirred for 105 minutes at 80°C while its pH was maintained at 8. Following 5 minutes of centrifugation, the solutions were dried in an oven for 24 hours.

Demulsification test

The demulsification efficiency of SiO_2@BKC was evaluated through a series of bottle tests. Different demulsifier concentrations (ranging from 8 to 1600 ppm) were added to the w/o emulsions

Table 1. List of chemicals used in the experiments

Components	Purity (%)	Company
Silica	98	Pars Silis
Benzalkonium Chloride solution	50	Padideh Jam
Sodium Hydroxide	99	Sigma-Aldrich

Table 2. Ratio of BKC to Silica in various demulsifiers

Demulsifier's name	BKC to Silica ratio
SBKC-5	5%
SBKC-10	10%
SBKC-15	15%
SBKC-20	20%
SBKC-25	25%

Table 3. Physiochemical properties of the crude oil at 25°C

Petroleum Characterization	Value
Density (kg/m^3)	870
API	31.1
IFT with water (mN/m)	18.59
Asphaltene (%)	10

Table 4. The XRF analysis result of Silica

Chemical name	SiO_2	L.O.I	CaO	Other compounds
(%)	98.636	0.63	0.154	0.580

and shaken for 100 times. The treatment was then examined to determine its efficiency.

Characterization

The purity of the industrial silica powder was measured using X-ray fluorescence (XRF) with a Philips XRF Analyzer PW2404. Photoinduced light scattering (PLS) technique was conducted (Dandong Bettersizer instrument) to study the size distribution of the demulsifier. The Brunauer-Emmett-Teller (BET) method was utilized to evaluate the surface area of the demulsifiers. FT-IR spectroscopy was applied to analyze the chemical structures in KBr pellets using a Nicolt 100 instrument. Scanning electron microscopy (SEM) was employed using TESCAN (MIRA 3) to study the morphology of SiO_2. The characteristics of the particles were further explored by X-ray diffraction (XRD) (Philips X'Pert MPD operating with Cu kά radiation (λ = 0.154 nm)).

Interfacial tension measurements

The interfacial tension (IFT) between the crude oil and water samples following the addition of demulsifiers was measured through the ring tensiometer method using a KRUSS K12 instrument. The results were then compared to the IFT between the crude oil and distilled water.

RESULTS AND DISCUSSION

Characterization

Table 3 presents the physicochemical features of the crude oil, measured at 25°C.

The purity of the industrial silica was determined using XRF analysis. The results indicated a purity greater than 98% (Table 4). According to the PLS findings, the size of over 90% of the industrial silica particles ranged from 1-100 µm, as depicted in Figure S1 of the Supporting Information.

XRD spectra of SiO_2 can be found in Fig. 1a in which most of the peaks are related to SiO_2 (Quartz) [30]. Few other peaks can be assigned to the impurities as the applied industrial silica includes $CaCO_3$. These results are consistent with XRF findings.

Fig. 1b displays the FT-IR results of SiO_2 and SBKC-20. The peaks at 461 and 796 cm^{-1} can be attributed to Si-O, while the peak at 1080 cm^{-1} can be assigned to the Si-O-Si group [31,32]. Additionally, the peak emerging at ~3422 cm^{-1} indicates the presence of hydroxyl groups [2,27]. Furthermore, the FT-IR spectrum of SBKC-20 shows some peaks at 2854 and 2923 cm^{-1}, suggesting the carbon-hydrogen stretching vibrations of the surfactant tail [33]. The FT-IR spectra of other demulsifiers can be found in Fig. S2 of the Supporting Information.

Fig. 1c displays the BET-BJH results. Based on the International Union of Pure and Applied

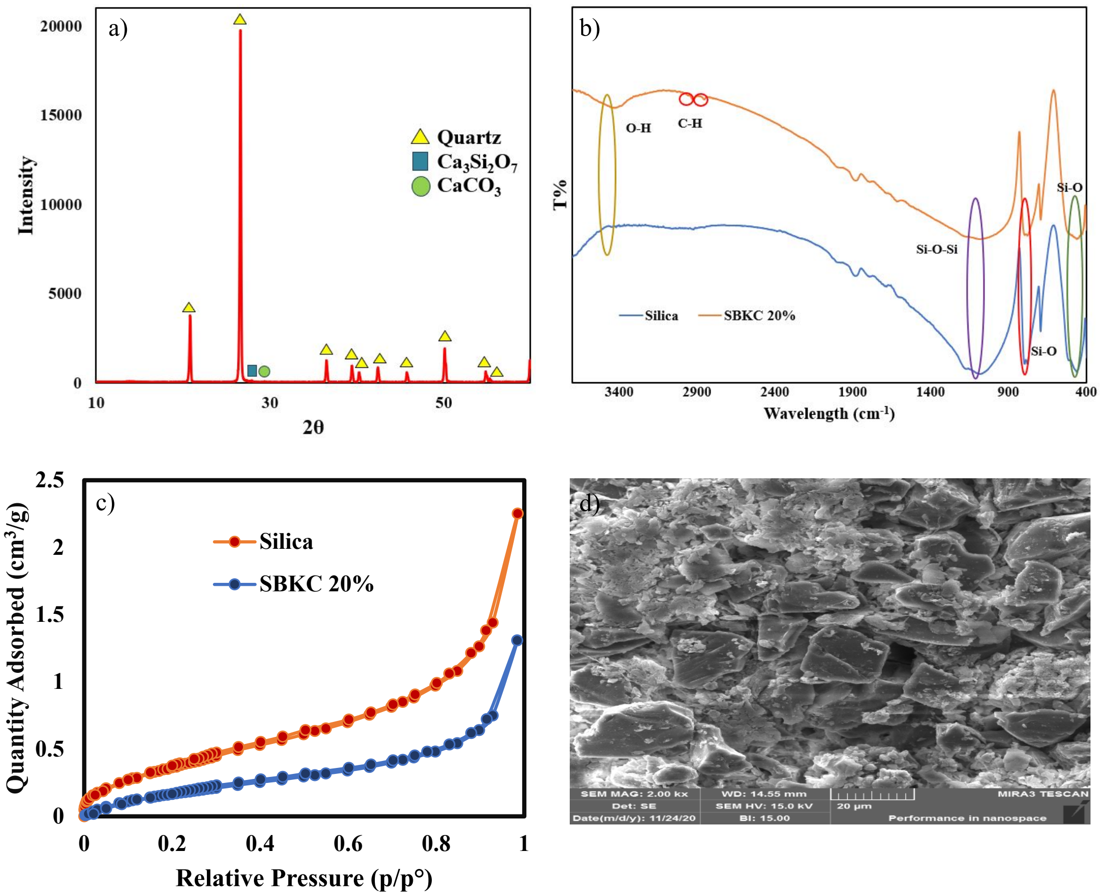

Fig. 1. a) XRD spectra of SiO_2 b) FT-IR spectra of silica and SBKC-20 c) Nitrogen adsorption-desorption isotherms for silica and SBKC-20 d) SEM image of SiO_2

Table 5. Surface area of the demulsifiers

Demulsifier	BET Specific Surface Area ($m^2.g^{-1}$)	t-Plot External Surface Area ($m^2.g^{-1}$)
Silica	1.48	1.65
SBKC-20	0.21	0.87

Chemistry (IUPAC) adsorption isotherm classification, the diagram exhibits a type IV isotherm, reflecting the mesoporous structure of the demulsifiers [34]. Mesoporous silica has large surface area [35]. Moreover, both SiO_2 and SBKC-20 exhibit an H3-type hysteresis loop according to the IUPAC classification [36], suggesting the presence of non-rigid aggregates composed of plate-like particles [37].

The specific surface area and external surface area of silica and SBKC-20 were characterized by the BET method, as presented in Table 5. The micropore and mesopore external surface areas and pore volumes are often defined based on the t-plot external surface area [38]. As indicated in Table 5, the introduction of benzalkonium chloride (BKC) to the industrial silica caused a reduction in the specific surface area of the demulsifier. Industrial silica has a specific surface area of 1.48 $m^2.g^{-1}$, which is in agreement with other reports [39]. After modification, SBKC-20 specific surface area was reduced to 0.21 $m^2.g^{-1}$. External surface area of silica also decreased from 1.65 to 0.87 $m^2.g^{-1}$ in SBKC-20. This reduction in specific surface area upon surfactant addition is consistent with previous reports [40].

Fig. 1d demonstrates the morphology of SiO_2. As the SiO_2 used in this study is industrial, its size

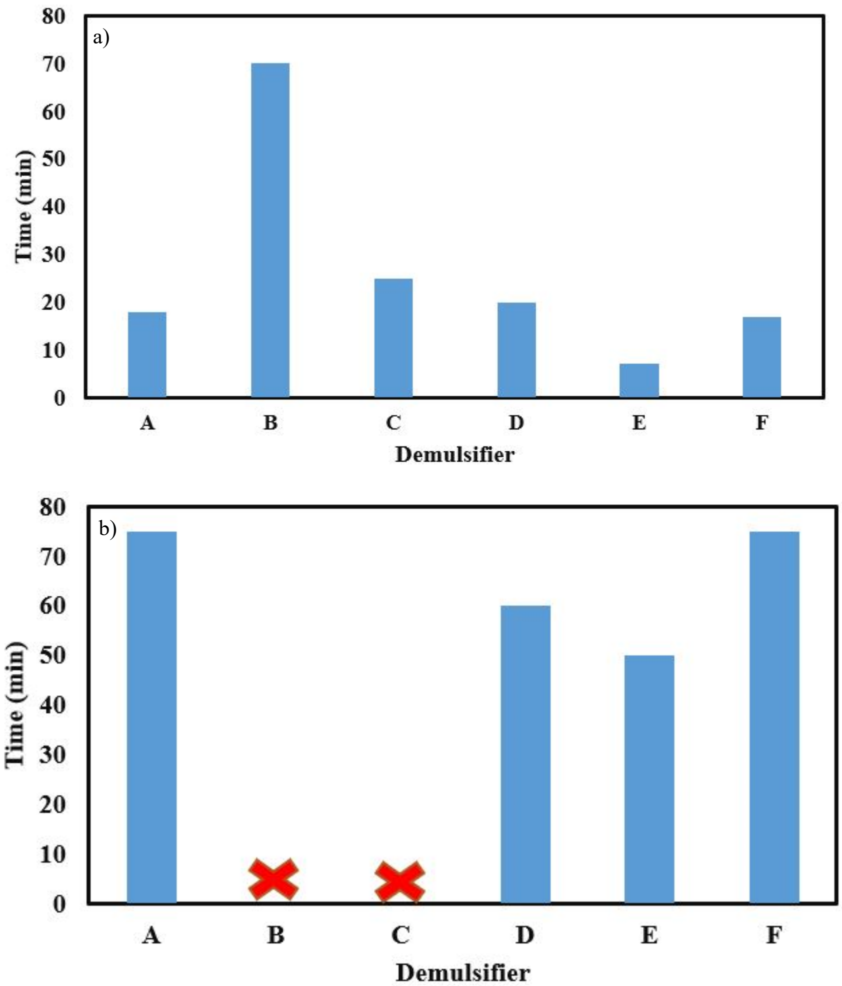

Fig. 2. Duration of a) 50% and b) 100% water separation by each demulsifer at optimum concentration (A, B, C, D, E, and F attribute to silica, SBKC-5, -10, -15, -20, and -25, respectively)

and shape are different. According to SEM images, the size of the particles varies from few microns to several tens of microns (below 100 microns), which is in agreement with the PLS results.

Demulsification test and possible demulsification mechanism

Demulsifier efficiency was examined using a standard bottle test. The performance of each demulsifier was evaluated over a concentration range of 8 to 1600 ppm. Figure S3 compares the performance of each demulsifier at different concentrations after 50 minutes. The water separation percentage was compared to determine the best concentration of each demulsifier. Fig. 2a illustrates the duration required for each demulsifier at optimum concentration to separate 50% of water from oil. Evidently, SBKC-20 has the highest efficiency, requiring only 7 minutes to achieve 50% separation. This is followed by SBKC-25 and silica, which require 17 and 18 minutes, respectively. SBKC-15 and SBKC-10 also need 20 and 25 minutes, respectively. In contrast, SBKC-5 need a significantly longer duration of 70 minutes to separate 50% of water from crude oil. Fig. 2b shows the time required for each demulsifier at best concentration to achieve complete water separation from oil. SBKC-20 is again the fastest demulsifier, requiring 50 minutes to achieve 100% water separation, followed by SBKC-15 which requires 60 minutes. It takes 75 minutes for silica and SBKC-25 to achieve complete water separation. In contrast, SBKC-5 and SBKC-10 do not achieve 100% water separation within an acceptable time frame.

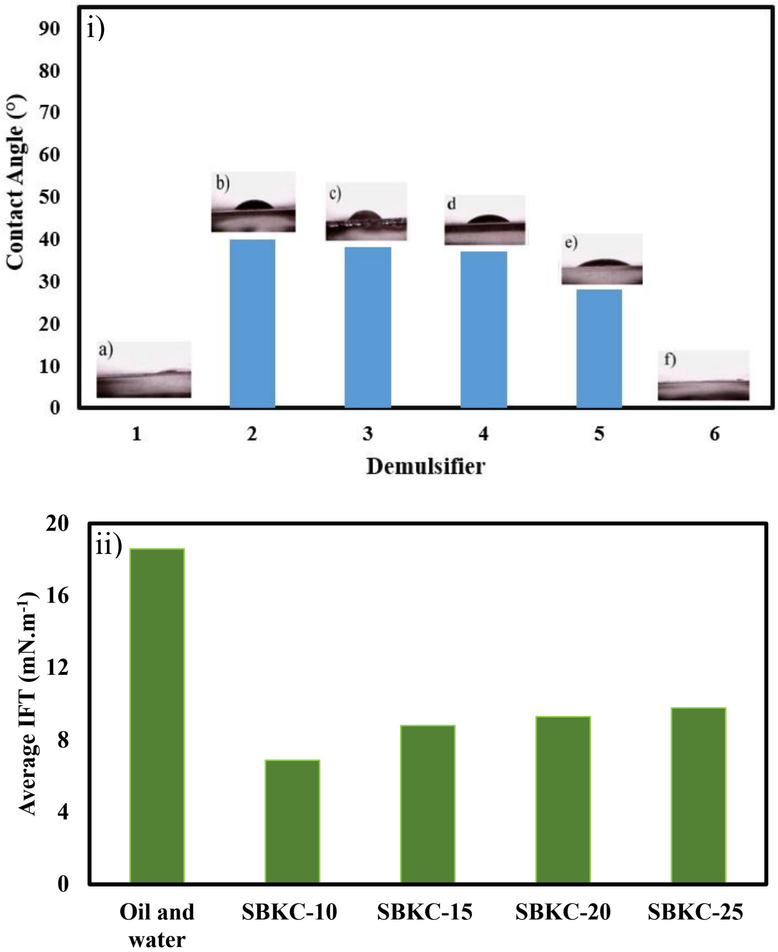

Fig. 3. i) Diagram of the CA formed between a water droplet and the surface of different demulsifiers. The inset photographs show water droplets on the surface of a) bare silica and b) SBKC-5, c) SBKC-10, d) SBKC-15, e) SBKC-20, and f) SBKC-25. ii) Average interfacial tension before and after adding demulsifiers at a concentration of 1600 ppm

The surface wettability of the demulsifiers was evaluated based on the CA of a water droplet on the surface of the demulsifier-coated glass, as depicted in Fig. 3i. Upon placing on the surface of bare silica-coated glass, water droplet was immediately absorbed, resulting in 0° CA. This implies that industrial silica is superhydrophilic due to the presence of the hydrophilic hydroxyl groups on its surface [3]. The CA values of the water droplet on SBKC-5, SBKC-10, SBKC-15, and SBKC-20 were 40°, 38°, 37°, and 28°, respectively. The SBKC-25, however, had the water droplet CA of 0°. This phenomenon can be assigned to the formation of a double layer of surfactant around the silica particles at high surfactant concentrations. In this double-layer configuration, the second layer of surfactant molecules is oriented with their hydrophilic head facing outward, making SBKC-25 superhydrophilic. The CA results also indicate that the introduction of benzalkonium chloride (BKC) alters the wettability of SiO_2 by reducing its hydrophilicity, making it amphipathic. The hydrophilic and hydrophobic ends of the demulsifier molecule interact with the aqueous and oil phases, respectively [4]. The amphipathic nature of the demulsifier molecule enables it to more effectively adsorb at the oil-water interface.

Reducing IFT is one of the most important factors in demulsification of crude oil emulsion, as it can show the ability of a demulsifier to penetrate into the interfacial layer [10]. Asphaltenes and resin of crude oil can affect IFT between the oil and water phases [14]. The IFT between crude oil and distilled water was measured to be 18.59 mN/m. As it can be seen in Fig. 3ii, the addition of demulsifier to the w/o emulsion led to a significant

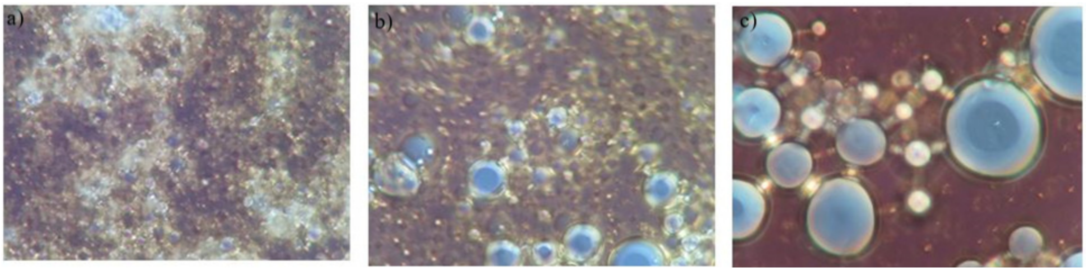

Fig. 4. Optical microscopic images of a water-in-crude oil emulsion: a) in the absence of a demulsifier, b) and c) following the addition of SBKC-20 after 25 and 60 minutes, respectively

decrease in the IFT between the separated water and crude oil phases for all tested demulsifiers. The introduction of silica particles into the emulsion can further reduce the IFT by accumulating at the oil-water interface and forming a layer [41]. All the tested demulsifiers exhibited good interfacial activity which can move to the oil-water interface. At the interface, the demulsifier can displace natural surface-active agents on the surface of water droplets and disrupt the asphaltene film, thereby, destabilizing the emulsion [2]. However, an optimal dosage of demulsifier is required for effective demulsification [42]. Although the IFT results obtained in the presence of demulsifier are somewhat close to each other, SBKC-10 was the most successful sample in decreasing the IFT between the oil and water phases. This result is consistent with the findings of the water contact angle section.

The mechanism of demulsification by silica particles can be described in several ways. Firstly, silica is hydrophilic and, in a w/o emulsion, water droplets are dispersed in a hydrophobic crude oil medium. As a result, silica particles are attracted to the water droplets and promote their coalescence. Secondly, the formation of hydrogen bonds by hydroxyl (OH) groups on the surface of SiO_2 with asphaltenes of the crude oil facilitate the demulsification process [2].

In general, an effective emulsion breaker should have amphiphilic properties to enable its diffusion into the oil-water interface and alter the properties of the interfacial film to promote droplet coalescence [43]. Surfactants can improve demulsification by replacing particles in the interfacial layer or being adsorbed onto the water droplets within the emulsion [44]. To enhance the demulsification ability and amphiphilic properties of silica, cationic benzalkonium chloride (BKC) was added to form SBKC. Upon adding to the emulsion, SBKC effectively moved to the oil-water interface. The reduction in the hydrophilicity of silica due to the addition of BKC also facilitated the movement of the new demulsifier within the crude oil medium. Despite the suboptimal adsorption of silica and SBKC-20, as indicated by the adsorption isotherm results, other factors such as interfacial tension play a more important role in the treatment. The separation performance of SBKC-25 reached 80% after 50 minutes of demulsification, which is lower than SBKC-20. Noteworthy, amphipathic demulsifiers can also stabilize emulsions. Cationic surfactants are effective in the removal of pollutants from wastewater [45]. The authors have recently [46] explored the effect of cationic surfactants such as alkyl trimethyl ammonium bromide (CTAB) on the dehydration of crude oil. The results demonstrated that at high concentrations of cationic surfactant, the counterion can significantly influence the demulsification efficiency. The presence of excess demulsifier can lead to steric repulsion between water droplets and interfere with the treatment of emulsions [16,28].

For further understanding of the demulsification process, microscopic imaging techniques were employed [8]. Fig. 4a illustrates optical microscope images of a stable water-in-crude oil emulsion, in which water droplets are dispersed throughout the crude oil medium. Upon the addition of SBKC-20, aggregates of water droplets began to form after 25 minutes, as shown in Fig. 4b. After 60 minutes, larger water droplets can be observed (Fig. 4c), indicating that the demulsifier disrupted the natural surfactants present at the oil-water interface and promoted demulsification [3]. Table 6 compares the efficiency of different eco-friendly water-in-oil demulsifiers with this work. It is important to note that these results are merely a compilation and therefore, a definite conclusion cannot be drawn as the oil type and emulsification method used in

Table 6. Comparison of different eco-friendly water in oil demulsifiers' efficiency

No.	Demulsifier	E (%)	Time (min)	Temperature (°C)	Reference no.
1	CNTs/SiO_2	87	30	70	[3]
2	GO-SiO_2	100	90	25	[2]
3	SiO_2@CS	8	150	40	[4]
4	partially hydrophobic SiO_2 NPs	100	90	70	[6]
5	Fe_3O_4@PDA@Polyether	98	N/A	N/A	[25]
6	Fe_3O_4/CNNs	92	10	25	[26]
7	SBKC-20	100	50	25	This work

CNT: Carbon Nanotubes, GO: Graphen Oxide, CS: Carbon Sphere, NPs: Nanoparticles, PDA: Polydopamine, CNNs: Carbon Nanospheres

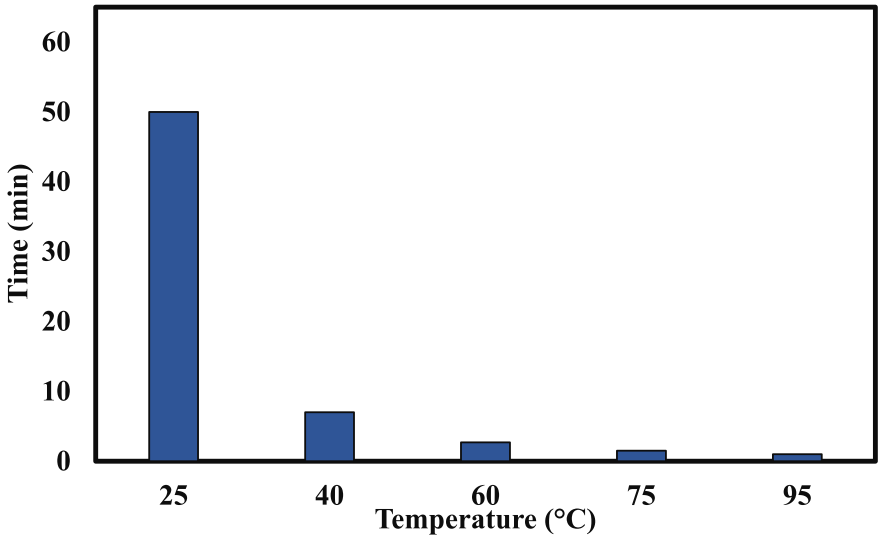

Fig. 5. The temperature effect on the duration required for 100% water separation using SBKC-20.

reports are not similar.

Temperature effect

The effect of temperature was studied by conducting bottle tests at 40, 60, 75, and 95°C using the optimal concentration of the most effective demulsifier (1600 ppm SBKC-20) to observe its impact on achieving 100% water separation (Fig. 5). The results indicate that an increase in temperature significantly reduced the demulsification time. At 95°C, the most rapid w/o treatment was observed, with 100% clean water visible after just one minute. Upon temperature elevation, the crude oil viscosity was lowered, facilitating the movement and coalescence of water droplets as the surrounding stabilizing film was weakened and the demulsifier migrated more rapidly to the water-crude oil interface [14]. Consequently, these factors enhanced the efficiency of the demulsifier in separating water from crude oil. The favorable impact of temperature on demulsification was previously reported in the literature [47].

Adsorption isotherms

The adsorption isotherms of asphaltene were first extracted using the IP-143 standard method [29]. Asphaltene was dissolved in toluene following the extraction. Samples containing 5 to 20 ppm asphaltene were prepared and 500 ppm of either bare silica or SBKC-20 was added to each one. Subsequently, UV tests were conducted. The results indicated that asphaltene adsorption did not exhibit significant adsorption on silica, possibly due to the large particle size and low specific surface area, as confirmed by BET analysis. Therefore, other mechanisms, such as interfacial tension (IFT), had a more pronounced effect on the demulsification mechanism. Other studies [6,38] also reported that the use of nanoparticles as demulsifiers can enhance asphaltene adsorption, in contrast to the silica particles utilized in this research.

CONCLUSION

In this study, industrial SiO_2 was modified by a commercial BKC cationic surfactant to achieve SBKC, a low-cost, non-toxic, and highly efficient demulsifier. SBKC-20 managed fully to separate water from crude oil in 50 minutes, representing a 33% improvement over bare silica. SBKC is highly active at the interface and significantly reduces the IFT between crude oil and water. The adsorption of asphaltene on the particles did not have a significant impact on demulsification because of the large size and low specific surface area of the demulsifiers, as confirmed by BET results. As such, SBKC can be considered a promising demulsifier for the removal of water in crude oil emulsions within the oil industry.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest relevant to the study.

REFERENCES

1. Wai MM, Khe CS, Yau XH, Liu WW, Sokkalingam R, Jumbri K, et al. Optimization and characterization of magnetite–reduced graphene oxide nanocomposites for demulsification of crude oil in water emulsion. 2019;9(41):24003-14.
2. Javadian S, Sadrpoor SM. Demulsification of water in oil emulsion by surface modified SiO2 nanoparticle. Journal of Petroleum Science and Engineering. 2020;184:106547.
3. Huang Z, Li P, Luo X, Jiang X, Liu L, Ye F, et al. Synthesis of a Novel Environmentally Friendly and Interfacially Active CNTs/SiO2 Demulsifier for W/O Crude Oil Emulsion Separation. Energy & Fuels. 2019;33(8):7166-75.
4. Yuan H, Zhang Z, Mi Y, Ye F, Liu W, Kuan J, et al. Demulsification of Water-Containing Crude Oil Driven by Environmentally Friendly SiO2@CS Composite Materials. Energy & Fuels. 2020;34(7):8316-24.
5. Ezzat AO, Al-Lohedan HA, Tawfeek AM, Faqihi NA. One-Step Synthesis of New Amphiphilic Nonionic Surfactants Based on Alkylamine and Poly(ethylene glycol) Dimethacrylate for Demulsification of Arabian Heavy Crude Oil Emulsions. ACS Omega. 2023;8(6):6030-9.
6. Dhandhi Y, Kumar Saw R, Singh R, Naiya TK. Application of a novel surface-active green demulsifier for demulsification of field crude oil emulsion. Separation Science and Technology. 2023;58(9):1654-78.
7. Faizullayev S, Adilbekova A, Kujawski W, Mirzaeian M. Recent demulsification methods of crude oil emulsions – Brief review. Journal of Petroleum Science and Engineering. 2022;215:110643.
8. Javadian S, khalilifard M, Sadrpoor SM. Functionalized graphene oxide with core-shell of Fe3O4@oliec acid nanospheres as a recyclable demulsifier for effective removal of emulsified oil from oily wastewater. Journal of Water Process Engineering. 2019;32:100961.
9. Yue X, Fu D, Zhang T, Yang D, Qiu F. Superhydrophobic Stainless-Steel Mesh with Excellent Electrothermal Properties for Efficient Separation of Highly Viscous Water-in-Crude Oil Emulsions. Industrial & Engineering Chemistry Research. 2020;59(40):17918-26.
10. Al-Janabi OYT, Abdulkareem HA, Waheed IF, Foot PJS. Fe3O4@SiO2 functionalized PEG-PPG-PEG triblock copolymer-grafted graphene oxide as novel magnetic nanodemulsifier for water-in-crude oil emulsion separation. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2023;676:132228.
11. Hemmati-Sarapardeh A, Ameli F, Ahmadi M, Dabir B, Mohammadi AH, Esfahanizadeh L. Effect of asphaltene structure on its aggregation behavior in toluene-normal alkane mixtures. Journal of Molecular Structure. 2020;1220:128605.
12. Khadim MA, Sarbar MA. Role of asphaltene and resin in oil field emulsions. Journal of Petroleum Science and Engineering. 1999;23(3):213-21.
13. Dhandhi Y, Chaudhari RK, Naiya TK. Development in separation of oilfield emulsion toward green technology – A comprehensive review. Separation Science and Technology. 2022;57(10):1642-68.
14. Alves CA, Romero Yanes JF, Feitosa FX, de Sant'Ana HB. Influence of asphaltenes and resins on water/model oil interfacial tension and emulsion behavior: Comparison of extracted fractions from crude oils with different asphaltene stability. Journal of Petroleum Science and Engineering. 2022;208:109268.
15. Yegya Raman AK, Aichele CP. Demulsification of Surfactant-Stabilized Water-in-Oil (Cyclohexane) Emulsions using Silica Nanoparticles. Energy & Fuels. 2018;32(8):8121-30.
16. Shen L, Hu W, Lei Z, Peng J, Zhu E, Zhang X, et al. Nanoscale silica-coated graphene oxide and its demulsifying performance in water-in-oil and oil-in-water emulsions. Environmental Science and Pollution Research. 2021;28(39):55454-64.
17. Pekdemir T, Akay G, Dogru M, Merrells RE, Schleicher B. Demulsification of Highly Stable Water-in-Oil Emulsions. Separation Science and Technology. 2003;38(5):1161-83.
18. Javadian S, Sadrpoor SM, Khosravian M. Taking a look accurately at the alteration of interfacial asphaltene film exposed to the ionic surfactants as demulsifiers. Scientific Reports. 2023;13(1):12837.
19. Zhang L, Bai C, Zhang Z, Wang X, Nguyen TV, Vavra E, et al. Application of magnetic nanoparticles as demulsifiers for surfactant-enhanced oil recovery. Journal of Surfactants and Detergents. 2023;26(3):401-8.
20. Yonguep E, Kapiamba KF, Kabamba KJ, Chowdhury M. Formation, stabilization and chemical demulsification of crude oil-in-water emulsions: A review. Petroleum Research. 2022;7(4):459-72.
21. Xia X, Ma J, Liu F, Cong H, Li X. A Novel Demulsifier with Strong Hydrogen Bonding for Effective Breaking of Water-in-Heavy Oil Emulsions. International Journal of Molecular Sciences [Internet]. 2023; 24(19).
22. Ogolo NA, Olafuyi OA, Onyekonwu MO. Enhanced Oil Recovery Using Nanoparticles. SPE Saudi Arabia Section Technical Symposium and Exhibition2012. p. SPE-160847-MS.
23. Ye F, Jiang X, Mi Y, Kuang J, Huang Z, Yu F, et al. Preparation of oxidized carbon black grafted with nanoscale silica and

its demulsification performance in water-in-oil emulsion. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2019;582:123878.
24. Ge B, Han L, Gao B, Zhang T, Li X, Zhu X, et al. A mesoporous SiO2/TiO2 composite used for various emulsions separation. Separation Science and Technology. 2019;54(6):962-9.
25. Feng X-J, He X, Lai L, Lu Q, Cheng L, Wu J. Polydopamine-anchored polyether on Fe3O4 as magnetic recyclable nanoparticle-demulsifiers. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2021;617:126142.
26. Guo S, Wei L, Zhang L. Preparation and Characterization of Magnetic Carbon Nanospheres for the Demulsification of Water-in-Oil Emulsion. ACS Omega. 2023;8(1):1548-55.
27. Enayati Ahangar L, Movassaghi K, Emadi M, Yaghoobi F. Photocatalytic application of TiO2/SiO2-based magnetic nanocomposite (Fe3O4@SiO2/TiO2) for reusing of textile wastewater. Nanochemistry Research. 2016;1(1):33-9.
28. Li B, Qi B, Guo Z, Wang D, Jiao T. Recent developments in the application of membrane separation technology and its challenges in oil-water separation: A review. Chemosphere. 2023;327:138528.
29. Shayan NN, Mirzayi B. Adsorption and Removal of Asphaltene Using Synthesized Maghemite and Hematite Nanoparticles. Energy & Fuels. 2015;29(3):1397-406.
30. Tavares LRC, Junior JFT, Costa LM, da Silva Bezerra AC, Cetlin PR, Aguilar MTP. Influence of quartz powder and silica fume on the performance of Portland cement. Scientific Reports. 2020;10(1):21461.
31. Bodaghifard MA, Faraki Z, Asadbegi S. Effective fabrication of poly(anilin-formaldehyde)-supported hybrid nanomaterial and catalytic synthesis of dihydropyridines. Nanochemistry Research. 2019;4(2):101-11.
32. Khodadadi B. TiO2/SiO2 prepared via facile sol-gel method as an ideal support for green synthesis of Ag nanoparticles using Oenothera biennis extract and their excellent catalytic performance in the reduction of 4-nitrophenol. Nanochemistry Research. 2017;2(1):140-50.
33. Farías T, de Ménorval LC, Zajac J, Rivera A. Benzalkonium chloride and sulfamethoxazole adsorption onto natural clinoptilolite: Effect of time, ionic strength, pH and temperature. Journal of Colloid and Interface Science. 2011;363(2):465-75.
34. Rahman MM, Muttakin M, Pal A, Shafiullah AZ, Saha BB. A Statistical Approach to Determine Optimal Models for IUPAC-Classified Adsorption Isotherms. Energies [Internet]. 2019; 12(23).
35. Lashgari N, Badiei A, Mohammadi Ziarani G. Modification of mesoporous silica SBA-15 with different organic molecules to gain chemical sensors: a review. Nanochemistry Research. 2016;1(1):127-41.
36. Donohue MD, Aranovich GL. Adsorption Hysteresis in Porous Solids. Journal of Colloid and Interface Science. 1998;205(1):121-30.
37. Thommes M, Kaneko K, Neimark AV, Olivier JP, Rodriguez-Reinoso F, Rouquerol J, et al. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). 2015;87(9-10):1051-69.
38. Desmurs L, Galarneau A, Cammarano C, Hulea V, Vaulot C, Nouali H, et al. Determination of Microporous and Mesoporous Surface Areas and Volumes of Mesoporous Zeolites by Corrected t-Plot Analysis. ChemNanoMat. 2022;8(4):e202200051.
39. Sdiri A, Higashi T, Bouaziz S, Benzina M. Synthesis and characterization of silica gel from siliceous sands of southern Tunisia. Arabian Journal of Chemistry. 2014;7(4):486-93.
40. Spataru CI, Ianchis R, Petcu C, Nistor CL, Purcar V, Trica B, et al. Synthesis of Non-Toxic Silica Particles Stabilized by Molecular Complex Oleic-Acid/Sodium Oleate. International Journal of Molecular Sciences [Internet]. 2016; 17(11).
41. Rayeni NS, Imanivarnosfaderani M, Rezaei A, Rezaei Gomari S. An experimental study of the combination of smart water and silica nanoparticles to improve the recovery of asphaltenic oil from carbonate reservoirs. Journal of Petroleum Science and Engineering. 2022;208:109445.
42. Kang W, Jing G, Zhang H, Li M, Wu Z. Influence of demulsifier on interfacial film between oil and water. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2006;272(1):27-31.
43. Wang D, Yang D, Huang C, Huang Y, Yang D, Zhang H, et al. Stabilization mechanism and chemical demulsification of water-in-oil and oil-in-water emulsions in petroleum industry: A review. Fuel. 2021;286:119390.
44. El-Aooiti M, de Vries A, Rousseau D. Demulsification of water-in-oil emulsions stabilized with glycerol monostearate crystals. Journal of Colloid and Interface Science. 2023;636:637-45.
45. Rajabi AA, Yamini Y, Faraji M, Nourmohammadian F. Modified magnetite nanoparticles with cetyltrimethylammonium bromide as superior adsorbent for rapid removal of the disperse dyes from wastewater of textile companies. Nanochemistry Research. 2016;1(1):49-56.
46. Javadian S, Bahri M, Sadrpoor SM, Rezaei Z, Kakemam J. Structure effect in the demulsification performance of cationic surfactants. Journal of Petroleum Science and Engineering. 2022;218:110895.
47. Fang S, Chen B, Chen T, Duan M, Xiong Y, Shi P. An innovative method to introduce magnetism into demulsifier. Chemical Engineering Journal. 2017;314:631-9.