



Adsorption of organic acids in oil on crushed marble at varying temperatures and ambient pressure

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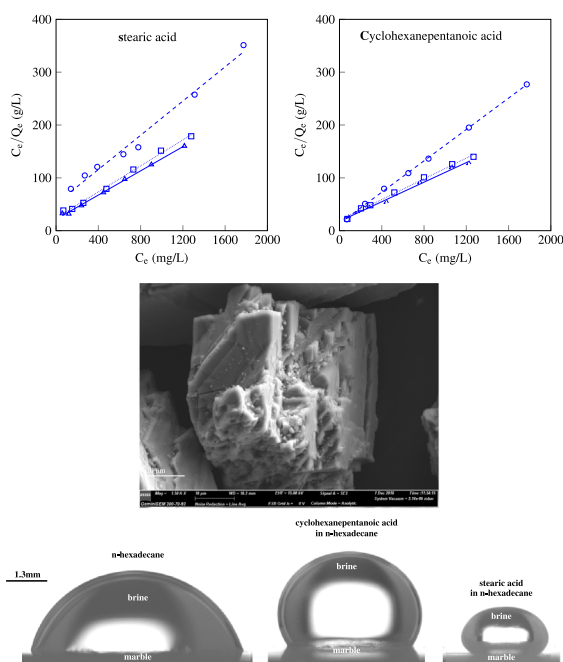
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HIGHLIGHTS

- Adsorption of stearic acid and cyclohexanepentanoic acid on carbonate rock is spontaneous.
- Adsorption of stearic acid and cyclohexanepentanoic acid alter wettability of carbonate rock.
- Maximum adsorption capacity of stearic acid and cyclohexanepentanoic acid on carbonate rock increases with temperature.
- Adsorption of stearic acid and cyclohexanepentanoic acid on carbonate rock involve both Physical and chemical mechanisms.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption of organic constituents of reservoir fluids onto the surface of grains constituting carbonate reservoirs is believed to determine reservoir wettability and, at the pore scale, the flow of fluids in them. In this study, the effect of grain surface modification, duration of exposure, and temperature on stearic acid and cyclohexanepentanoic acid adsorption and their adsorption strengths on crushed marble, our model for carbonate reservoir rock, is investigated. The amount of stearic acid or cyclohexanepentanoic acid adsorbed onto the marble grains was determined using Gas Chromatography-Flame Ionization Detector (GC-FID). To characterize marble grains, Particle Size Analysis (PSA), Nitrogen Adsorption-desorption analysis (NAD),

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Wettability alteration

Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) were performed. Adsorption of stearic acid and cyclohexanepentanoic acid reached equilibrium after 336 h and altered the contact angle of the marble from water-wet to oil-wet. The amount of adsorption for both acids on marble increased with temperature. Adsorption results indicated that adsorption mechanisms are a combination of physical and chemical adsorption for both acids on marble grains. The adsorption strength experiments also showed that stearic acid adsorption on the marble is stronger than cyclohexanepentanoic acid adsorption. The results suggest that understanding the impact of temperature on adsorption and adsorption strength of polar components in the oil phase on rock surface is essential in carbonate reservoirs to reduce remaining oil saturation.

1. Introduction

Displacement of one fluid by another within a porous medium is relevant to many processes such as oil and gas recovery from hydrocarbon reservoirs. Immiscible displacement encountered in the oil and gas recovery is influenced, at the pore scale, by the properties of the grains (size distribution, roughness, mineralogy) and how they are arranged (pore topology and geometry) [1–5], the fractional volumes of the fluids initially occupying the pores [6–8], the velocity of the fluids [9,10], and the properties of the fluids (chemical and physical constituents, which in turn alter fluid–fluid–grain contact angle, fluid–fluid interfacial tension, viscosity, and density) [6,11,12]. Constituents in the oil phase can affect pore scale displacement via several pathways, one of which is sorption and subsequent alteration of the wettability of grain surfaces towards hydrophobic conditions.

The wettability of a carbonate reservoir depends on how and to what extent organic components are adsorbed to the solid phase [13–20]. Engineered wettability alteration from oil-wet condition to more water-wet is one of the main mechanisms to increase oil extraction from these reservoirs [14,21–33]. For carbonate reservoirs, naphthenic and carboxylic acids are recognized as the most common acidic components adsorbed on the rock surface that alter the wettability [34–37]. A shift in wettability of mineral surfaces due to adsorption of specific components present in oil phase, including carboxylic acid groups on calcite surfaces, has been reported in the literature [38–48].

Temperature controls both fluid–fluid and fluid–rock interactions [49–51]. A number of studies have explored the impact of adsorption of stearic acid and cyclohexanepentanoic acid on the calcite surface at varying temperatures by measuring contact angle and interfacial tension [15,41–44].

Rezaei Gomari et al. [41], Rezaei Gomari and Hamouda [44], Jarrahian et al. [45], Norrman et al. [46], Haagh et al. [47] and Al-Shirawi et al. [48] studied the effect of carboxylic acids (stearic acid and cyclohexanepentanoic acid) structure and chemical composition, water composition, temperature and pH on calcite, mica, dolomite and limestone surface wettability using advancing and receding contact angles, interfacial tension measurements, zeta potential measurements, Thermogravimetric Analysis, vapor adsorption isotherm, Fourier Transform Infrared, Atomic Force Microscopy, X-ray Photoelectron Spectroscopy, Time-Of-Flight Secondary Ion Mass Spectrometry and Gas Chromatography Mass Spectrometry. They concluded that stearic acids changed calcite surface wettability from water-wet to strongly oil-wet at pH less than 7 and were more strongly adsorbed on the calcite compared to the mica, the limestone and the dolomite.

The aim of this paper is to improve our understanding of adsorption of stearic acid and cyclohexanepentanoic acid on marble (carbonate rock) as well as their adsorption strength through a series of adsorption experiments at various times. Stearic acid and cyclohexanepentanoic acid have been investigated in the literature to determine the impact of organic compounds available in the reservoir oil on carbonate rock [42–48]. Although there is a large body of research available about organic compounds available in the reservoir oil, stearic acid and cyclohexanepentanoic acid adsorption has not been comprehensively investigated.

This paper presents impact of time and temperature on adsorption of stearic acid or cyclohexanepentanoic acid on marble at ambient

pressure. The amount of adsorbed acids on the marble grains was measured using GC-FID. Contact angles were measured to demonstrate the impact of adsorption of stearic acid or cyclohexanepentanoic acid on the wettability of the marble. The adsorption kinetics, isotherm adsorption parameters using common models in literature and thermodynamic parameters were calculated. PSA, SEM, and BET were also performed to characterize substrate (marble).

2. Materials and methods

In this study marble was used to represent carbonate rock as it is a common form of CaCO_3 under ambient conditions. Carbonate pore spaces are mainly rounded and marble was used to obtain rounded calcite when is crushed [52,53]. Crushing most limestones would produce semi-rounded and partially rhombic calcite of a mixture of grain sizes. Marble often has rounded more-equally dimensioned grains of calcite (sometimes called sucrosic or homoblastic).

Solutions of stearic acid or cyclohexanepentanoic acid in n-hexadecane was prepared to model oil phase. N-hexadecane was used to simplify the complexity of crude oil composition and minimize oil evaporation due to running the experiments at elevated temperature for a long period of time, whereas n-decane and toluene were used as model oil/solvent in previous researches [15,37,42,44]. A simple synthetic brine was also used for contact angle measurements.

2.1. Materials

2.1.1. Model carbonate rock

Following Bowden et al. [3], Tanino et al. [9] and Zacarias-Hernandez et al. [54], marble from Carrara, Italy was used as an analogue for carbonate rock. A block of marble was first ground by use of Tema mill (Fritsch) and then sieved to collect the fraction which was finer than $45 \mu\text{m}$. Grains were cleaned with methanol, dichloromethane and methanol, sequentially [3]. The grains were then air dried in a fume hood for 24 h before being heated at 373 K for 48 h to evaporate any residual methanol.

The marble grains were subsequently submerged in low concentration (approximately 2 vol.%) hydrochloric acid solution at 298 K for approximately 5 min to remove fine fractions [3] and then rinsed with distilled water. On completion of treatment, the grains were submerged in methanol, dichloromethane and methanol for 24 h, sequentially. Finally, the grains were then allowed to dry in a fume hood for 24 h prior to heating to 333 K for 48 h to evaporate any residual methanol.

The SEM images at different magnifications, particle size distribution of marble are shown in Figs. A.1(b,d,f) and A.2b, respectively. BET surface area calculated from NAD measurement was $0.13 \pm 0.01 \text{ m}^2/\text{g}$ (Table A.1). XRD result for treated marble is also shown in Fig. A.3b. The main mineral constituents on treated marble is calcium carbonate. The result confirms that the sample is predominately calcium carbonate with approximately 0.5% of dolomite and 1%–2% of potassium aluminosilicate.

Marble from Carrara, Italy was also used for contact angle measurements. Marble was cut into pieces approximately $10 \times 10 \times 5 \text{ mm}$ in size with a diamond saw (Malvern Lapidary, 245 mm diameter) and a horizontal grinder (Jones & Shipman 1400). The two $10 \times 10 \text{ mm}$ surfaces were polished using a lap wheel with a solution of MicroPolish II Alumina $0.3 \mu\text{m}$ (Kent 3 Automatic Lapping and Polishing Unit, Engis Ltd).

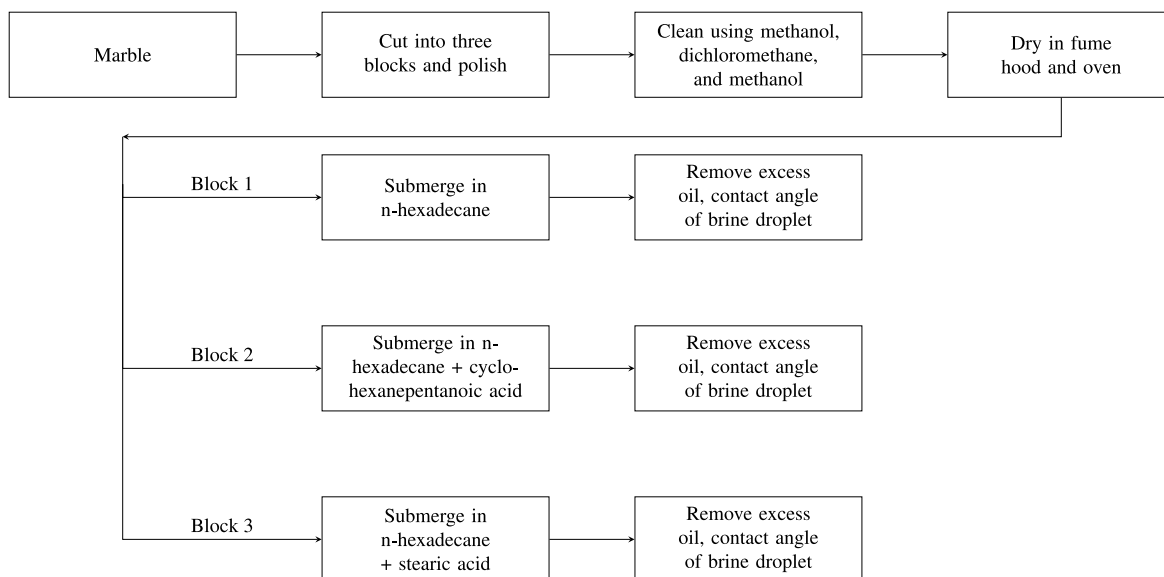


Fig. 1. Marble block preparation for contact angle measurements.

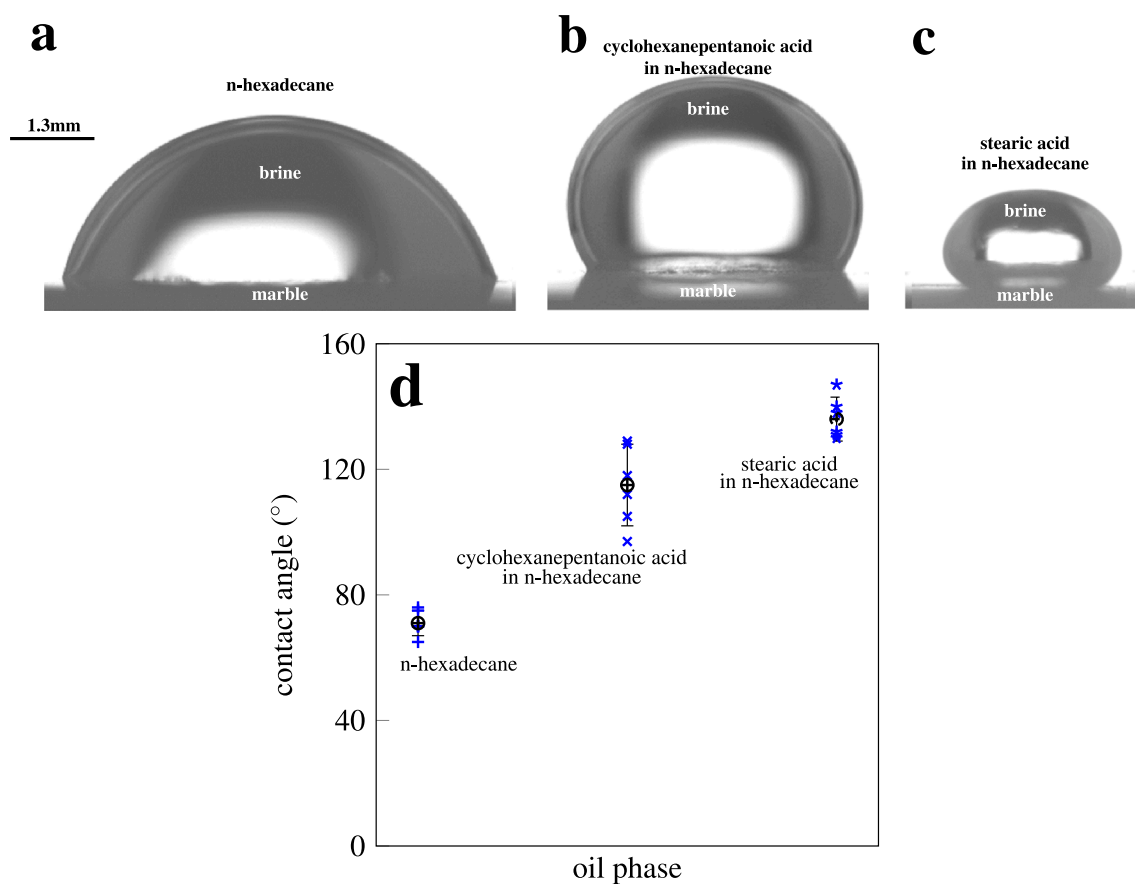


Fig. 2. Contact angle of a brine droplet on marble surface aged in (a) n-hexadecane, (b) 2000 mg/L cyclohexanepentanoic acid in n-hexadecane, (c) 2000 mg/L stearic acid in n-hexadecane for 72 h at 298 K and (d) contact angle measurements for each solution; vertical bars depict standard deviation. Note that the brine droplet volumes differ between in (a), (b) and (c). N-hexadecane, cyclohexanepentanoic acid in n-hexadecane and stearic acid in n-hexadecane are depicted by +, × and * respectively. Measurement means are also shown in ⊕.

2.1.2. Test fluids

Test oils comprised various concentrations (200 to 2200 mg/L) of stearic acid (Sigma-Aldrich, ≥98.5%) or cyclohexanepentanoic acid

(Sigma-Aldrich, 98%) dissolved in n-hexadecane (Fisher Scientific, 99%). The molecular structure of stearic acid and cyclohexanepentanoic acid are shown in Table 1. The brine in the contact angle

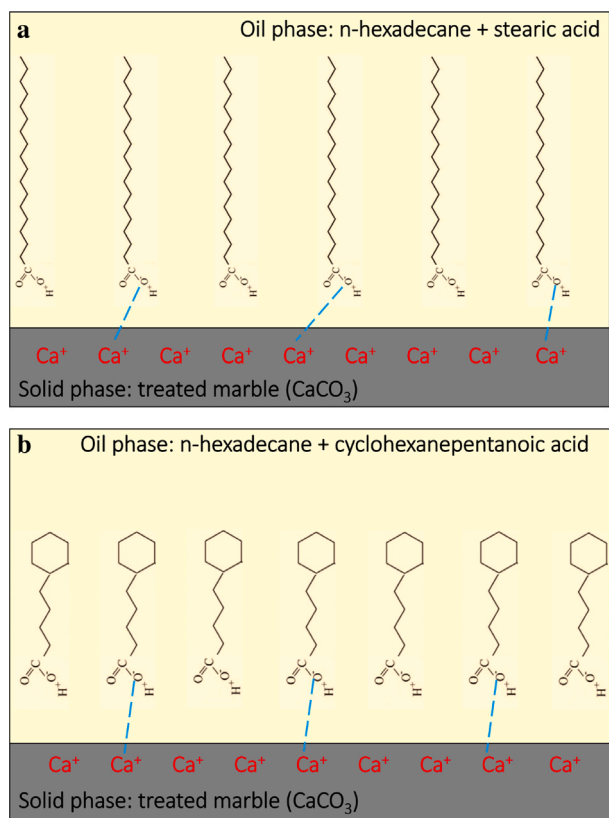


Fig. 3. Adsorption mechanisms of (a) stearic acid and (b) cyclohexanepentanoic acid on marble. Surface area is $0.13 \text{ m}^2/\text{g}$ for marble. The blue dashed line depicts the bonding between marble with positive charge and oxygen with negative charge in stearic acid or cyclohexanepentanoic acid.

Table 1
Structural formula and molar masses of the organic acids considered.

Organic component	Molecular structure	Molar mass (g/mol)
Stearic acid		284.48
Cyclohexanepentanoic acid		184.27

measurements were 5 wt.% NaCl and 1 wt.% KCl [2] in deionized water. The density and viscosity of test fluids used in this paper are listed in Tables B.1 to B.3.

2.2. Methods

2.2.1. Contact angle measurements

Three polished marble blocks were cleaned with methanol (Fisher Scientific, $\geq 99.8\%$), dichloromethane (Fisher Scientific, $\geq 99.8\%$) and methanol sequentially to remove any hydrocarbons, salt and water. After drying in an oven at 333 K, one of the blocks was fully submerged in n-hexadecane in a glass cuvette, and the other two were fully submerged in 2000 mg/L of cyclohexanepentanoic acid or stearic acid in n-hexadecane for 72 h at 298 K following the procedure developed by Christensen and Tanino [55]. After 72 h, a drop of brine (equilibrated with test oils for 72 h) was manually dispensed onto the substrate using sessile drop method with FTA instrument (FTA100, First Ten Angstroms) and imaged using a camera (FLIR USB 2.0-FMVU-03MTM-CS: 0.3 MP, 60 FPS, Aptina MT9V022, Mono) (Fig. 1). At least six oil-brine contact angle measurements for each of the three oil phases were performed.

2.2.2. Adsorption and adsorption strength experiments

Three sets of experiment were designed to simulate the rock and fluid interactions and determine adsorption and adsorption strengths of stearic acid and cyclohexanepentanoic acid. Approximately 0.50 g of marble grains were placed into glass vials and exposed to 4 mL of model oils for 336 h (the required time to achieve equilibrium). The mixture was agitated using a shaking water bath (Grant GLS Aqua Plus) at constant temperature of either 298, 313, 333 K. An aliquot of 100 μL was taken after 168, 336, and 504 h and analyzed by GC-FID (varian cp-3800, ZB-FFAP GC column $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) to measure the amount of stearic acid or cyclohexanepentanoic acid adsorbed on the substrate.

333 K was chosen as the maximum temperature considered as approximately 25% of world oil reservoirs are around 333 K [56]. The adsorption experiments were performed at ambient pressure. To do adsorption experiments at reservoir pressure, it was required to design a high pressure vessel, capable to homogenize fluids prior to sampling and take aliquots at reservoir pressure. The experiments at reservoir conditions are also very time consuming. We could not outsource a setup or fabricate it internally to meet our experimental requirements in short term. Investigating the impact of pressure on the adsorption of stearic acid and cyclohexanepentanoic acid is a topic for future work using more sophisticated laboratory apparatus.

To determine the amount of strongly held adsorbates and its dependence on temperature, the remaining mixtures from adsorption experiments were centrifuged and liquid was decanted. The remaining grain was then exposed to 4 mL of fresh n-hexadecane. The mixture was agitated using a shaking water bath (Grant GLS Aqua Plus) at constant temperature (298, 313, or 333 K) and aliquots of 100 μL were taken after 168, 336, and 504 h and analyzed using GC-FID.

The equilibrium concentrations (C_e), mass of adsorbate per volume of adsorbent, was calculated using GC-FID and the adsorbent loading (Q_e), the mass of adsorbate per adsorbent mass, was also determined using the following expression:

$$Q_e = \frac{C_i m_i - C_e m_r}{\rho X} \quad (1)$$

where C_i is the initial concentration of the solution, ρ is the density of the solvent, m_i and m_r are the initial and remaining mass of the solution, and X is the mass of marble which is assumed to remain constant.

2.2.3. Adsorption kinetics, Langmuir model and thermodynamic parameters

Interaction mechanism between adsorbate and adsorbent are determined from kinetics of adsorption. Adsorption kinetics could predict adsorption rate and provide information about the mechanism of adsorption [50]. Pseudo-first-order, pseudo-second-order and intra particle diffusion are the most common adsorption kinetic models used to understand the mechanism of adsorption of stearic acid and cyclohexanepentanoic acid on the marble [57,58].

Pseudo-first-order kinetic model was introduced by Lagergren (1898) for solid-liquid interface adsorption process as given in below [50]:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (2)$$

where Q_e (mg/g) is the equilibrium adsorbing loading and Q_t (mg/g) represents the amount of adsorption on the marble at time t . K_1 (1/min) is constant rate of pseudo-first-order model and is calculated from slope of $\ln(Q_e - Q_t)$ versus t .

Pseudo-second-order kinetic model was also introduced by Lagergren at 1898 as below [50]:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (3)$$

where K_2 is constant rate of pseudo-second-order model and is obtained from the plot of t/Q_t versus t .

The first and second-order kinetic models are used to understand the type of reaction and constant rates during adsorption of stearic acid

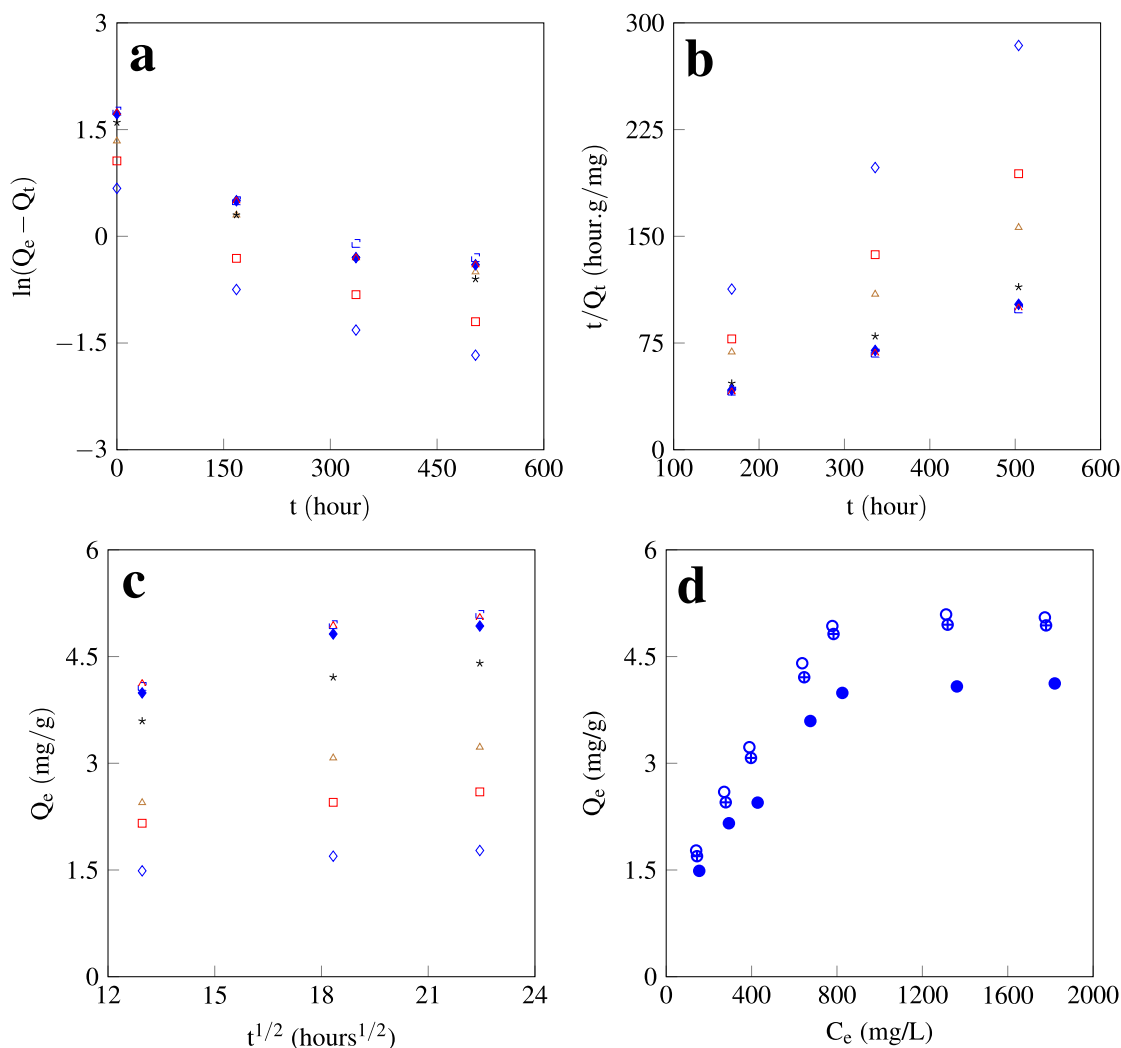


Fig. 4. Stearic acid adsorption (a) pseudo-first-order adsorption kinetic (b) pseudo-second-order adsorption kinetic (c) intra-particle diffusion adsorption kinetic (d) adsorption isotherm after 168 (●), 336 (⊕) and 504 (○) hours. All data collected at 298 K on treated marble. Stearic acid concentrations in n-hexadecane are 230 (◇), 402 (■), 550 (△), 844 (*), 1024 (◆), 1566 (□), and 2026 mg/L (▲).

and cyclohexanepentanoic acid on the marble. Intra-particle diffusion model is used for internal and external diffusion mechanisms [59–61].

$$Q_t = k_i t^{1/2} + P_i \quad (4)$$

where k_i is the intraparticle diffusion rate constant [M/MT^{1/2}] and P_i [M/M] is the value of Q_t at $t = 0$. Intra particle diffusion is the main mechanism if $P_i = 0$ and the other mechanisms (external diffusion and adsorption onto the active sites) are involved in adsorption process if $P_i \neq 0$ [62].

There are several models in the literature to quantify adsorption processes and evaluate adsorption equilibriums such as Henry's, Freundlich's, Temkin's and Langmuir's isotherm. Crocker and Marchin [63], Madsen et al. [64] and Dubey and Waxman [65] suggested that the Langmuir's isotherm is the most suitable model to investigate the adsorption of crude oil organic components on reservoir rocks. Based on the results obtained in this paper Langmuir's isotherm is a reliable model to examine adsorption of stearic acid and cyclohexanepentanoic acid on a marble surface after sufficient time (Section 3.3).

The general form of Langmuir's model [66] for solid–liquid adsorption processes is given by:

$$Q_e = \frac{Q_m K_v C_e}{1 + K_v C_e} \quad (5)$$

where Q_m is the maximum adsorption capacity (mass of adsorbate per mass of adsorbent) and K_v is the volumetric adsorption constant (volume of adsorbent per mass of adsorbate). Rearranging Eq. (5) yields the linear form of the Langmuir equation:

$$\frac{C_e}{Q_e} = \frac{1 + K_v C_e}{Q_m K_v} \quad (6)$$

Freundlich model proposes a multi-layer adsorption onto a heterogeneous surface [67] and defined by:

$$Q_e = K_f C_e^{1/n} \quad (7)$$

where K_f is Freundlich constant and shows the adsorption capacity of stearic acid or cyclohexanepentanoic acid on the marble and $1/n$ is heterogeneity factor and relates to adsorption intensity [66–68].

Temkin model is also a linear isotherm and represent as follows [50, 69]:

$$Q_e = B \ln K_t + B \ln C_e \quad (8)$$

where B is the adsorption surface capacity per unit binding energy and K_t is adsorption constant.

Thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) are a key parameter to determine the spontaneity of adsorption process and can be calculated

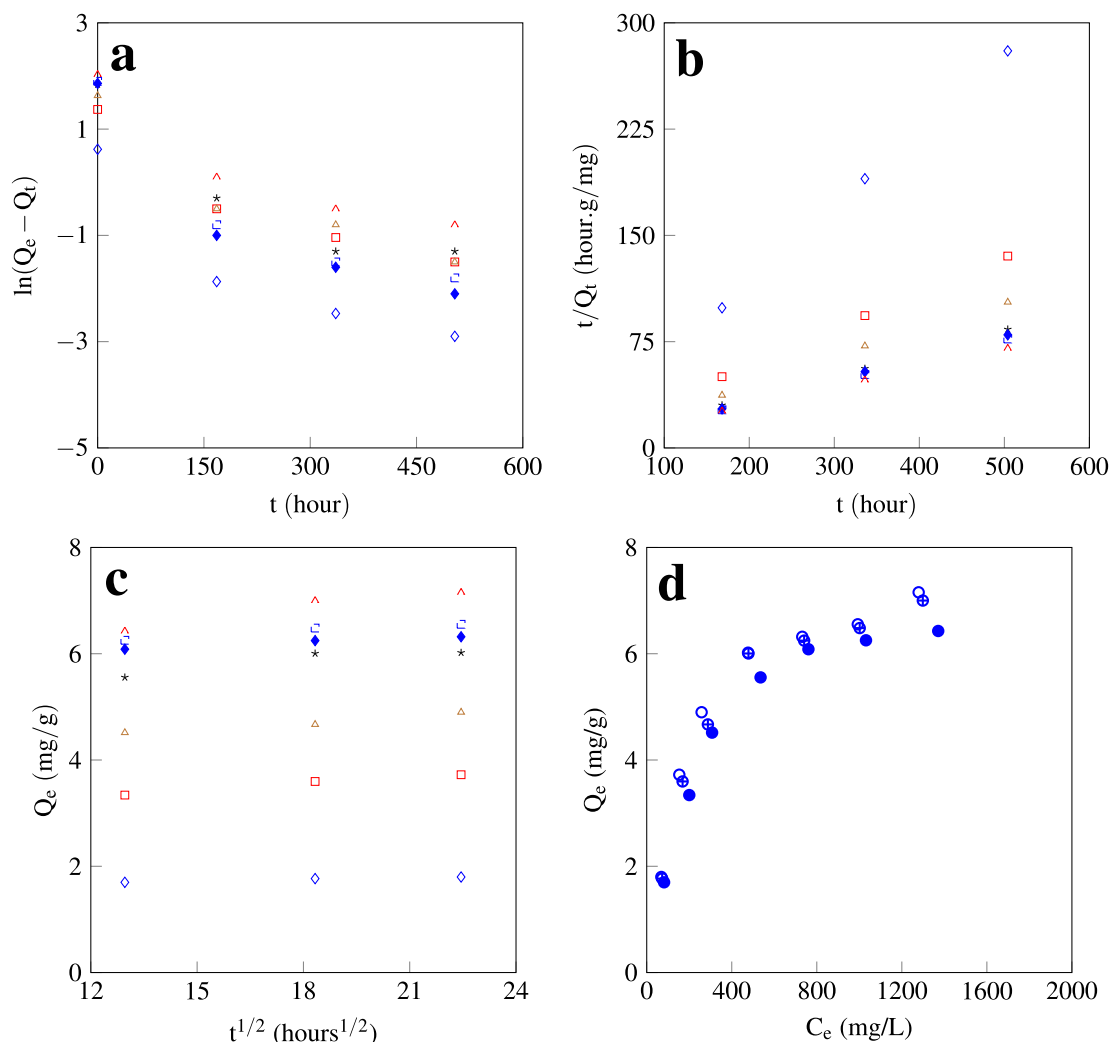


Fig. 5. Stearic acid adsorption (a) pseudo-first-order adsorption kinetic (b) pseudo-second-order adsorption kinetic (c) intra-particle diffusion adsorption kinetic (d) adsorption isotherm after 168 (●), 336 (⊕) and 504 (⊙) hours. All data collected at 313 K on treated marble. Stearic acid concentrations in n-hexadecane are 300 (◇), 610 (■), 888 (△), 1238 (★), 1516 (◆), 1832 (□), and 2184 mg/L (▲).

from the variation of the thermodynamic equilibrium constant K_T with the change in temperature and given by:

$$K_T = \frac{\alpha_s}{\alpha_e} = \frac{v_s C_s}{v_e C_{em}} \quad (9)$$

where α_s is the activity of the adsorbed adsorbate, α_e is the activity of adsorbate in the equilibrium solution, C_s is the amount of adsorption in mmol of adsorbate per gram of adsorbent, C_{em} is the adsorbate concentration in the equilibrium solution (mmol/mL), v_s is the activity coefficient of the adsorbed adsorbate and v_e is the activity of adsorbate in the equilibrium solution. As adsorbate concentration in the solution decreases and approaches to zero, K_T is obtained by plotting $\ln(C_s/C_{em})$ vs. C_s [70,71]. With calculating K_T , thermodynamic parameters (ΔG° , ΔH° , and ΔS°) can be calculated by Van't Hoff equations [72–74]:

$$\Delta G^\circ = -RT \ln(K_T) \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

where T is absolute temperature and R is the universal gas constant (8.314 J/(K mol))

3. Results and discussion

3.1. Impact of stearic and cyclohexanepentanoic acid on contact angle

Images of selected static brine droplets dispensed on marble surfaces aged for 72 h in n-hexadecane, 2000 mg/L of cyclohexanepentanoic acid in n-hexadecane, and 2000 mg/L of stearic acid in n-hexadecane at 298 K, are presented in Fig. 2(a, b and c). The mean of contact angles measured in n-hexadecane, 2000 mg/L of cyclohexanepentanoic acid in n-hexadecane, and 2000 mg/L of stearic acid in pure n-hexadecane were $71^\circ \pm 4$, $115^\circ \pm 13$, and $136^\circ \pm 7$ respectively (Fig. 2d). This demonstrates that the wettability of marble surface is altered from water-wet to oil-wet through exposure to cyclohexanepentanoic acid or stearic acid solutions, consistent with previous measurements [2,55, 75].

3.2. Effect of time on adsorption

In wettability studies, the duration a substrate and fluid are in contact is regarded as an important parameter. The effect of time on adsorption studies is not fully understood and has not been studied by many authors [50]. The time required for adsorption of organic components in the oil phase on rock surface, can be used as an index

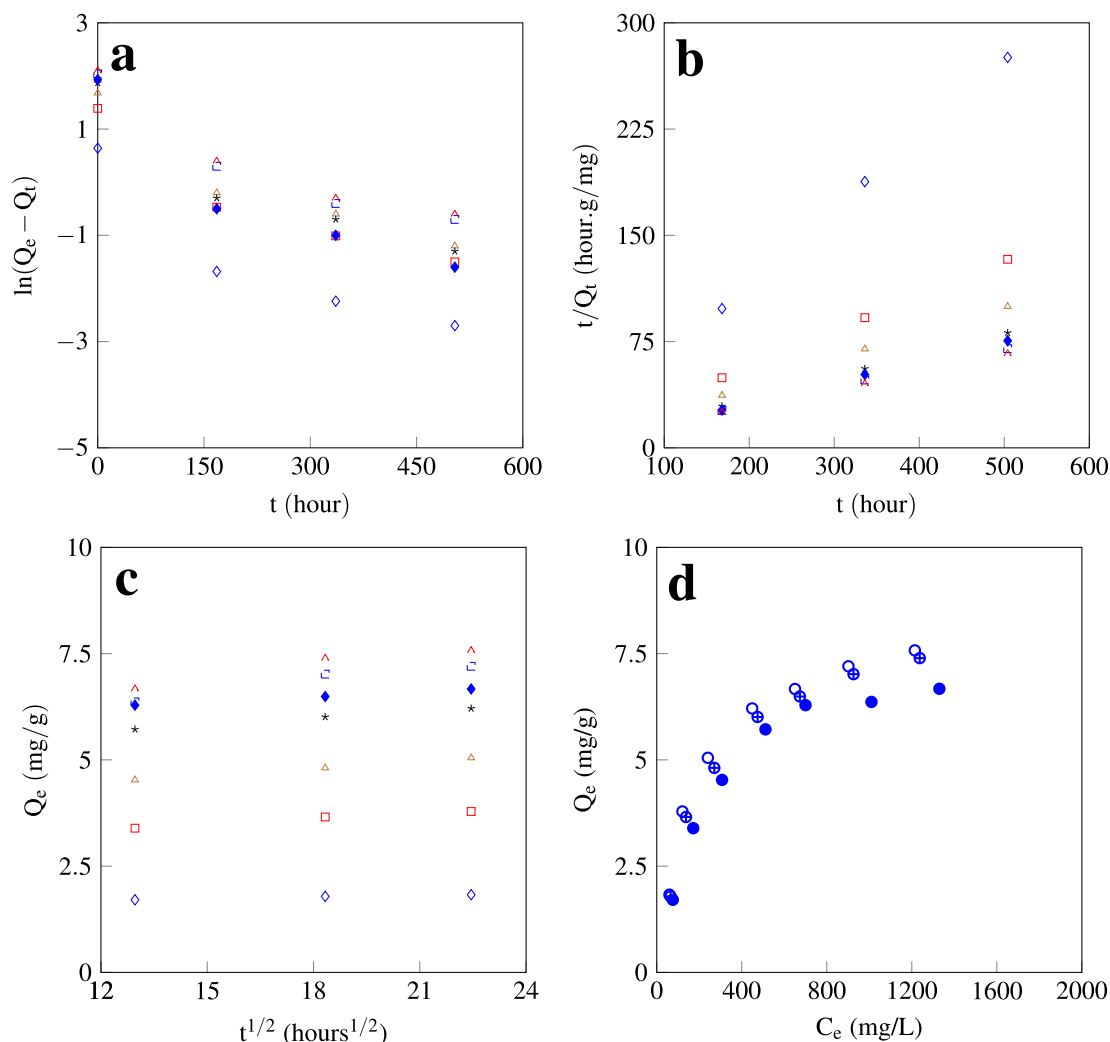


Fig. 6. Stearic acid adsorption (a) pseudo-first-order adsorption kinetic (b) pseudo-second-order adsorption kinetic (c) intra-particle diffusion adsorption kinetic (d) adsorption isotherm after 168 h (●), 336 h (⊕) and 504 h (○) hours. All data collected at 333 K on treated marble. Stearic acid concentrations in n-hexadecane are 300 (◇), 610 (■), 888 (△), 1238 (★), 1516 (◆), 1832 (□), and 2184 mg/L (▲).

to restore the wettability of the geological samples to their initial state in the laboratory [34].

Alotaibi et al. [76] reported in their study, Isoelectric point (IEP) for carbonate at (101.35 kPa, 298.15 K) falls within the range 9.8–11.9, and Farooq et al. [77] stated the range is between 8.2–8.5 at (101.35 kPa, 298.15 K). The rock surface charge will be positive if the pH of the flowing fluid adjacent to the reservoir rock surface is below IEP of the rock. Since the pH of the brine used in this study was measured 7.85, the marble grain surface carries positive charges and, accordingly, the adsorption layer is formed with the carboxyl group oriented towards it for both acids (Fig. 3).

With having adsorbed amounts for stearic acid and cyclohexanepentanoic acid on marble and surface area measured for marble, surface area per molecule can be calculated from the following correlation [78]:

$$\sigma = \frac{S_A}{\Gamma N_A} \quad (12)$$

where σ is surface area per molecule, S_A is specific surface of marble (0.13 m²/g), Γ is the adsorbed amount of stearic acid or cyclohexanepentanoic acid (moles per marble mass) and N_A is Avogadro's number, 6.022×10^{23} molecules per mole. For example, surface area of a molecule of stearic acid on marble is 2.98×10^{-2} nm². The equivalent value for cyclohexanepentanoic acid is 1.43×10^{-2} nm².

Figs. 4 and 7 show the impact of time on adsorption of stearic acid or cyclohexanepentanoic acid on marble grains at 298 K using pseudo-first-order, pseudo-second-order and intra-particle diffusion models [79]. As shown, adsorption of stearic acid and cyclohexanepentanoic acid are in good agreement with pseudo-second-order model. From intra-particle diffusion model result for both acids in Figs. 4c and 7c, it can be understood that adsorption mechanism is mainly due to intra-particle diffusion (linear portion of curve). The intercept of the plot reflects boundary layer effect and relates to boundary layer thickness. The adsorption rates for stearic acid and cyclohexanepentanoic acid increase substantially in first 168 h at different initial concentrations, and then reach equilibrium gradually after 336 h. A significant increase in adsorption is observed for both acids when the experimental time is increased from 168 to 336 h. Subsequently, the adsorption capacities do not change significantly when increasing the experiment time from 336 h to 504 h, this suggests that the system is approaching equilibrium conditions at some point after the 336 h experiment. The equivalent adsorption isotherms for both acids are also shown in Figs. 4d and 7d.

The impact of time on stearic acid or cyclohexanepentanoic acid adsorption at 313 and 333 K are also shown in Figs. 5, 6, 8, 9. Likewise Figs. 4 and 7, the adsorption rates increase substantially in first 168 h at different initial concentrations, and then reach equilibrium gradually after 336 h for the majority of concentrations. The adsorption kinetic

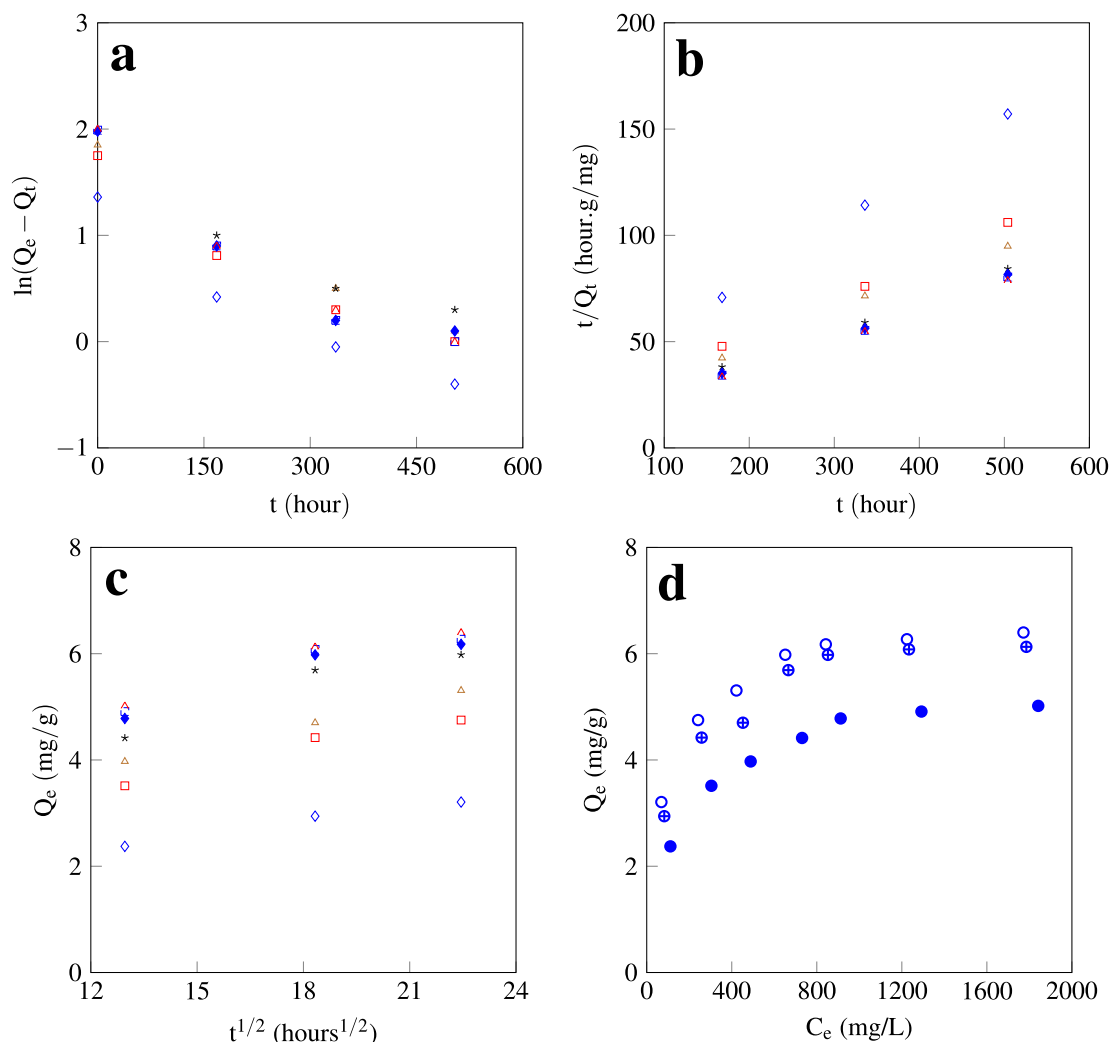


Fig. 7. Cyclohexanepentanoic acid adsorption (a) pseudo-first-order adsorption kinetic (b) pseudo-second-order adsorption kinetic (c) intra-particle diffusion adsorption kinetic (d) adsorption isotherm after 168 (●), 336 (⊕) and 504 (○) hours. All data collected at 298 K on treated marble. Stearic acid concentrations in n-hexadecane are 232 (◇), 482 (■), 688 (△), 954 (★), 1152 (◆), 1538 (□), and 2094 mg/L (△).

parameters for stearic acid and cyclohexanepentanoic acid on marble for variable concentrations and temperatures are given at Table 2.

Barati et al. [50] studied the impact of time on the adsorption of a nonionic surfactant with varying concentrations on carbonate surfaces. They found that the adsorption increases with exposure time and reached an equilibrium after a certain time. As mentioned previously, due to the low BET surface area measured for treated marble, the mass of adsorption to unit mass is expected to be low.

3.3. Effect of temperature on adsorption and strength of adsorption

Fig. 10 presents adsorption capacities at three temperatures for various concentrations of stearic acid or cyclohexanepentanoic acid dissolved in n-hexadecane on an treated marble substrate. The adsorption of stearic acid and cyclohexanepentanoic acid on marble was observed to follow a Langmuir model at all three temperatures considered, in line with literature [13,50]. Adsorption was found to increase for all concentrations with increasing temperature which is in agreement with the results obtained by Strand et al. [80] and Barati et al. [50]. The increase in adsorption capacities with temperature was observed to be significant from 298 to 313 K for both acids, with more modest increase observed when increasing the temperature from 313 to 333 K.

Table 2
Adsorption kinetic parameters for stearic acid or cyclohexanepentanoic acid on marble grains.

T K	Stearic acid				Cyclohexanepentanoic acid			
	Ci mg/L	K1 1/min	K2 g/(mg min)	Ki	Ci mg/L	K1 1/min	K2 g/(mg min)	Ki
298	230	0.272	0.574	0.082	232	0.203	0.143	0.148
	402	0.263	0.355	0.120	482	0.204	0.098	0.220
	550	0.218	0.171	0.150	688	0.204	0.087	0.241
	844	0.255	0.192	0.205	954	0.207	0.080	0.279
	1024	0.255	0.171	0.231	1152	0.230	0.103	0.289
	1566	0.248	0.154	0.238	1538	0.236	0.108	0.294
	2026	0.260	0.177	0.237	2094	0.235	0.105	0.298
313	300	0.399	2.083	0.084	400	0.268	0.281	0.152
	610	0.326	0.484	0.173	650	0.272	0.213	0.223
	888	0.349	0.458	0.227	886	0.244	0.123	0.283
	1238	0.374	0.481	0.283	1232	0.283	0.158	0.338
	1516	0.445	0.922	0.296	1578	0.360	0.323	0.370
	1832	0.424	0.726	0.307	1912	0.309	0.177	0.391
	2184	0.332	0.268	0.335	2158	0.291	0.139	0.422

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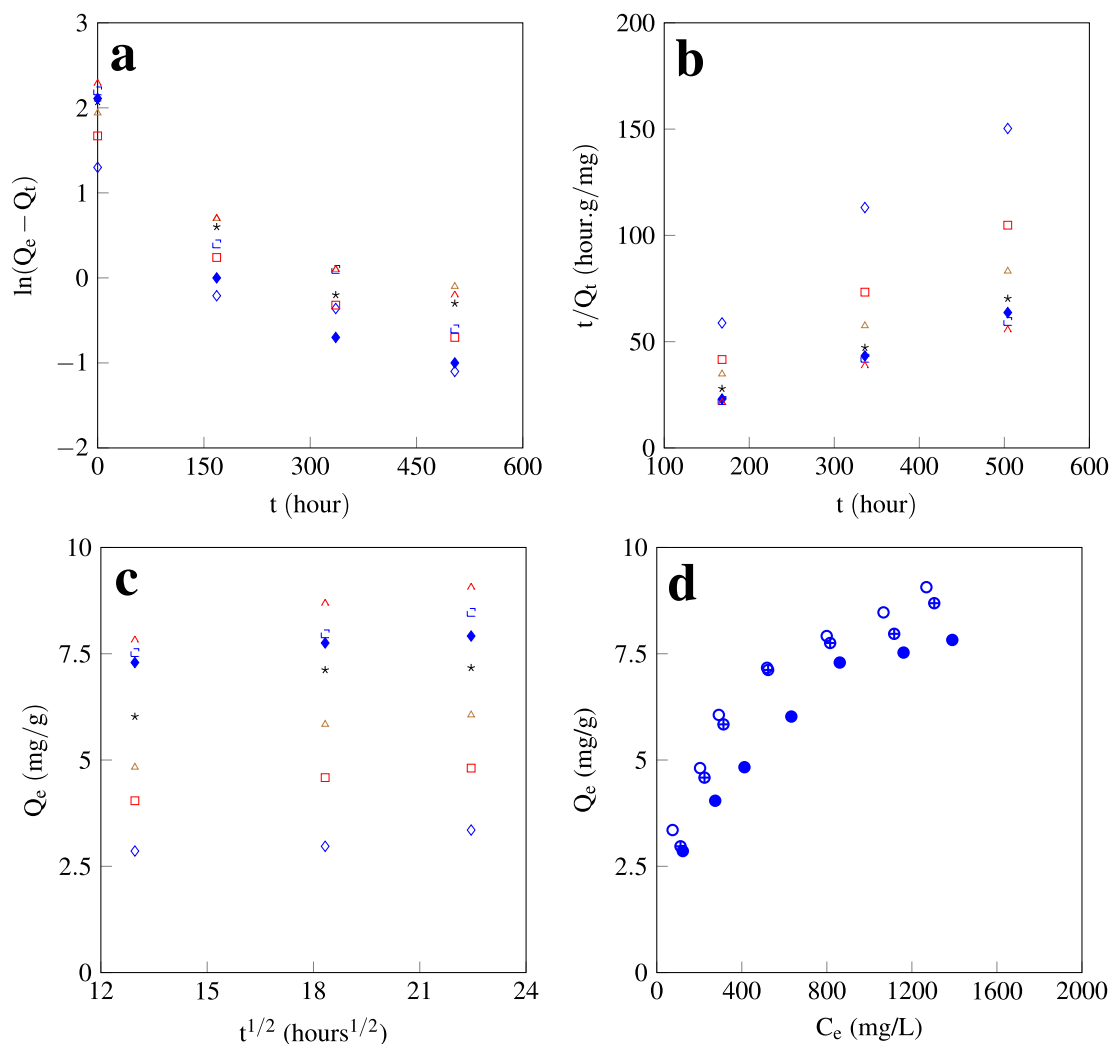


Fig. 8. Cyclohexanepentanoic acid adsorption (a) pseudo-first-order adsorption kinetic (b) pseudo-second-order adsorption kinetic (c) intra-particle diffusion adsorption kinetic (d) adsorption isotherm after 168 (●), 336 (◻) and 504 (◊) hours. All data collected at 313 K on treated marble. Stearic acid concentrations in n-hexadecane are 400 (◇), 650 (■), 886 (△), 1232 (*), 1578 (◆), 1912 (□), and 2158 mg/L (▲).

Table 2 (continued).

T	Stearic acid				Cyclohexanepentanoic acid			
	Ki	K1	K2	Ki	Ki	K1	K2	Ki
K	mg/L	1/min	g/(mg min)		mg/L	1/min	g/(mg min)	
333	300	0.379	1.675	0.085	400	0.305	0.433	0.153
	610	0.325	0.469	0.176	650	0.339	0.401	0.226
	888	0.321	0.338	0.234	886	0.291	0.191	0.286
	1238	0.354	0.385	0.289	1232	0.226	0.073	0.371
	1516	0.390	0.508	0.311	1578	0.304	0.167	0.382
	1832	0.315	0.224	0.337	1912	0.309	0.171	0.411
	2184	0.313	0.208	0.354	2158	0.314	0.162	0.440

For stearic acid, the change in adsorption was 2.301 mg/g at $C_e = 270$ mg/L when the temperature was increased from 298 to 313 K; whereas from 313 to 333 K the increase was 0.149 mg/g at $C_e = 260$ mg/L. Similarly, for cyclohexanepentanoic acid, the change in adsorption was 1.310 mg/g at $C_e = 290$ mg/L compared to 0.246 mg/g at $C_e = 280$ mg/L from 313 to 333 K. Key adsorption parameters for stearic acid and cyclohexanepentanoic acid on marble grain such as Langmuir maximum adsorption capacity (Q_m), Langmuir adsorption constant (K_L), Freundlich adsorption constant (K_f), and Temkin adsorption constant (K_t) are given in Table 3. As shown in Table 3.

To further compare, the uptake of stearic acid or cyclohexanepentanoic acid on grain marbles, thermodynamic parameters (ΔG° , ΔH° ,

Table 3

Isotherm adsorption parameters for stearic acid or cyclohexanepentanoic acid on marble grains.

Isotherms	T	Stearic acid			Cyclohexanepentanoic acid		
		K	Q_m mg/g	k_L L/mg	R^2	Q_m mg/g	k_L L/mg
Langmuir	298	6.693	0.0025	0.987	6.504	0.0138	0.986
	313	9.354	0.0036	0.984	9.033	0.0490	0.965
	333	9.858	0.0040	0.977	10.853	0.0051	0.993
		K_f L/mg	n	R^2	K_f L/mg	n	R^2
Freundlich	298	0.00023	2.293	0.909	0.00137	4.591	0.938
	313	0.00037	2.322	0.889	0.00078	2.879	0.983
	333	0.00040	2.301	0.902	0.00070	2.652	0.933
		K_t	B	R^2	K_t	B	R^2
Temkin	298	0.0259	1.45	0.928	0.3948	1.03	0.965
	313	0.0511	1.75	0.970	0.0643	2.02	0.990
	333	0.0551	1.86	0.985	0.0546	2.29	0.964

and ΔS°) were calculated (Table 4). ΔG° , ΔH° , and ΔS° were calculated using different models in the literature. From Table 4, adsorption of stearic acid or cyclohexanepentanoic acid on marble grains is a spontaneous process as ΔG° is negative [81,82]. The adsorption of stearic acid

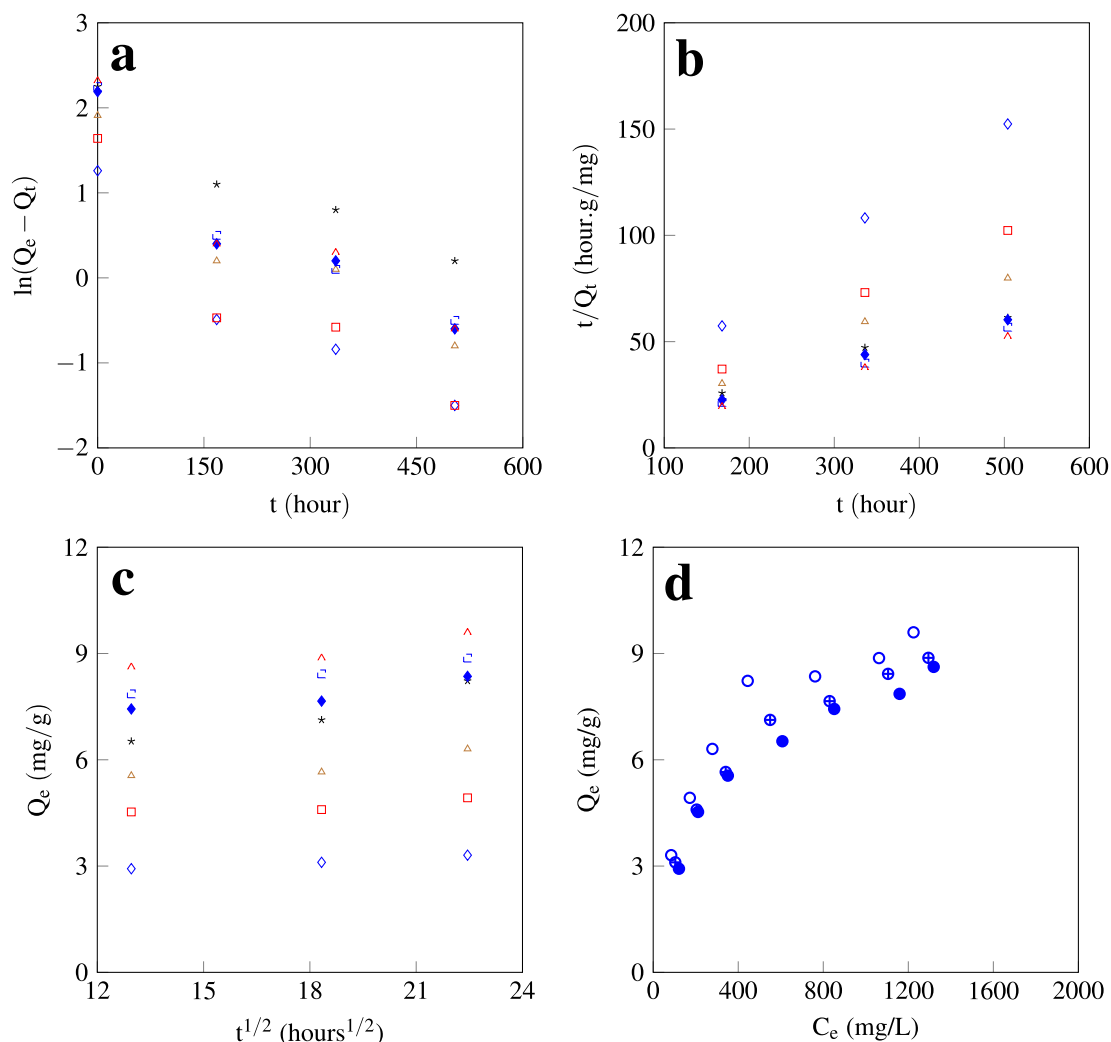


Fig. 9. Cyclohexanepentanoic acid adsorption (a) pseudo-first-order adsorption kinetic (b) pseudo-second-order adsorption kinetic (c) intra-particle diffusion adsorption kinetic (d) adsorption isotherm after 168 (●), 336 (⊕) and 504 (○) hours. All data collected at 333 K on treated marble. Stearic acid concentrations in n-hexadecane are 400 (◇), 650 (■), 886 (△), 1232 (*), 1578 (◆), 1912 (□), and 2158 mg/L (▲).

Table 4

Thermodynamic parameters for adsorption of stearic acid or cyclohexanepentanoic acid on marble grains.

T K	Stearic acid			Cyclohexanepentanoic acid		
	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° J/(mol K)	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° J/(mol K)
298	-33.25	16.47	167.60	-36.35	-22.13	46.8
313	-36.46			-36.29		
333	-39.13			-37.98		

on marble grains is an endothermic reactions (negative sign of ΔH°), whereas for cyclohexanepentanoic acid shows an exothermic reactions (positive sign of ΔH°) [81]. Affinity of stearic acid adsorption is greater than cyclohexanepentanoic acid based on ΔS° calculated [81,82].

Some of the stearic acid and cyclohexanepentanoic acid adsorbed on the marble grains returned to solution after exposure to fresh n-hexadecane for 504 h, with the amount returned increased with

temperature. The remaining stearic acid (mass) is greater than cyclohexanepentanoic acid on the marble after 504 h at 298, 313 and 333 K as listed in Table 5 (data for earlier times can be found in Appendix C, Tables C.1 and C.2). This shows that stearic acid bounds to marble grains are stronger than cyclohexanepentanoic acid.

Physical and chemical adsorption process can also be determined from ΔG° value. The free energy change ranges from $\Delta G^\circ = 20$ to 0 kJ/mol for physical adsorption, and for chemical adsorption, it ranges between -80 and -400 kJ/mol. ΔG° values fall within the range -20 to -80 kJ/mol (Table 4), which suggests that both physical and chemical adsorption is involved [82,83].

It has previously been reported that stearic acid and naphthenic acids adsorbed on calcite [15,37,75] and dolomite [45] desorbed into distilled water [37,75]. Following Thomas et al. [84]'s observation, the high-temperature loss corresponded to a monolayer of the adsorbate (chemisorption), and the low-temperature loss was interpreted as physisorption on top of the monolayer and readily removed. Our interpretation of the present experiments is that the acid returned into the fresh n-hexadecane is physisorbed mass, and what remains on the grains comprise a monolayer of chemisorbed acids.

Table 5

Stearic acid and cyclohexanepentanoic acid returned to the solution at 298, 313, and 333 K after 504 h.

T K	Stearic acid		Cyclohexanepentanoic acid	
	Ce mg/L	Qe mg/g	Ce mg/L	Qe mg/g
298	136	0.710	291	1.296
	217	1.074	351	2.348
	246	1.397	391	2.487
	313	2.014	431	2.943
	322	2.446	432	3.065
	325	2.647	444	3.104
	328	2.659	459	3.080
	313	143	0.709	279
330		1.202	409	1.636
450		1.354	508	2.089
531		1.982	598	2.609
546		2.111	673	2.673
549		2.327	725	2.805
576		2.451	784	2.971
333		145	0.708	285
	391	0.795	461	1.346
	498	1.168	579	1.692
	587	1.618	780	2.275
	614	1.957	772	2.281
	666	2.100	802	2.507
	700	2.122	863	2.861

4. Conclusions

The effect of time and temperature on the adsorption behavior of organic acids in n-hexadecane on marble as well as their adsorption strengths were investigated in this study. Organic acids in the crude oil were represented by stearic acid and cyclohexanepentanoic acid. PSA, NAD, SEM and XRD were utilized to examine the properties of marble. The wetting properties of the marble surface were also evaluated using adsorption and adsorption strength measurements. The main findings are as follows:

1. Stearic acid and cyclohexanepentanoic acid adsorb on marble in the absence of water. Adsorption for both acids increases with temperature over the range considered presently, i.e., from 298 to 333 K.
2. Cyclohexanepentanoic acid mass adsorbed on marble is slightly greater than stearic acid. This may be attributed to the molecule surface area of cyclohexanepentanoic acid being smaller than that of stearic acid.
3. Contact angle measurements indicate that adsorption of stearic acid and cyclohexanepentanoic acid alters the wettability of marble even in the absence of an aqueous phase.
4. A portion of acid adsorbed on the marble surface was removed when submerged in fresh n-hexadecane, indicating that stearic acid and cyclohexanepentanoic acid adsorbed on marble grains are desorbed to an extent. Value of ΔG° calculated also suggests that both physical and chemical adsorption were involved for adsorption of stearic acid or cyclohexanepentanoic acid on marble grains. Greater adsorption affinity of stearic acid on marble grains compared to cyclohexanepentanoic acid was resulted from ΔS° calculated. This is also confirmed by less stearic acid returned to solution compared to cyclohexanepentanoic acid.

CRediT authorship contribution statement

Mohammad Sarlak: Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Khosro Jarraghan:** Writing – original draft, Writing – review & editing. **Alan J. McCue:** Resources, Writing – original draft, Writing – review & editing.

Table A.1

BET surface area on marble prior to and after hydrochloric acid treatment. The reported range represents uncertainty in measurements and calculations.

	BET surface area (m ² /g)
Untreated marble	0.32 ± 0.01
Treated marble	0.13 ± 0.01

James A. Anderson: Methodology, Resources. **Yukie Tanino:** Conceptualization, Methodology, Resources, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Mohammad Sarlak reports financial support was provided by Premier Corex (UK) LTD. Mohammad Sarlak reports a relationship with Premier Corex (UK) LTD that includes: employment.

Data availability

Data will be made available on request.

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Appendix A. Impact of HCl treatment on crushed marble properties

Particle size distribution was measured using a laser diffraction analyzer (Beckman Coulter LS13 320 with an aqueous liquid module attachment) to characterize the size distribution of treated marble. Laser diffraction spectrometry gives an estimation of the percentage of particles belonging to a certain size using the principle of light scattering. On completion of cleaning, the grains were dispersed in water to separate particles individually.

The textural properties of treated marble were investigated using NAD technique and Brunauer–Emmett–Teller (BET) surface areas were calculated. The samples were analyzed using a BET instrument (Micromeritics ASAP 2020). Approximately 0.50 g was placed into a glass cell and degassed under reduced pressure and elevated temperature

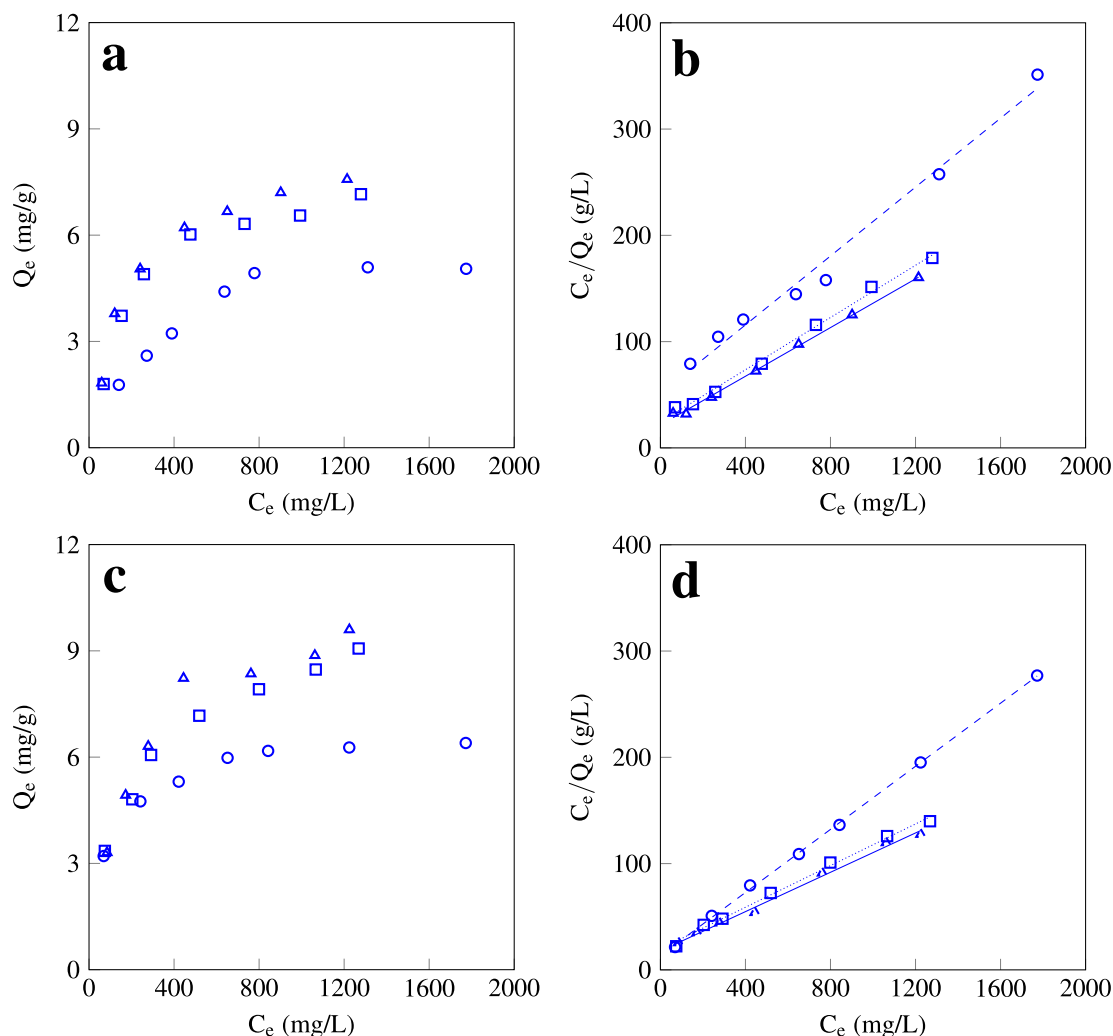


Fig. 10. Stearic acid adsorption (a) adsorption isotherm (b) linearized Langmuir isotherm and cyclohexanepentanoic acid adsorption (c) adsorption isotherm (d) linearized Langmuir isotherm at 298 (o), 313 (□) and 333 K (△). All data collected after 504 h on treated marble. (---) linear regression at 298 K, (...) linear regression at 313 K, and (—) linear regression at 333 K.

(approximately 473 K) using a heating mantle to remove water and other contaminants. After the sample was degassed, the cell was moved to the analysis port and a dewars of liquid nitrogen was used to cool the sample and maintain it at a constant temperature.

For SEM, approximately 0.50 g of treated marble was mounted onto aluminum stubs and carbon coated. The measurements were carried out using a Carl Zeiss Gemini SEM 300- high resolution Field Emission SEM (FESEM) with Secondary Electron (SE), Back Scattered Electron (BSE) and Cathodoluminescence (CL) detectors at magnifications from 100 to 1500x.

XRD was performed using a Panalytical Empyrean powder diffractometer with Johansson monochromator to quantify/identify the types of minerals present within treated marble. Approximately 2.0 g of dried and cleaned samples were used. Each sample was analyzed between 5° and 80° 2-theta (θ) and a step size of 0.013° . Samples were exposed to x-ray radiation, which was emitted from a copper anode at 35 kV, 30 mA.

Fig. A.1 shows the SEM images of untreated and treated marble grain surface. It is readily evident that exposure to hydrochloric acid removed fine grains (sizes $< 0(1) \mu\text{m}$). Fig. A.2 shows particle size distribution for untreated and treated marble. Exposure to hydrochloric acid preferentially removed particles smaller than $20 \mu\text{m}$.

BET surface area for untreated and treated marble was calculated from NAD measurements. As expected, exposure to hydrochloric acid reduced the surface area (Table A.1), consistent with the removal of the finest marble grains captured in SEM images (Fig. A.1). This also corresponds well with PSA result, as the loss of the smallest particles in the system correlates with a significant drop in surface area.

XRD results for untreated and treated marble are shown in Fig. A.3. It can be clearly observed that the main mineral constituents on untreated and treated marble is calcium carbonate. The result for untreated marble confirms approximately 95% calcium carbonate, 2% calcium magnesium carbonate (dolomite), and 3% magnesium silicate. On treated marble, the sample is predominately calcium carbonate with a much-reduced proportion of dolomite (approximately 0.5%) and 1%–2% of potassium aluminosilicate. Comparing the XRD result for both untreated and treated marble shows that there is no significant difference in mineralogy. As discussed previously, acid has only removed the fine fractions which are mainly calcium carbonate.

Appendix B. Basic properties of the test fluids

Dynamic viscosities and densities of each test fluid (Tables B.1–B.3) were measured by rotational viscometry at 298, 313, and 333 K (Anton Paar SVMTM 3000).

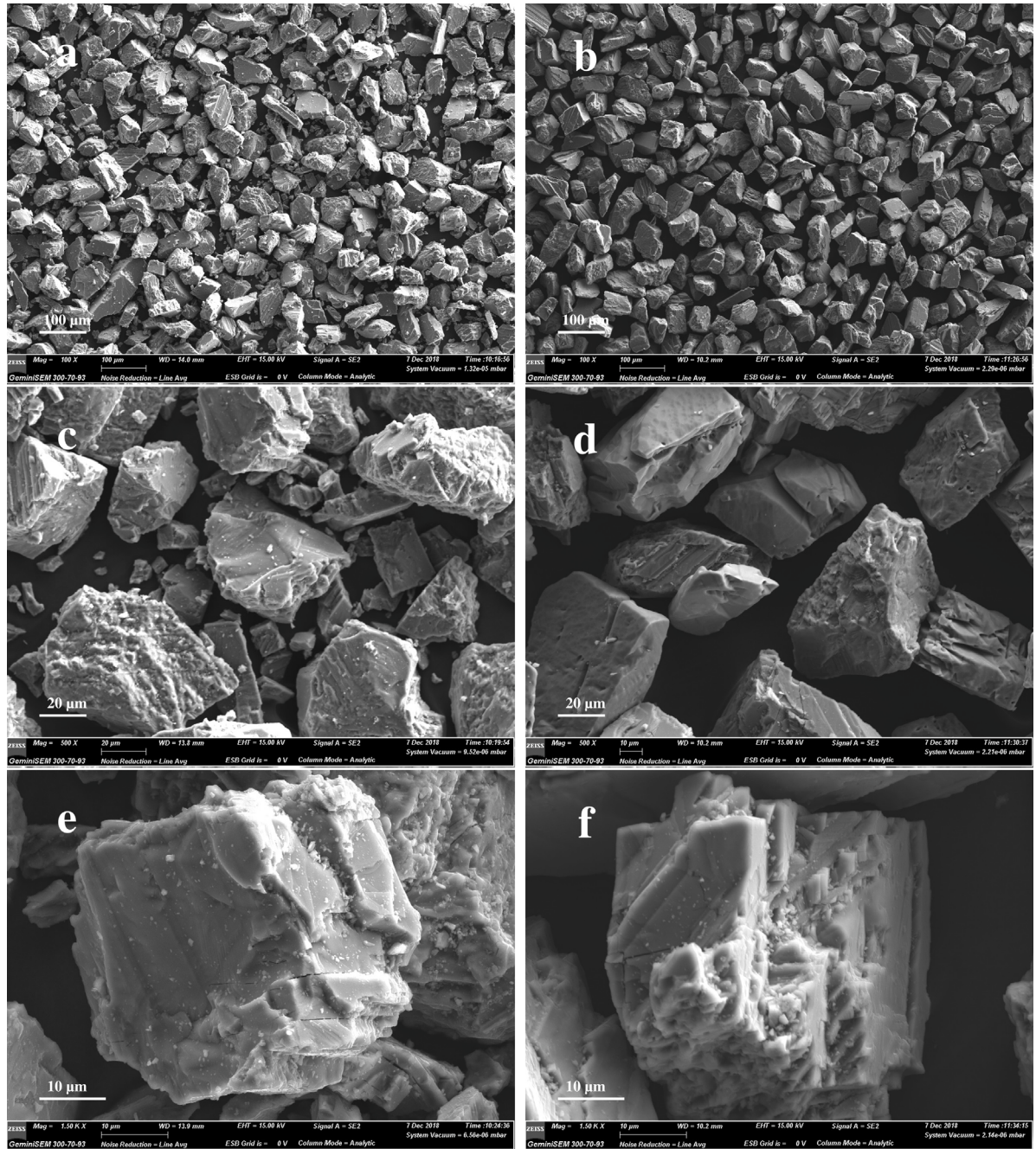


Fig. A.1. SEM images of (a, c, e) untreated marble and (b, d, f) treated marble at 100, 500, and 1500× magnifications.

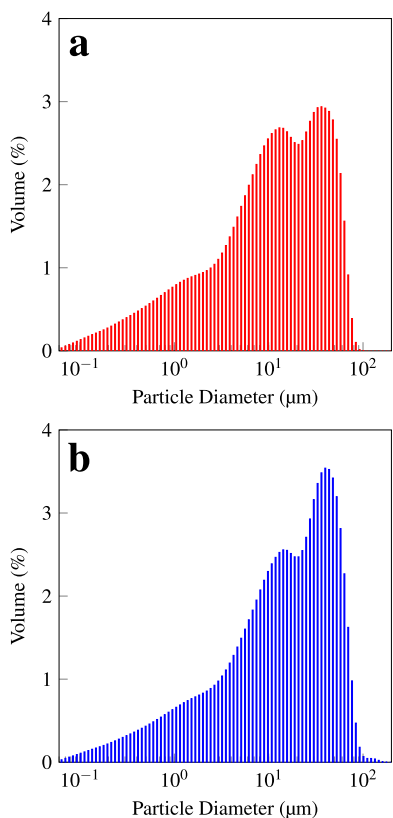


Fig. A.2. Particle size distribution of crushed marble before (a) and after (b) treatment in HCl.

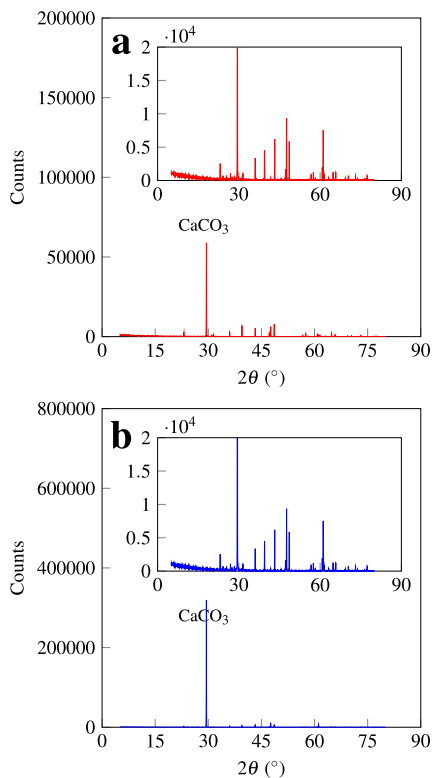


Fig. A.3. XRD analysis for (a) untreated marble and (b) treated marble. Inset graph is plot magnification counts ranging from 0 to 20000.

Table B.1
Densities and viscosities of the synthetic brine.

<i>T</i> K	Density g/mL	Viscosity mPa s
298	1.0379	1.0218
313	1.0312	0.7824
333	1.0220	0.5693

Table B.2
Densities and viscosities of the stearic acid solutions.

<i>C_e</i> mg/L	<i>T</i> K	Density g/mL	Viscosity mPa s
0	298	0.7707	3.0270
300		0.7707	3.0280
610		0.7708	3.0390
888		0.7708	3.0410
1238		0.7709	3.0440
1516		0.7709	3.0460
1912		0.7710	3.0490
2184	0.7710	3.0510	
0	313	0.7602	2.1990
300		0.7602	2.2000
610		0.7603	2.2190
888		0.7603	2.2210
1238		0.7604	2.2240
1516		0.7604	2.2260
1912		0.7605	2.2290
2184	0.7605	2.2310	
0	333	0.7463	1.4850
300		0.7463	1.4860
610		0.7464	1.5220
888		0.7464	1.5240
1238		0.7465	1.5260
1516		0.7465	1.5280
1912		0.7466	1.5300
2184	0.7466	1.5320	

Table B.3
Densities and viscosities of the cyclohexanepentanoic acid solutions.

<i>C_e</i> mg/L	<i>T</i> K	Density g/mL	Viscosity mPa s
0	298	0.7707	3.0270
400		0.7707	3.0351
650		0.7708	3.0367
886		0.7708	3.0381
1232		0.7709	3.0399
1578		0.7709	3.0414
1912		0.7710	3.0433
2158	0.7711	3.0449	
0	313	0.7602	2.1990
400		0.7603	2.2147
650		0.7603	2.2156
886		0.7604	2.2165
1232		0.7604	2.2176
1578		0.7605	2.2185
1912		0.7606	2.2197
2158	0.7606	2.2206	
0	333	0.7463	1.4850
400		0.7464	1.5191
650		0.7464	1.5203
886		0.7465	1.5214
1232		0.7466	1.5228
1578		0.7466	1.5239
1912		0.7467	1.5253
2158	0.7468	1.5265	

Appendix C. Stearic acid and cyclohexanepentanoic acid returned to the solution at 298, 313, and 333 K

The remaining stearic acid and cyclohexanepentanoic acid on the marble after 168 and 336 h at 298, 313 and 333 K are listed in Tables C.1 and C.2.

Table C.1

Stearic acid and cyclohexanepentanoic acid returned to the solution at 298, 313, and 333 K after 168 h.

T K	Stearic acid		Cyclohexanepentanoic acid	
	Ce mg/L	Qe mg/g	Ce mg/L	Qe mg/g
298	142	0.807	256	1.565
	221	1.332	324	2.560
	255	1.522	342	2.872
	328	2.45	372	3.394
	331	2.714	383	3.445
	346	2.985	390	3.518
	350	3.013	396	3.557
313	130	0.805	251	1.401
	323	1.258	373	1.916
	434	1.485	470	2.386
	501	2.209	546	3.002
	516	2.342	624	3.048
	521	2.537	681	3.150
	551	2.658	738	3.328
333	132	0.803	265	1.238
	366	0.985	407	1.769
	483	1.281	553	1.901
	543	1.968	736	2.611
	577	2.171	725	2.650
	642	2.289	767	2.783
	678	2.299	832	3.098

Table C.2

Stearic acid and cyclohexanepentanoic acid returned to the solution at 298, 313, and 333 K after 336 h.

T K	Stearic acid		Cyclohexanepentanoic acid	
	Ce mg/L	Qe mg/g	Ce mg/L	Qe mg/g
298	129	0.753	272	1.444
	189	1.107	336	2.466
	239	1.469	369	2.662
	276	2.139	386	3.289
	296	2.516	399	3.324
	303	2.814	405	3.401
	305	2.836	413	3.428
313	137	0.752	264	1.303
	326	1.239	396	1.736
	443	1.411	490	2.232
	515	2.105	591	2.660
	526	2.272	641	2.922
	532	2.456	690	3.075
	556	2.613	741	3.304
333	139	0.750	275	1.161
	388	0.819	447	1.456
	492	1.217	565	1.802
	574	1.718	760	2.432
	597	2.013	742	2.519
	651	2.216	772	2.750
	683	2.262	847	2.979

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