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Fatemah Alhamad  
*Edith Cowan University*

Mujahid Ali  
*Edith Cowan University*

Nurudeen P. Yekeen  
*Edith Cowan University*

Muhammad Ali

Hussein Hoteit

*See next page for additional authors*

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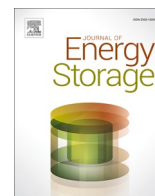
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**Authors**

Fatemah Alhamad, Mujahid Ali, Nurudeen P. Yekeen, Muhammad Ali, Hussein Hoteit, Stefan Iglauer, and Alireza Keshavarz



## Research Papers

# Effect of methylene blue on wetting characteristics of quartz/H<sub>2</sub>/brine systems: Implication for hydrogen geological storage

Fatemah Alhammad<sup>a,b,\*</sup>, Mujahid Ali<sup>a,b</sup>, Nurudeen Peter Yekeen<sup>a,b</sup>, Muhammad Ali<sup>c</sup>, Hussein Hoteit<sup>c</sup>, Stefan Iglauer<sup>a,b</sup>, Alireza Keshavarz<sup>a,b,\*</sup>

<sup>a</sup> School of Engineering, Edith Cowan University, Joondalup, WA 6027, Australia

<sup>b</sup> Centre for Sustainable Energy and Resources, Edith Cowan University, Joondalup, WA 6027, Australia

<sup>c</sup> Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia



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## ABSTRACT

Hydrogen (H<sub>2</sub>) is considered a promising replacement for fossil fuels due to its enormous potential as an environmentally friendly and sustainable option compared to carbon-based fossil fuels. However, storing the vast quantity of H<sub>2</sub> required to satisfy the global energy demand on the earth's surface can be difficult due to its compressibility and volatility. The best option for large-scale storage is underground H<sub>2</sub> storage (UHS), which can be retrieved when needed. Rock wettability is vital in UHS because it determines the H<sub>2</sub> storage capacity, containment security, and potential withdrawal and injection rates. Organic acid inherent in storage formations could make the storage rock H<sub>2</sub>-wet and reduce the residually trapped H<sub>2</sub>; thus, recent research efforts have concentrated on modifying sandstone formations contaminated with organic acid through chemical injections, such as nanofluids and methyl orange. However, previous research has not considered applying methylene blue (MB) as a rock wettability modifier to promote successful UHS. In addition, MB is a toxic constituent of wastewater, causing pollution. This research aims to dispose of MB in underground reservoirs to alter the wettability and increase the H<sub>2</sub> storage capacity, mitigating anthropogenic carbon dioxide emissions. We assess the application of MB as a chemical agent for altering the wettability of quartz contaminated with stearic acid to promote H<sub>2</sub> geological storage. Based on the contact-angle measurements, quartz aged with the optimum concentration of MB (100 mg/L) has the least advancing ( $\theta_a = 35^\circ$ ), and receding ( $\theta_r = 32^\circ$ ) angles at 13 MPa and 50 °C, changing the wettability to strongly water-wet. We demonstrate that an injection of MB into geological formations could make the rock water-wet, promoting H<sub>2</sub> containment security and assisting in the large-scale implementation of UHS.

## 1. Introduction

The world relies on carbon-based fossil fuels to satisfy the increasing demand for energy because of expanding global populations and the high rate of industrialization [1,2,80]. However, burning fossil fuels is the primary contributor to increased carbon dioxide (CO<sub>2</sub>) gas emissions and global warming [3–5]. Investment in renewable energy, such as solar panels and wind turbines, has been considered a feasible alternative to carbon-based fuels, but renewable energy sources are not available at all times of the day and vary seasonally [6,7].

Hydrogen (H<sub>2</sub>) is considered a clean and sustainable fuel compared to fossil fuel alternatives and burns cleanly to produce water vapor, unlike fossil fuels that produce carbon on combustion [8,9]. Although

H<sub>2</sub> has a high energy density (141.86 MJ·kg<sup>-1</sup>), it is a gaseous molecule with a very low density of 0.0084 kg/m<sup>3</sup> at 20 °C and 1 atm [10,11]. In addition, liquid H<sub>2</sub> exists between the critical and triple points, and the rate of boil-off and losses of H<sub>2</sub> from a liquid storage vessel due to leakages from heat have been estimated at 0.4 % per day for a storage volume of 50 m<sup>3</sup> [12,13], suggesting that H<sub>2</sub> storage in liquid form could be very challenging.

Hydrogen can be stored at the surface or underground [14], but the challenges of surface storage of H<sub>2</sub> are enormous [15]. It is difficult to keep O<sub>2</sub> or air from mixing with H<sub>2</sub> within confined spaces because H<sub>2</sub> is a highly flammable fuel requiring a smaller proportion of around 5 % oxygen for combustion compared to the 12 % for fossil fuel equivalents [16]. It also has a broad flammability range of 4 % to 75 % in air and 4 %

\* Corresponding authors at: School of Engineering, Edith Cowan University, Joondalup, WA 6027, Australia.

E-mail addresses: [f.alhammad@ecu.edu.au](mailto:f.alhammad@ecu.edu.au) (F. Alhammad), [a.keshavarz@ecu.edu.au](mailto:a.keshavarz@ecu.edu.au) (A. Keshavarz).

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to 94 % in O<sub>2</sub> [17]. The flammability range of H<sub>2</sub> could result in explosion and fire if the surface storage of H<sub>2</sub> is not properly handled. Along with the maintenance costs and the ability of H<sub>2</sub> to penetrate other substances and diffuse faster, the combination of these factors makes surface storage a very challenging task [18,19].

Consequently, underground H<sub>2</sub> storage (UHS) in subsurface geological formations has been proposed as a potential solution to achieve industrial-scale H<sub>2</sub> storage [20–22]. The advantages of storing H<sub>2</sub> underground in a reservoir are its cost-effectiveness, safety, and security because of the absence of oxygen that could lead to an explosion during surface storage. The stored gas is covered by several kilometers of overlying sealing rock (caprock), permitting high pressure of up to 20 MPa and beyond, with a massive storage volume at a fairly low investment cost [23]. Moreover, UHS provides ample space while requiring relatively moderate ground installations compared to surface facilities. Constructing UHS facilities is cheaper than similar surface facilities; for instance, storing crude oil in salt caverns was estimated at 3 USD per barrel, compared to 15 USD to 18 USD per barrel for above-ground tanks [23].

The feasibility of large-scale H<sub>2</sub> storage in UHS facilities, such as salt caverns, aquifers, and depleted hydrocarbon reservoirs, has been evaluated. Researchers and stakeholders are optimistic that industrial-scale UHS in these storage sites could be achieved based on the experience with successful natural gas storage in these media. For instance, >24 depleted gas reservoir bases have been built in China for seasonal storage [23]. Among the subsurface geological storage (geo-storage) sites, salt caverns have diverse applications for various energy carriers, such as compressed air, crude oil, methane (CH<sub>4</sub>), nitrogen (N<sub>2</sub>), CO<sub>2</sub>, and H<sub>2</sub> [23]. Salt caverns have distinctive benefits and simple structures that could promote favorable UHS. They require a lower quantity of cushion gas because the withdrawal rate and efficiency of injected H<sub>2</sub> are higher than in other geo-storage media. Moreover, biochemical reactions are lower because the saline environments restrict bacterial activities [23,24].

However, the storage volume of salt caverns is lower than depleted oil and gas reservoirs, and the locations of storage facilities are secluded from commercial H<sub>2</sub> utilization centers. Saline aquifers have a huge storage capacity after the depletion of their reservoirs, whereas depleted hydrocarbon reservoirs contain the largest porous space and impermeable overlying rock [25]. Generally, we are more acquainted with the features and working conditions of depleted oil and hydrocarbon reservoirs because of prior experience in storing natural gas. However, the stored H<sub>2</sub> in depleted reservoirs could be contaminated by the remaining hydrocarbon in the storage sites [26,27].

Although the successful storage of CH<sub>4</sub> and air in different underground structures provides valuable insight for H<sub>2</sub> storage, the unique characteristics of H<sub>2</sub>, such as lower density and viscosity and higher volatility, chemical reactivity, and diffusibility, require careful identification of the most suitable storage methods [23]. The idea of UHS is like the underground storage of CH<sub>4</sub>. However, certain differences in the chemical and physical properties of H<sub>2</sub> must be considered to ensure that H<sub>2</sub> can be stored safely underground.

Storage formation wettability and rock-fluid interactions are the main physiochemical parameters governing the potential withdrawal and injection rates of H<sub>2</sub> [28–30]. In a three-phase system comprising rock, H<sub>2</sub>, and brine, the terms *hydrophilic* and *hydrophobic* are commonly used to denote the preference of the brine phase to cover or not cover the rock surface, respectively. When the rock surface is hydrophobic (wetted by H<sub>2</sub>), the H<sub>2</sub> wettability of such rock is high. Conversely, when the rock is hydrophilic (water-wet), the H<sub>2</sub> wettability of such rock is low. The most popular direct method of inferring the H<sub>2</sub> wettability of the rock employs advancing and receding contact-angle measurements.

The classification of wettability of the H<sub>2</sub>-brine-rock system based on contact angles is provided in Table 1 [31–35]. Higher contact angles signify poor water-wetting conditions and lower residual and structural trapping capacities of storage/caprocks [7,32].

**Table 1**

Wettability based on contact angles for H<sub>2</sub>/brine/mineral systems.

Wettability state	Contact angles $\theta$ (°C)
Complete wetting	0
Strongly water-wet	0–50
Weakly water-wet	50–70
Intermediate-wet	70–110
Weakly H <sub>2</sub> -wet	110–130
Strongly H <sub>2</sub> -wet	130–180
Complete H <sub>2</sub> -wet	180

The success of UHS in porous geo-storage formations, such as depleted saline caverns, aquifers, and hydrocarbon reservoirs, is restrained by insufficient information on H<sub>2</sub>/host rock/brine reactivity, host-rock wettability, and rock-fluid interfacial tension, which determines the residual trapping and migration of H<sub>2</sub> in porous formations. The diffusion of stored H<sub>2</sub> via the storage and caprocks also depends on the rock-wetting phenomenon [36].

Capillary/residual trapping and structural trapping are important mechanisms for H<sub>2</sub> immobilization in geo-storage formations [37–40]. During H<sub>2</sub> injection schemes (brine imbibition), the upward migration of the H<sub>2</sub> plume traps H<sub>2</sub> bubbles (ganglia) in the pore space, known as residual trapping, which plays a crucial role in H<sub>2</sub> containment security and the storage efficiency of the storage formations. Structural trapping depends on the integrity and effectiveness of the overlying seal to stop buoyant H<sub>2</sub> migration across the caprock [32].

The rock wettability and capillarity govern the residual trapping phenomenon. The capillarity is expressed via the characteristic capillary pressure equation [41,42,79] (equation 1):

$$P_c = P_{H_2} - P_{water} = \frac{2\gamma \cos(\theta)}{r},$$

where  $P_c$  represents the capillary pressure,  $\theta$  denotes the contact angle (°),  $\gamma$  indicates the H<sub>2</sub>-brine interfacial tension (mN/m), and  $r$  represents the capillary radius or rock pore (m). The leakage and upwelling of the buoyant H<sub>2</sub> across the caprock are high if the buoyancy pressure of the H<sub>2</sub> plume becomes higher than the capillary force [43]. A lower  $\theta$  and high  $\gamma$  guarantee that the threshold capillary pressure is not surpassed.

The rock wettability, usually described by the contact angles of H<sub>2</sub>/brine systems on the mineral surface, has been the subject of recent studies. Previous studies have focused on measuring  $\theta_a$ ,  $\theta_r$ , and equilibrium contact angles at different temperature and pressure values for various rock substrates, such as quartz [44–50], calcite [51], mica [28,30,52], clay [53], basalt [54], and shale [32,55]. The structural and residual trapping capacities of clean and organic-acid-aged storage and caprocks were inferred directly from contact-angle datasets to account for the organic acids inherent in storage formations [2,28,30,52].

These previous studies generally concluded that the residual trapping of H<sub>2</sub> is feasible and that the caprock forms an impenetrable overlying seal if the reservoir rocks remain strongly water-wet (i.e., contact-angle values <90°). However, the containment of H<sub>2</sub> in subsurface rocks could be more complicated due to the influence of biological and geochemical interactions that could result in microbial H<sub>2</sub> consumption and H<sub>2</sub> loss [56,57].

The initial assessment of rock-wetting behavior from contact-angle data was conducted through empirical correlations due to the safety concerns associated with using H<sub>2</sub> in the laboratory, such as H<sub>2</sub> volatility/reactivity and H<sub>2</sub>-induced metal-embrittlement damage. Further, H<sub>2</sub> contact angles were determined at various pressure and temperature values from the empirical relationship between the contact angles and densities of other gases (CH<sub>4</sub>, CO<sub>2</sub>, argon (Ar), N<sub>2</sub>, and helium (He)).

Al-Yaseri et al. [32,53,54] used this technique and predicted that the wetting conditions of the shale, basalt, and clay constituents of geo-storage rock remain strongly water-wet in UHS. Specifically, the equilibrium contact angles of montmorillonite, illite, and kaolinite were

generally lower than  $40^\circ$ , whereas those of shale (with varying total organic carbon) and basalt were lower than  $20^\circ$  at 343 K and differing pressures (5–20 MPa). Based on these findings, Al-Yaseri et al. [32,53,54] concluded that storage rocks and caprocks should remain hydrophilic during UHS because of the low molecular density of  $H_2$ , resulting in little interaction between the  $H_2$  molecules and rock surfaces.

Likewise, Hashemi et al. [58] measured the contact angles of  $H_2$ /brine systems on Bentheimer and Berea sandstone rocks using the captive-bubble technique and observed that all measured angles ranged from  $21.1^\circ$  to  $43^\circ$ , irrespective of the changing geo-storage conditions. Recently, Hashemi et al. [33] further observed that the contact angles of  $CH_4$ -brine and  $H_2$ -brine systems on Bentheimer sandstone ranged between  $25^\circ$  and  $45^\circ$  with varying temperatures ( $30^\circ C$  and  $50^\circ C$ ) and pressures (20–100 bar). They reported that the wetting characteristics of the  $H_2/CH_4$  mixture are like those of pure  $CH_4$  and  $H_2$  gas.

Higgs et al. [49] reported that the in situ contact-angle data measured using the captive-bubble technique for Bentheimer sandstone and quartz ranged from  $39.77^\circ$  to  $59.75^\circ$  at 6.89 to 20.68 MPa. Van Rooijen et al. [59] applied a microscopic technique for measuring the contact angles of  $H_2$  on borosilicate glass and found that the microfluidics remained strongly water-wet at 10 bar, and that  $\theta_a$  varied from  $13^\circ$  to  $39^\circ$  and  $\theta_r$  varied from  $6^\circ$  to  $23^\circ$ . These results generally agreed with those by Al-Yaseri: that underground  $H_2$  sites and the overlying caprocks could remain hydrophilic at downhole conditions. However, these experiments were conducted without accounting for the presence of organic acid contamination inherent in geo-storage rocks.

In contrast, Iglauer et al. [45] measured three-phase contact angles of  $H_2$ /brine/rock systems using the tilted plate method and reported that, although the clean quartz was relatively hydrophilic at geo-storage temperatures ( $20^\circ C$ – $70^\circ C$ ) and pressures (1–250 bar), the rock surface turned weakly water-wet (attaining a contact angle of  $70^\circ$ ) in the presence of  $10^{-2}$  mol/L of stearic acid. Likewise, Ali et al. [44] measured  $\theta_a$  and  $\theta_r$  for the  $H_2$ /brine system on mica as  $106.2^\circ$  and  $97.3^\circ$ , respectively, for  $10^{-2}$  mol/L of lignoceric-acid-aged mica at 25 MPa. They also found that contact angles were higher at high pressure for mica and quartz, whereas contact angles were higher at lower temperatures for mica but were higher at higher temperatures for quartz. These results generally suggest that the organic-acid-modified quartz surface has less water-wet conditions than pure quartz; thus, the rock storage potential and containment safety of  $H_2$  should be lower in the presence of organic acid.

The injection of various chemicals into geo-storage formations prior to  $H_2$  injection has been suggested as a promising technique to reverse the wettability of organic-acid-aged rocks into the original water-wet state to achieve successful UHS [29,60,61]. Ali et al. [29] found that increasing the concentrations of  $Al_2O_3$  nanofluids from 0.05 to 0.25 wt% increases solid-gas interfacial tension and decreases the equilibrium contact angles of mica contaminated with organic acids. Similarly, Pan et al. [61] also found that increasing the  $SiO_2$  nanofluid concentration from 0.05 to 0.1 wt% results in higher rock-gas interfacial tension (for  $H_2$ ,  $CO_2$ , and  $CH_4$ ) for basalt and quartz.

Alhammad et al. [62,63] aged quartz with methyl orange (a toxic wastewater dye usually discharged into the hydrosphere in large quantities) and observed that the hydrophobicity of oil-wet sandstone rock reduced, enhancing oil recovery and increasing gas storage capacity. Methylene blue (MB) is chemical wastewater widely discharged into surface and ground waters, harming human health and the environment. Various research studies have used different methods, such as precipitation, coagulation, chemical oxidation, flocculation, and membrane processes, to remove MB dyes from aqueous solutions [64–68]. Contact-angle data related to using MB to alter rock wettability to promote UHS are scarce. We evaluated the application of MB as an agent for wettability alteration by disposing of it in an underground reservoir. Thus, MB from wastewater can be minimized, ensuring a cleaner environment and increasing the gas storage capacity of underground rock.

Thus, we assess the influence of MB on the  $H_2$  wettability of stearic-acid-aged quartz from contact-angle measurement ( $\theta_a$  and  $\theta_r$ ) using the tilted plate method. The quartz was initially aged in stearic acid ( $10^{-2}$  mol/L) and then in various concentrations of MB (10–100 mg/L). Afterward,  $\theta_a$  and  $\theta_r$  for the stearic acid and MB-modified quartz were measured at varying pressures (1–13 MPa), salinities (0.1–0.3 M), and temperatures ( $25^\circ C$  and  $50^\circ C$ ) to evaluate the effect of MB on  $H_2$  storage capacity and the contaminant security of  $H_2$  in quartz contaminated with organic acid.

## 2. Experimental methodology

### 2.1. Materials

Sodium chloride (NaCl;  $\geq 99.9\%$  pure), n-decane and hydrochloric acid (HCl;  $\geq 99.9\%$  mol% purity), stearic acid ( $\geq 95\%$  mol%), and MB ( $C_{16}H_{18}ClN_3S$ ; Fig. 1) were purchased from Sigma-Aldrich. Quartz chips (20x15x5 mm) were supplied by Ward's Science (Rochester, NY). Deionized water (with electrical conductivity of 0.02 mS/cm; Ultrapure) was from David Grey,  $H_2$  (99.9 mol%), and  $N_2$  ( $\geq 99.9\%$ ) were supplied by Coregas (Perth, Australia). The chemical structure of MB is presented in Fig. 1.

### 2.2. Quartz sample preparation

The quartz substrates were washed with deionized water to remove contamination and dust from their surfaces. Subsequently,  $N_2$  was used to dry the quartz samples, and then they were placed in an oven to dry for 1 h at  $80^\circ C$  to remove the remaining contaminants. Afterward, the cleaned substrates were immersed in NaCl brine (2 wt%), droplets of HCl were added to maintain a pH of 4, and the samples were left for approximately half an hour at ambient conditions. This process can increase the adsorption of stearic acid in quartz substrates [62,71,72].

Then, the substrate was aged in  $10^{-2}$  mol/L stearic acid/n-decane solutions for one week at  $50^\circ C$  to stimulate the adsorption of organics onto the storage rock at realistic geo-storage conditions. Last, the stearic-acid-aged samples were placed in different solutions of MB (10–100 mg/L) to measure their effects on  $H_2$  wettability.

### 2.3. Contact-angle measurement

Fig. 2 illustrates the detailed schematic setup of a contact-angle experiment. The  $\theta_a$  and  $\theta_r$  measurements were performed via a tilted plate goniometric technique at a  $17^\circ$  tilted angle. The substrate was positioned in a high-pressure, high-temperature (HPHT) optical cell, followed by  $H_2$  gas injection at various pressures (1–13 MPa). The HPHT cell was connected to two ISCO pumps. One of the pumps supplied brine, and the other supplied  $H_2$  gas. Teledyne ISCO 250D supplied these two high-precision ISCO syringe pumps with a pressure accuracy of 0.001 MPa [30]. The temperature was equilibrated, and brine droplets ( $6 \pm 1 \mu L$ ) of various concentrations (0.1–0.3 M) were dispensed via a needle onto the quartz surfaces.

The values of  $\theta_a$  and  $\theta_r$  were recorded at the leading and trailing edges of the brine droplet, respectively, using a high-quality video

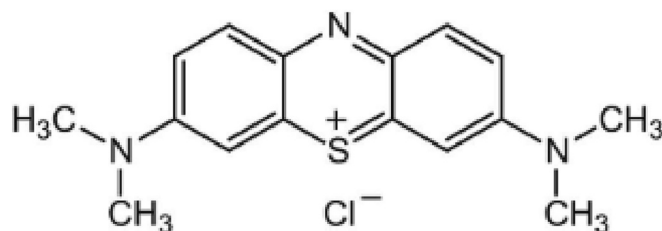


Fig. 1. Chemical structure of methylene blue [69,70].

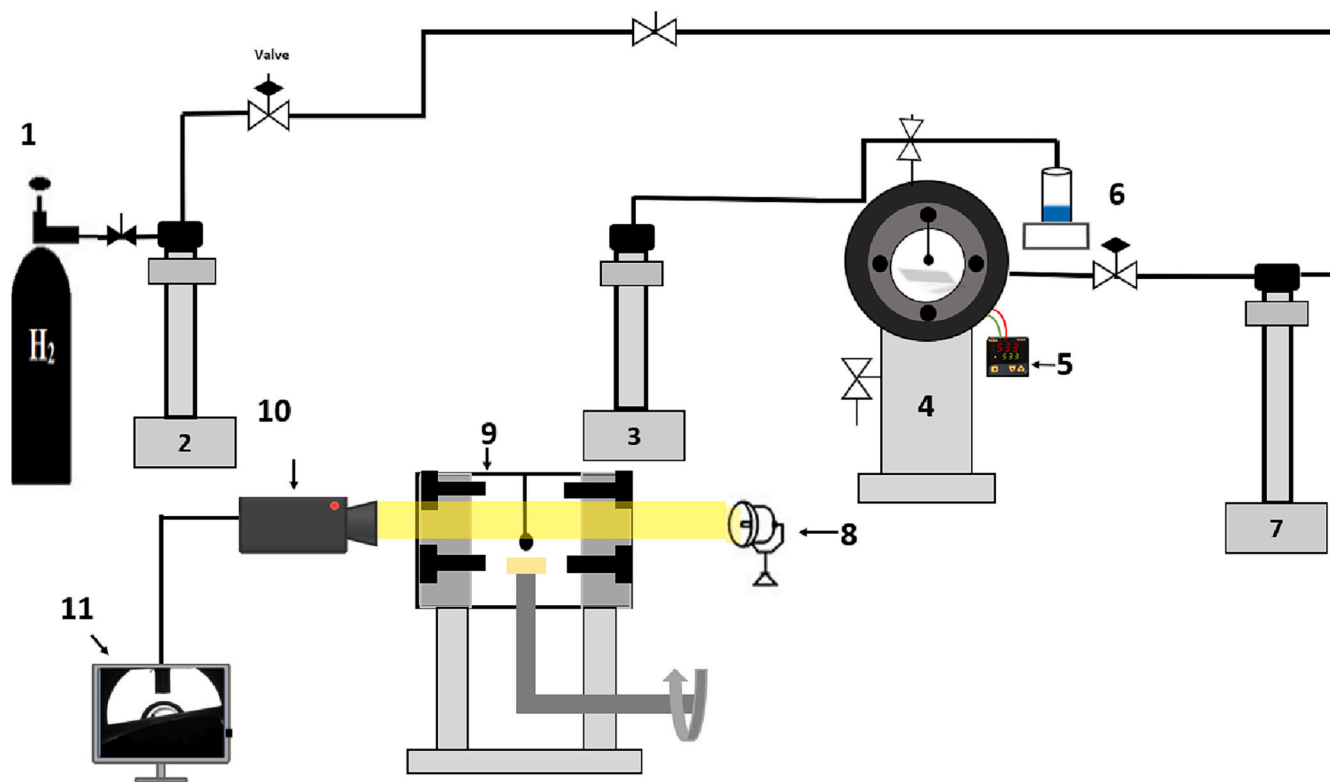


Fig. 2. Graphic of the setup for contact-angle measurement: (1) H<sub>2</sub> tank, (2) syringe pump (H<sub>2</sub>), (3) syringe pump (brine), (4) high-pressure, high-temperature (HPHT) cell with the tilted plate inside, (5) temperature controller, (6) refill/drainage system, (7) HPHT syringe pump to inject H<sub>2</sub> into the cell, (8) light source, (9) HPHT cell with the tilted plate inside (side view), (10) high-speed capturing camera, and (11) ImageJ software for contact-angle analysis.

camera (Basler ace acA640–90 um monochrome USE 3.0) fitted with a Ricoh television lens of 50 mm 1:1.4 with a frame rate of 30 fps and a resolution of 656 × 480 pixels). Contact-angle measurement was conducted in different conditions, and the contact-angle values were estimated using ImageJ software at a standard deviation of  $\pm 3^\circ$  [73].

#### 2.4. Rock surface roughness analysis

Atomic force microscopy (Nanosurf, model C3000) with an NCLAUD cantilever was used to estimate the quartz surface roughness. Atomic force microscopy is an effective technique that uses a cantilever with a sharp tip to scan the quartz substrate and obtain image characteristics, whether the surface is soft or rough. Fig. 3(a) reveals that the surface of the pure quartz is relatively smooth (1.4 nm), which agrees with the literature. Al-Yaseri et al. [74] obtained the surface roughness of pure quartz as 1 nm, whereas Iglauer et al. [45] reported that the pure quartz surface roughness ranged from 1 to 2 nm.

When quartz was aged in stearic acid, the surface roughness increased to 35.5 nm (Fig. 3(b)) due to the chemisorption of the carboxylic group on the quartz surface [74]. Previous research results similarly found that the surface roughness value of quartz increased to 160 to 330 nm when pure quartz was aged in organic acids [44]. However, modifying the stearic-acid-aged quartz surface with 100 mg/L of MB reduced the surface roughness to 18.3 nm, suggesting MB adsorption on the quartz surface. However, the overall change in surface roughness of the quartz aged in organic acid and MB was  $<1 \mu\text{m}$ ; thus, the change in surface roughness due to aging quartz in stearic acid and MB does not significantly affect contact-angle measurements [75,76].

### 3. Results and discussion

#### 3.1. Pressure and temperature effects on contact angles

The influence of temperature and pressure on contact angles is presented in Fig. 4. The results demonstrate that increasing H<sub>2</sub> pressure from 1 to 13 MPa and the temperature from 25 °C to 50 °C results in significant increases in  $\theta_a$  and  $\theta_r$ . For instance, at 25 °C,  $\theta_a$  increased from 86° to 108°, and  $\theta_r$  rose from 80° to 104° with pressures from 1 to 13 MPa. Similarly, at 50 °C and similar pressure conditions,  $\theta_a$  increased from 93° to 115°, and  $\theta_r$  rose from 88° to 110°. These results are consistent with the literature, and previous research has revealed that contact angles are higher at an elevated pressure because of the increased H<sub>2</sub>/quartz surface intermolecular interactions and cohesive energy density due to higher values of H<sub>2</sub> density at high pressures [44–50].

Higher contact angles of H<sub>2</sub>/quartz/brine systems have also been reported in the literature. They are attributed to the increasing tendency of -OH bonds between the silanol group of quartz substrates and H<sub>2</sub>O molecules to be broken at elevated temperatures, resulting in retraction (withdrawal) of water from the quartz surface and a high tendency of the water to become wetted by H<sub>2</sub> [28,30,52].

However,  $\theta_a$  and  $\theta_r$  were generally lower in the presence of 100 mg/L MB. All contact-angle measurements indicated that the quartz substrate remained strongly water-wetting in the presence of MB. For instance,  $\theta_a$  slightly increased from 26° to 35°, whereas  $\theta_r$  barely changed from 20° to 32° with a change in pressure from 1 to 13 MPa at 25 °C. A similar trend occurred at 50 °C;  $\theta_a$  changed from 31° to 44° and  $\theta_r$  changed from 22° to 39° when the pressure rose from 1 to 13 MPa. This result suggests that MB was considerably adsorbed on the stearic-acid-aged quartz altering the H<sub>2</sub>-wet quartz to an initially water-wet condition [62].



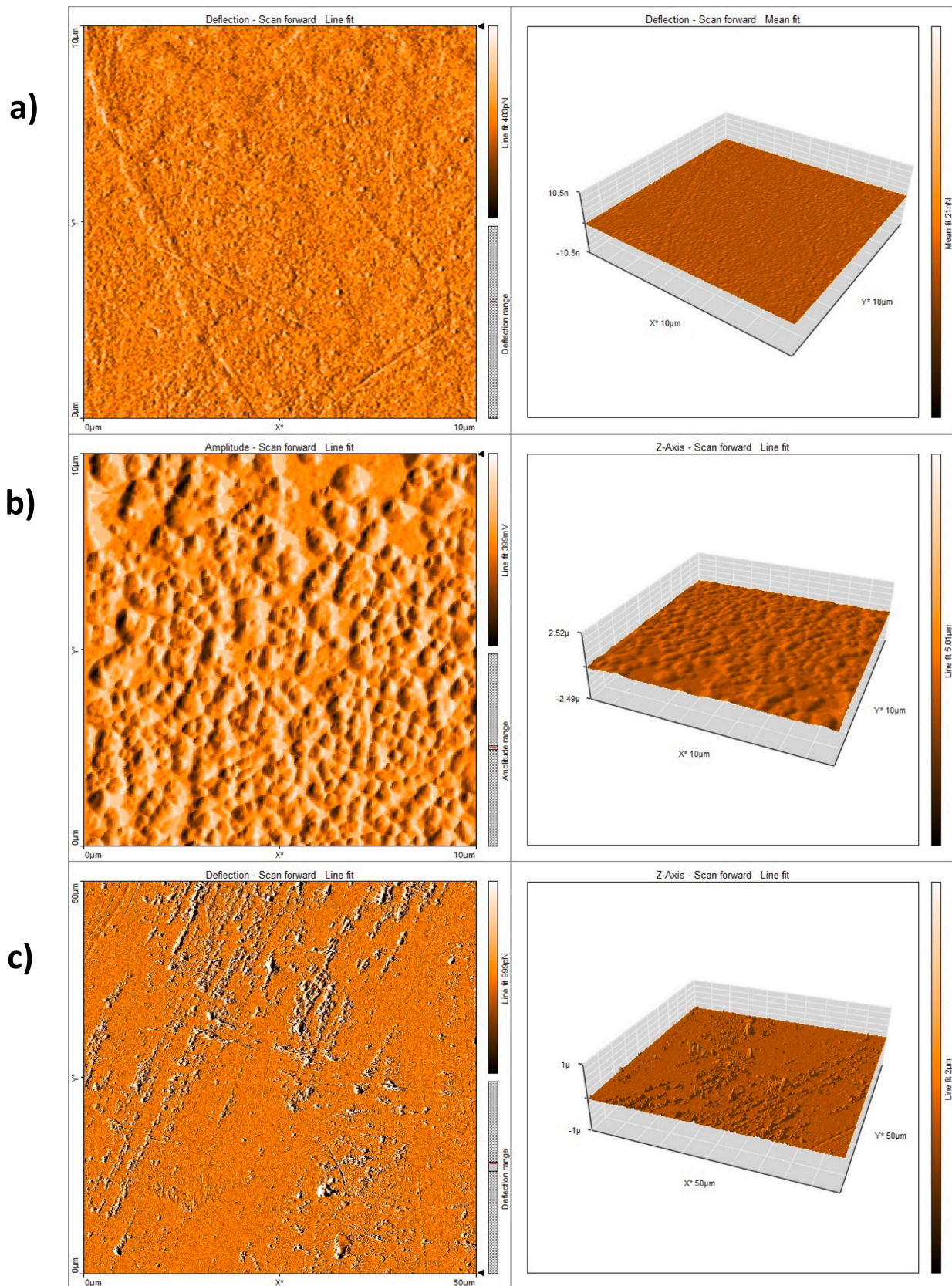


Fig. 3. Micrographs of (a) clean quartz, (b) stearic-acid-aged quartz, and (c) quartz aged with 100 mg/L of methylene blue. Left: two-dimensional; Right: three-dimensional.

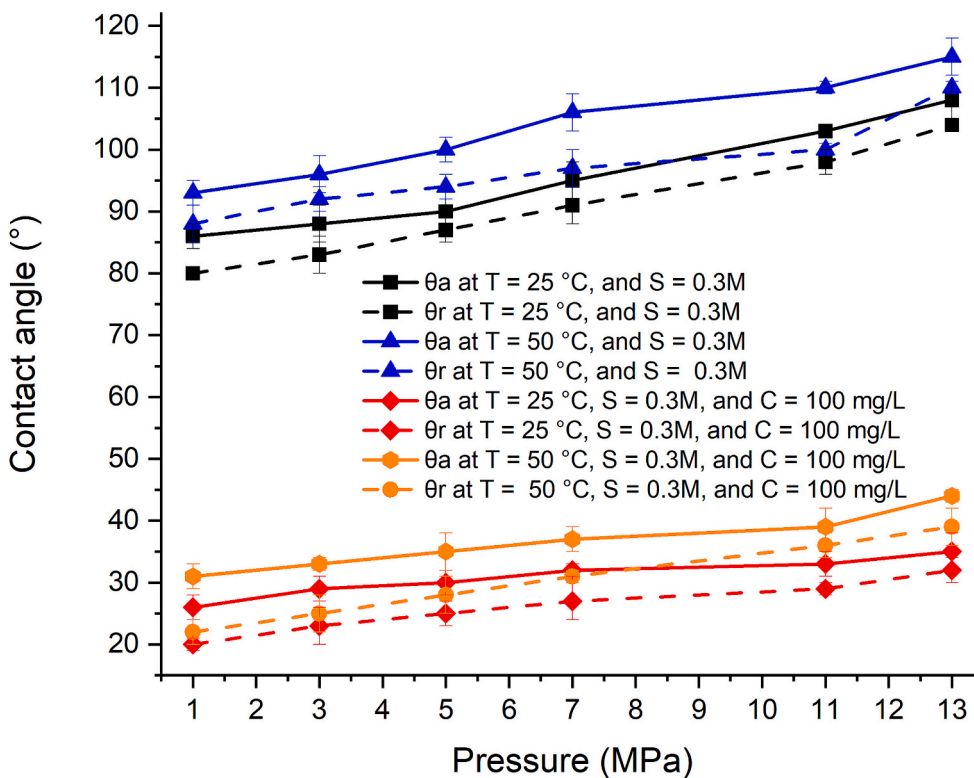


Fig. 4. Influence of temperature and pressure on H<sub>2</sub> wettability of stearic-acid-aged quartz and MB-modified quartz (T = temperature, S = salinity, and C = methylene blue concentration).

3.2. Methylene blue concentration effects on H<sub>2</sub> wettability of organic-acid-aged quartz

Methylene blue is a toxic dye that occurs at a large scale in the textile industry and wastewater. In this research, we used MB to change the wettability of oil-wet stearic-acid-aged quartz to water-wet to promote the storage potential of quartz rock and increase H<sub>2</sub> containment security. Fig. 4 indicates that the pure quartz lost its water-wetness when aged in organic acid. At 13 MPa, the quartz became fully H<sub>2</sub>-wet in the presence of organic acid: ( $\theta_a = 108^\circ$  and  $\theta_r = 104^\circ$  at 25 °C and  $\theta_a = 115^\circ$  and  $\theta_r = 110^\circ$  at 50 °C). The pure quartz surface became hydrophobic in the presence of organic acid due to the esterification of organics on the hydroxyl group of rock surfaces, replacing the hydroxyl group with the silanol group [73].

However, the contact angle of stearic-acid-aged quartz generally decreased with increasing MB concentrations, and  $\theta_a$  and  $\theta_r$  reached the values of 35° and 32°, respectively, at 50 °C and 13 MPa at the optimum concentration of MB (100 mg/L; Fig. 5). The adsorption of MB on the stearic-acid-aged quartz surfaces involves hydrophobic and van der Waals interactions. The molecules of MB bear phenyl rings, methyl groups (hydrophobic group), and the aminopropyl group (hydrophilic group) [77].

The surface accessibility to water increased in the presence of MB, and the chemisorption of MB on stearic-acid-aged quartz surface increased the rock hydrophilicity and reduced the contact angles. The results demonstrated that injecting MB into sandstone geo-storage formations prior to H<sub>2</sub> storage could increase the residual trapping and containment safety of H<sub>2</sub> in such formations.

The illustration of the wettability alteration of pure quartz using stearic acid to H<sub>2</sub>-wet and the modification of stearic-acid-aged quartz with MB to the water-wet state are provided in Fig. 6.

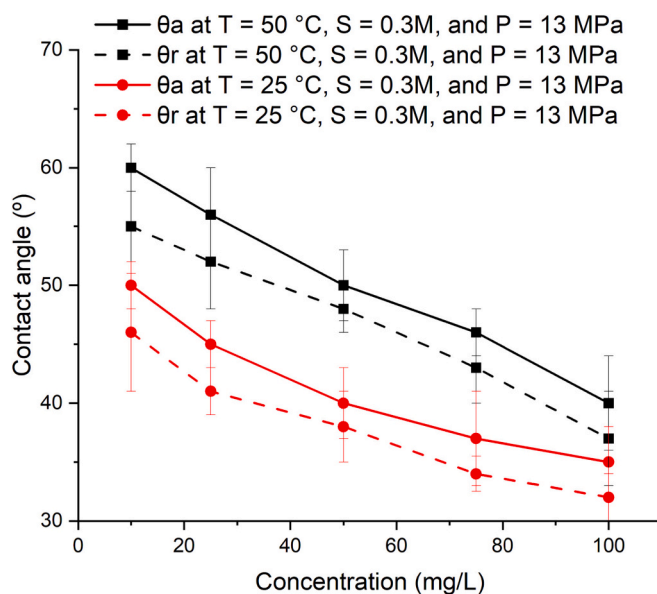


Fig. 5. Effects of concentrations of methylene blue on contact angles (T = temperature, S = salinity, and P = pressure).

3.3. Effects of salinity on quartz aged with stearic acid and methylene blue

The effects of salinity on quartz aged in stearic acid and MB in two salinity scenarios (0.1–0.3 M) presented in Fig. 7 indicate that contact angles generally increase with increasing brine concentration. For instance,  $\theta_a$  changed from 95° to 108° and  $\theta_r$  increased from 90° to 104° when the NaCl concentration increased from 0.1 to 0.3 M at 13 MPa and 25 °C for the stearic-acid-aged quartz. Likewise, at 50 °C with a constant



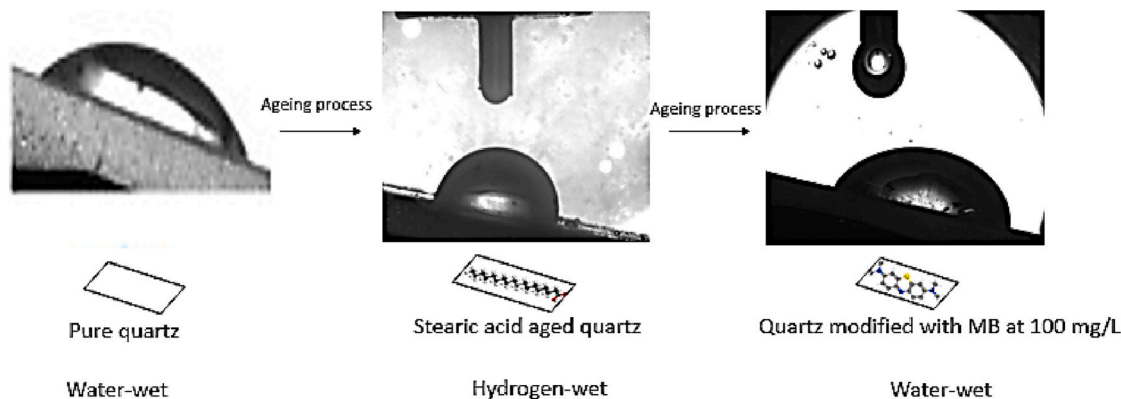


Fig. 6. Wettability alteration mechanisms of pure quartz using stearic acid to reach an H<sub>2</sub>-wet state and modification of stearic-acid-aged quartz using MB to a water-wet state.

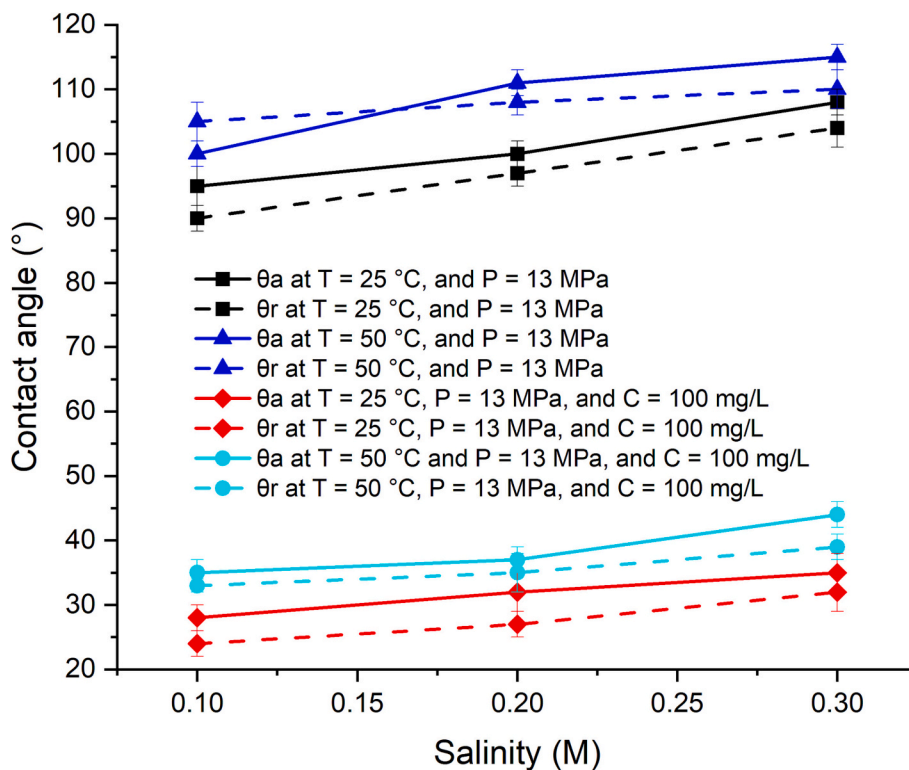


Fig. 7. Salinity effects on contact angles for stearic-acid-aged quartz and methylene blue (MB)-modified quartz (T = temperature, C = MB concentration, and P = pressure).

pressure of 13 MPa,  $\theta_a$  increased from 100° to 115° and  $\theta_r$  increased from 105° to 110°.

A similar trend was observed for the effect of brine salinity on the H<sub>2</sub> wettability of MB-modified quartz, where  $\theta_a$  rose from 28° to 35° and  $\theta_r$  rose from 24° to 32° with increasing salinity from 0.1 to 0.3 M at a pressure of 13 MPa and temperature of 25 °C. At 50 °C and 13 MPa,  $\theta_a$  changed from 35° to 44°, and  $\theta_r$  changed from 33° to 39° with an increasing salinity from 0.1 to 0.3 M. These results are consistent with the literature data. Hou et al. [28] studied the effect of salinity on the H<sub>2</sub> wettability of carbonate rocks and observed that contact angles increased from 48.3° to 71.3° with an increasing concentration of NaCl from 0.1 to 5 wt%.

Pan et al. [78] highlighted that the zeta potential of the shale surface increased due to the addition of NaCl and CaCl<sub>2</sub> into the shale suspension, and the adsorption of divalent ions onto the shale surface resulted in more positive charges. The increased contact angles with increased

salinity were attributed to the compression of the electric double layer by salt, which decreased brine wettability. The surface charge on quartz decreased in salt, decreasing interactions between water molecules and the quartz surface and enhancing the H<sub>2</sub> molecule-quartz surface interaction.

#### 4. Conclusion

The wettability of quartz-H<sub>2</sub>-brine systems is a critical thermophysical parameter that governs the H<sub>2</sub> injection and withdrawal rate, fluid flow behavior, and rock storage potential during UHS. Real geological sandstone formations contain organic acids, which negatively influence residual/capillary trapping of H<sub>2</sub>. This research aimed to evaluate the effects of MB (a toxic wastewater dye that can cause serious damage to the environment) on the H<sub>2</sub> wettability of organic-acid-aged quartz to increase the storage capacity of H<sub>2</sub>. Thus, we measured  $\theta_a$  and  $\theta_r$  for H<sub>2</sub>/

brine systems on stearic-acid-aged quartz, before and after modifying the quartz substrate with MB at geo-storage pressure (1–13 MPa), salinity (0.1–0.3 M), and temperature (25 °C and 50 °C) values. At 50 °C and 13 MPa, the quartz substrate turned completely hydrophobic (H<sub>2</sub>-wet) when aged in stearic acid (10<sup>-2</sup> mol/L) with  $\theta_a$  and  $\theta_r$  values of 115° and 110°. However, in the same conditions, the adsorption of MB on stearic-acid-aged quartz restored the original hydrophilic state (strongly water-wet) of the pure quartz as the  $\theta_a$  and  $\theta_r$  were significantly reduced to 40° (about 65 %) and 37° (about 66 %), respectively. The contact-angle values increased with increasing pressure, salinity, and temperature, suggesting that a hotter reservoir, increased storage depth, and high formation brine concentration could be unfavorable for large-scale UHS in sandstone formations. The injection of MB into underground sandstone formations preceding UHS is an innovative and promising approach for maximizing H<sub>2</sub> geo-storage and minimizing the adverse effects of MB disposal on the environment.

### CRedit authorship contribution statement

**Fatemah Alhammad:** Conceptualization, Methodology, Investigation, Data curation, Writing – original draft. **Mujahid Ali:** Methodology, Visualization, Writing – review & editing, Formal analysis. **Nurudeen Peter Yekeen:** Validation, Writing – review & editing. **Muhammad Ali:** Conceptualization, Validation, Data curation, Methodology, Writing – review & editing, Supervision. **Hussein Hoteit:** Validation, Writing – review & editing. **Stefan Iglauer:** Validation, Writing – review & editing, Supervision. **Alireza Keshavarz:** Resources, Writing – review & editing, Project administration, Supervision.

### Declaration of competing interest

There is no conflict of interest regarding the submitted manuscript.

### Data availability

Data will be made available on request.

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