INTRODUCTION

The enormous demand for crude oil and its extractions from various industrial plants is vitally essential to increase the oil production from hydrocarbon oilfields or develop new wells to supply the requested demand.\(^1\)\(^-\)\(^18\) In this regard, it should be noted that novel methods and techniques that can have a minimal environmental impact\(^19\)\(^-\)\(^31\) and virtually eliminate the unnecessary expenses have always been noticed by petroleum industries.\(^32\)\(^-\)\(^48\) Many companies and industries have proposed novel methods to capture carbon dioxide and store it. It is called carbon capture and underground storage (CCUS). This captured carbon can be injected and stored in underground formations.\(^49\)\(^-\)\(^67\) Due to the complexity of oil production from unconventional reservoirs, selecting optimum oil recovery methods would be of interest as production from conventional reservoirs would be finished in the following decades.\(^68\)\(^-\)\(^80\) Therefore, these reservoirs would be necessary for petroleum industries to be used as fundamental crude oil production.\(^80\)\(^-\)\(^90\)

Carbon dioxide (CO\(_2\)) injection is a well-known EOR method regarding its feasible application rather than other conventional methods.\(^91\)\(^-\)\(^95\) Its application in shale reservoirs is of importance in recent decades. In this method, carbon dioxide has interacted with the formation fluid (oil phase). It is adsorbed on the shale rock, which can be used as a useful guideline for developing unconventional hydrocarbon reservoirs. Thereby, pressure increase would be an essential parameter to increase CO\(_2\) storage capacity; however, temperature increase has a reverse pattern and has caused to decrease the CO\(_2\) storage capacity. The essence of the oil recovery factor from shale reservoirs is another crucial factor that depends on the pressure, temperature, and soaking time factors. CO\(_2\) injection would be a proper (EOR) method to increase the oil recovery factor for higher pressures and temperatures. Therefore, the applicability of CO\(_2\) injection in shale reservoirs could provide efficient results rather than other EOR techniques.

KEYWORDS
CO\(_2\) adsorption, CO\(_2\) injection, pressure impact, shale particle size
way to store CO₂ in underground formation. To nurture the importance of CO₂ adsorption on the oil recovery enhancement and CO₂ storage capacity, crucial parameters such as pressure, temperature, soaking time, and stimulation procedure should be considered. The methods of CO₂ injection contained huff-n-puff (cyclic CO₂ injection) or regular CO₂ injection. Using CO₂ reduces the oil viscosity that can cause the mobilization of more oil volume. Another crucial factor that plays an essential role in the performances of CO₂ is shale mineralogy (due to their high adsorption capacity), shale total organic content (TOC), and interactions of different formation and injected fluids. According to Zhao et al (2015), during the carbon dioxide displacement in low permeable reservoirs, pressure increase has caused to increase the oil mobilization through porous media. This concept was investigated for different pressures in this paper, and it is concluded that due to the more mobilization of the oil phase in higher pressures, the oil recovery factor has been increased.

Although there are few research proposal and field application has been made to improve the oil recovery factor from shale reservoirs, in this paper, it is aimed to experimentally investigate the influential factors such as pressure, shale particle size, and reservoir temperature on the CO₂ adsorption and how it affects the CO₂ storage capacity in underground formations. As pressure and temperature have a potential impact on the CO₂ adsorption, they can cause the mobilization of the oil phase and improve the oil recovery factor. Moreover, the effect of soaking time and stimulation phenomenon would be a proper guideline for the petroleum industries, which is studied and discussed in more detail in this paper.

2 | MATERIALS AND METHODS

2.1 | Materials

Core samples: as each experimental test needs a new shale core sample, about 35 samples were provided from one of the southwest Iranian oilfields. The reservoir characteristics of samples are statistically depicted in Table 1.

| Core Type No. | No. of samples | Diameter and length, cm | Porosity, % | Permeability, mD |
|---------------|----------------|-------------------------|-------------|-----------------|
| Core Type#1   | 10             | 2.54 * 25               | 23.12       | 3.25            |
| Core Type#2   | 10             | 2.54 * 25               | 24.15       | 3.22            |
| Core Type#3   | 5              | 2.54 * 25               | 23.68       | 3.21            |
| Core Type#4   | 5              | 2.54 * 25               | 23.94       | 3.26            |
| Core Type#5   | 5              | 2.54 * 25               | 24.35       | 3.24            |

TABLE 1 | Reservoir characteristics for studied core samples

Shale particle sizes: to consider shale particle sizes during carbon dioxide injection processes, it is necessary to investigate different particle sizes experimentally. It is given to us how different particle sizes influence carbon dioxide adsorption or if the particles can be a proper representative of the shale core samples. To do this, shale core samples pulverized into micro-sized of 50, 200, 400, and 800 μm.

Carbon dioxide: to provide high purity for CO₂, a high-pressurized cylinder was administered. It can provide CO₂ with the purity of 99.9% that used in the experiments.

Crude oil: crude oil composition for this experiment is statistically depicted in Table 2. Oil viscosity and density are 315 mPa s and 1.015 g/cm³, respectively.

2.2 | Experimental methods

To measure carbon dioxide adsorption and carbon dioxide injectivity performances on the oil recovery, two different systems were prepared, as in Figure 1.

The carbon dioxide adsorption and injection process are explicitly explained in Tables 3 and 4 in more detail.

3 | RESULTS

3.1 | CO₂ adsorption

3.1.1 | Shale particle size

Shale core samples with various sizes of 50, 200, 400, and 800 μm. It is given to us how different particle sizes influence carbon dioxide adsorption or if the particles can be a proper representative for shale core samples. The process was performed under reservoir conditions of 60°C and 1500 psi. Core type#1 was used for this experiment. According to the results of our experiments, it is evident that CO₂ adsorption for shale particle sizes of 50, 200, 400, and 800 μm is 87.4, 87, 86.7, and 86.5 SCF/ton, respectively. It is indicated that pulverized shale samples in micro-sized grains would not change the CO₂ adsorption significantly. Therefore, to save the required time for CO₂ measurement in oilfield applications, it
is recommended to use smaller-sized pulverized shale grains to obtain the results.

### 3.1.2 Temperature and pressure impact

To consider the considerable influence of reservoir temperature and injected pressure on the CO₂ adsorption, it is noted that 50 μm of shale particle size was selected for 6 hours to perform the experiments. Core type#1 was used for this experiment. Temperatures of 20, 60, and 100°C under 1500 Psi were implemented in the system to measure CO₂ adsorption. CO₂ adsorption is measured 90, 84, and 80 SCF/ton, respectively, indicating that temperature increase has a decreasing pattern in CO₂ adsorption. Therefore, the capacity of CO₂ storage has been decreased in hydrocarbon reservoirs that can be studied in more detail before any oilfield application processes as it has affected the oil recovery. The pressure parameter is another crucial factor in the CO₂ adsorption measurement performed under the reservoir temperature of 60°C for various 750, 1500, and 3000 psi pressures. Core type#1 was used for this experiment. It is observed that by the increase in pressure, CO₂ adsorption has been increased. It is about 93, 87, and 82 SCF/ton for 3000, 1500, 750 psi, respectively, indicating a higher capacity of CO₂ storage for higher pressures.

### 3.2 Oil recovery

#### 3.2.1 Phase behavior

To perform the profound impact of gas-phase behavior on the recovery factor, supercritical gas phase, liquid phase, and gas phase with the pressures of 1500 psi, 750 psi, and 500 psi were considered in this experiment. The experiment was done under 60°C and 6 hours of soaking time and core type#3. The supercritical gas phase has provided a higher oil recovery factor due to the lower density and can be mobilized more feasible. Another reason for this issue is related to the pressure that has caused more CO₂ adsorption by increasing pressure. Although pressure is a crucial factor in increasing CO₂ adsorption and oil recovery, density would play an important role. For the liquid and gas phase, as gas has a lower density than the liquid phase, its mobilization through pores and cracks was difficult due to the lower pressure. Therefore, the oil recovery factor was lower than the liquid phase.

On the other hand, when the CO₂ is in the liquid phase with higher pressure, the oil recovery factor has been approximately reached a plateau due to the remaining some liquid volumes in the small pores, and this is why it has increased slightly. The highest oil recovery factor is about 40%, 31%, and 24% for the supercritical, liquid, and gas phases (see Figure 2). To ensure the efficiency of the measurements in the experiments, a sensitivity analysis was performed for the gas phase. This experiment was done three times to observe the oil recovery variations.

#### 3.2.2 Pressure and temperature

As explained in Section 3.1, the CO₂ adsorption has increased by the increase in pressure. Therefore, the CO₂ storage capacity has been increased, helping to mobilize more oil volume through porous media. This section wants to experimentally investigate various pressures and their impact on the oil recovery factor. Core type#4 was used for this experiment. The experiments were done under 60°C, 6 hours of soaking time for pressures of 500, 1500, 2500, and 3000 psi to observe the total number of cycles needed for each pressure and measure the oil recovery factor. Due to the higher adsorption and storage capacity of CO₂ in higher pressures (higher CO₂ diffusion through the porous medium), it needs more CO₂ cycles by the pressure increase. Recovery factor is 62 (12 CO₂ cycles), 52 (10 CO₂ cycles), 44 (8 CO₂ cycles), and 28 (6 CO₂ cycles) % for 3000, 2500, 1500, and 500 psi in the maximum point (see Figure 3). To ensure the efficiency of the measurements in the experiments, a sensitivity analysis was performed for 2500 psi. This experiment was done three times to observe the oil recovery variations.

Temperature is another crucial factor in determining CO₂ adsorption and oil recovery factor; in this part, we experimentally investigate the effect of various temperatures. Therefore, the experiments were performed under 1500 psi, 6 hours of soaking time, by utilizing core type#5 for 20, 60, 100, and 120°C. As explained in section 3.1, temperature increase has caused a decrease in CO₂ adsorption; however, it is a reverse pattern with oil recovery. The temperature increase increases it. The reason for this phenomenon is related to the pore size expansion and viscosity reduction in higher temperatures. Moreover, as carbon dioxide has been changed its phase to

| Table 2: Crude oil composition |
|--------------------------------|
| Composition  | Mole%  |
| C₁           | 79.4  |
| C₂           | 8.51  |
| C₃           | 4.6   |
| C₄           | 3.54  |
| C₅           | 1.2   |
| C₆           | 0.35  |
| C₇+          | 0     |
| CO₂          | 0     |
| H₂S          | 0     |
| N₂           | 2.4   |

| Crude oil composition | Mole% |
|-----------------------|-------|
| C₁                    | 79.4  |
| C₂                    | 8.51  |
| C₃                    | 4.6   |
| C₄                    | 3.54  |
| C₅                    | 1.2   |
| C₆                    | 0.35  |
| C₇+                   | 0     |
| CO₂                   | 0     |
| H₂S                   | 0     |
| N₂                    | 2.4   |
FIGURE 1  (A) Carbon dioxide adsorption system and (B) carbon dioxide injection system
supercritical and liquid phase in higher temperatures, it can vaporize retrograde hydrocarbon due to the more content of CO2. Thereby, oil density has been reduced, and it can mobilize more feasible through porous media (see Figure 4). In initial CO2 cycles, the gas might be in the liquid phase, and the reason for the oil recovery factor increase at low temperatures corresponds to the more mobilization of the liquid phase, and then it decreased slightly. Maximum oil recovery factor is 62 (12 CO2 cycles), 47 (10 CO2 cycles), 37 (8 CO2 cycles), and 27 (6 CO2 cycles) for 120, 100, 60, and 20°C. To ensure the efficiency of the measurements in the experiments, a sensitivity analysis was performed for 60°C. This experiment was done three times to observe the oil recovery variations. As temperature increase would be a good point for oil recovery increase, there is an inverse pattern in CO2 storage capacity. Thereby, the reservoir should be studied in more detail that might not be a good choice for CO2 storage.

3.2.3 | Soaking time

To select the optimum soaking time (appropriate interaction time between CO2-oil), different soaking times were considered in the system to observe the oil recovery factor (RF) for each soaking time. All the experiments were done under 60°C, and 1500 Psi and core type#2 were used for this experiment. Soaking time of 4, 8, 12, and 24 hours were performed in the system for 12 CO2 cycles. It is observed that an increase in soaking time has caused to increase in the oil recovery factor. It corresponds to the more interaction time between oil and CO2 that can cause the mobilization of more oil volumes through the porous medium. Another finding of this observation is the soaking time of 12 and 24 hours that there is no significant alteration in recovery factor. It can be used as a guideline for petroleum industries to eliminate the extra expenses of soaking time as the performances can be done in 12 hours and provide relevant results. The highest recovery factor is 58%, 58%, 43%, and 30% for 24, 12, 8, and 4 hours of soaking time, respectively (see Figure 5). To ensure the efficiency of the measurements in the experiments, a sensitivity analysis was performed for 8 hours soaking time.97-107 This experiment was done three times to observe the oil recovery variations.

3.2.4 | Stimulation phenomenon

Due to the fracture’s conductivity impact on more oil mobilization through the shale core samples, it should be noted that making new fractures in the core could provide a higher recovery factor in the less CO2 cycles. The stimulation phenomenon is known as hydraulic fracturing, which can be done by injecting a fracturing fluid to create new fractures or reopening the blocked fractures.105,106 It can provide better conductivity between rock and production point in the shale core samples. The experiments were done under 60°C, and 1500 Psi and core type#2 were used for this experiment. Therefore, it can be concluded that if the cores have more fractures or are stimulated before CO2 injection, it has provided better results by performing fewer CO2 cycles (see Figure 6). To ensure the efficiency of the measurements in the experiments, a sensitivity analysis was performed for unstimulated cores. This experiment was done three times to observe the oil recovery variations.

4 | DISCUSSION

CO2 adsorption is considered one of the critical issues in CO2 storage capacity. It is affected by pressure and temperature. The pressure increase can provide higher CO2 adsorption as CO2 has changed to a supercritical phase, and its density would become lower. Therefore, it can reduce the oil viscosity, and the oil recovery factor has been increased. According to the findings of Davarpanah A. and Mirshekari B. (2019), the solubility of CO2 in crude oil can help to increase oil
### Table 4

| Carbon dioxide injection procedure |
|-----------------------------------|
| **Step** | **Procedure** |
| 1 | Saturate the shale core samples with crude oil in a high temperature-high pressure oven to use the appropriate pore volume injection. This process has been done for seven months to measure the pore volume correctly |
| 2 | Shale cores were vacuumed for 12 h in the presence of a water bath |
| 3 | The syringe pump was used to transfer the pressurized CO₂ into the system. To soak the system with the desired temperature and pressure, CO₂ should be present in the system. Soaking time can be measured at this stage |
| 4 | Oil recovery was measured by weighing the core samples |
| 5 | New cycles were continued to measure oil recovery until the incremental oil recovery was 1% |

**Figure 2** Oil Recovery factor measurement vs CO₂ cycles for different gas-phase behavior

**Figure 3** Oil Recovery factor measurement vs CO₂ cycles for different pressures
mobilization and oil recovery factors due to the oil viscosity reduction. This paper observed that pressure increase would be crucial for the CO₂ storage capacity and oil recovery factor. Thereby, it is concluded that high-pressurized wells would be a good choice for CO₂ storage and performing the CO₂ injection as more oil volumes can be produced.

In contrast, temperature increase has provided a reverse pattern for oil recovery and CO₂ storage capacity. By the
temperature increase, CO₂ adsorption has been decreased, while oil recovery has increased. Therefore, it is indicated that whether a hydrocarbon reservoir might be a good choice for CO₂ injection to improve the oil recovery factor should be checked for CO₂ storage capacity as it might not be a good choice for CO₂ storage capacity. The number of cycles and soaking time effect is another important factor during CO₂ adsorption and injection, which is utterly dependent on the pressure and temperature. Gamadi et al (2013 and 2014) experimentally investigated the soaking time impact on the pressure and temperature. They concluded that soaking time increase has caused to increase the oil recovery factor as the interaction time between oil-CO₂ has been increased. Therefore, the oil phase can be mobilized more feasible, and the oil recovery factor has been increased. In this paper, we observed that the soaking time increase has a limit, and after that, there is no significant increase in the oil recovery enhancement. This point can be used as an oilfield application guideline to reduce the soaking time during operational performances. Furthermore, it is concluded that increasing the number of cycling would propose an industrial point for petroleum industries to produce more oil volumes.

5 | CONCLUSION

Due to the importance of oil production from shale reservoirs, it is vital to provide efficient enhanced oil recovery techniques to improve the oil recovery factor. As CO₂ adsorption is a crucial factor in CO₂ storage and oil recovery, influential factors that affect these phenomena are experimentally investigated in this paper. The main findings of this study are as follows:

- Pulverized shale samples in micro-sized grains would not change the CO₂ adsorption significantly. CO₂ adsorption is measured 90, 84, and 80 SCF/ton for 20, 60, and 100°C, respectively, indicating that temperature increase has a decreasing pattern in CO₂ adsorption. CO₂ adsorption is about 93, 87, and 82 SCF/ton for 3000, 1500, 750 psi, respectively, indicating a higher capacity of CO₂ storage for higher pressures.
- The supercritical gas phase has provided a higher oil recovery factor due to the lower density and can be mobilized more feasible. Due to the higher adsorption and storage capacity of CO₂ in higher pressures (higher CO₂ diffusion through the porous medium), it needs more CO₂ cycles by the pressure increase. The temperature increase has caused to decrease the CO₂ adsorption; however, it is a reverse pattern with an oil recovery factor.
- If the cores have more fractures or are stimulated before CO₂ injection, it has better results by performing fewer CO₂ cycles.

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