

Article

Mitigating Asphaltene Deposition in CO₂ Flooding with Carbon Quantum Dots

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Abstract: Carbon capture, utilization, and storage (CCUS) technology has emerged as a pivotal measure in mitigating global climate change. Notably, CO₂-EOR is esteemed for its dual function of sequestering CO₂ and enhancing oil recovery. However, this process presents challenges related to asphaltene deposition during CO₂ flooding, leading to reservoir damage, such as pore plugging. This study systematically manipulated the factors inducing CO₂-induced asphaltene deposition, elucidating the mechanisms and magnitudes of asphaltene precipitation. Additionally, the study investigated the efficacy of carbon quantum dots (CQDs) in mitigating asphaltene deposition. Experimental findings indicated a positive correlation between asphaltene deposition and level of asphaltene content, CO₂ injection ratio, and temperature. Moreover, with an increase in experimental pressure, the asphaltene deposition rate demonstrated an initial increase followed by a subsequent decline. Leveraging their favorable compatibility with asphaltene, CQDs effectively suppressed the aggregation behavior of asphaltene. In the presence of CQDs, the onset of asphaltene precipitation was delayed from 45 V% to 55 V%, with the highest inhibition rate reaching approximately 36% at an optimal CQD concentration of 20 mg/L. This study proposes a novel approach to address asphaltene deposition issues in CO₂-EOR processes, contributing to the enhancement of recovery rates in low-permeability reservoirs.

Keywords: CCUS; CO₂-EOR; asphaltene deposition; carbon quantum dots; inhibition



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1. Introduction

Carbon dioxide (CO₂) is a major greenhouse gas driving global warming, with energy-related emissions reaching 36.8 Gt in 2022 [1]. Effective CO₂ utilization and removal technologies are crucial for achieving carbon neutrality [2,3]. Carbon capture, utilization, and storage (CCUS) is regarded as a viable option for significantly reducing CO₂ emissions while facilitating the energy transition towards carbon neutrality in the foreseeable future [4]. Among CCUS technologies, CO₂-Enhanced Oil Recovery (CO₂-EOR) stands out because of its dual benefits of CO₂ sequestration and enhanced oil recovery [5]. However, it faces challenges from asphaltene deposition, asphaltene being a complex component of crude oil known for its strong self-association and adsorption properties [6,7]. This deposition leads to issues such as wettability alteration, reduced permeability, and pore throat plugging, ultimately decreasing oil recovery rates and potentially causing reservoir

damage [6,8]. Previous studies have indicated a close correlation between the deposition of asphaltene and operational conditions during CO₂ flooding, such as injection pressure, CO₂ content, and temperature [9–12]. While adjusting operational conditions can mitigate asphaltene-related issues, the detailed mechanisms of asphaltene deposition remain unclear and warrant further investigation.

To address asphaltene precipitation/deposition issues, two primary methods are employed: (1) mechanical or chemical cleaning to eliminate deposited asphaltene and (2) the use of chemical inhibitors or dispersants [13–15]. Nevertheless, mechanical techniques are costly, labor-intensive, and typically restricted to removing deposits near the wellbore. Asphaltene inhibitors are typically surfactants, polymers, ionic liquids, or nanomaterials with specific functional groups and molecular structures that can interact strongly with asphaltene molecules, reducing their aggregation [16]. Surfactants can modify the interfacial properties between fluids, enabling asphaltenes to remain stably dispersed in crude oil. While widely used, they often require high concentrations and have limited applicability [17]. Ionic liquids have excellent stability and solubility in various solvents, and they demonstrate outstanding performance in inhibiting asphaltene deposition. However, their high costs hinder large-scale application [18]. In recent years, nanomaterials have shown great potential in addressing asphaltene deposition due to their unique physicochemical properties. They are considered one of the most promising solutions for asphaltene deposition.

The process of nanoparticle inhibition of asphaltene deposition is complex and influenced by various factors, including nanoparticle type, concentration, and preparation methods, as well as operating temperature, duration, and other relevant parameters. Nasar et al. [19] conducted a comparative analysis of various nanoparticles for inhibiting asphaltene deposition. The results indicated that metal oxides exhibit specificity in adsorbing asphaltene, with the adsorption capacity ranking as follows: CaO > Co₃O₄ > Fe₃O₄ > MgO > NiO > TiO₂. Kazemzadeh et al. [8] demonstrated that SiO₂, NiO, and Fe₃O₄ nanoparticles possess the ability to adsorb asphaltene, with SiO₂ nanoparticles showing the highest efficacy. The research conducted by Hassanpour et al. [20] suggested that Co₃O₄ nanoparticles enhanced the binding of asphaltene to the particle surface, forming more stable asphaltene nanoclusters. The inhibitory effect was concentration-dependent, with Co₃O₄ nanoparticles exhibiting superior inhibitory effects compared to Fe₃O₄ nanoparticles under similar conditions. Mohammed et al. [21], through molecular dynamics simulations, investigated the interaction of asphaltene with the surface of SiO₂. The simulation results suggested that van der Waals interactions and electrostatic attractions to the SiO₂ surface were the primary factors enabling asphaltene adsorption. The response surface methodology (RSM) modeling results found by Mohammadi et al. [22,23] suggested that introducing SiO₂ nanoparticles during the surface treatment of TiO₂ nanoparticles could lead to the formation of Ti-O-Si bonds. This modification improved the nanofluid's stability and increased asphaltene adsorption on the particle surface, leading to a more pronounced inhibition of asphaltene deposition. Bai et al. [24], through numerical simulations, revealed that the incorporation of heteroatoms intensified the interaction between asphaltene and silica. The effectiveness of this interaction was contingent upon the nature and placement of the heteroatoms.

While there are numerous research findings on the use of nanoparticles to control asphaltene precipitation, there is a scarcity of literature specifically addressing the inhibitory effects of carbon nanomaterials on asphaltene deposition. Carbon quantum dots (CQDs), also referred to as “carbon dots” or “carbon nanodots”, are typically defined as carbon nanoparticles with diameters smaller than 10 nm, featuring various surface passivation alterations [25]. Additionally, CQDs exhibit excellent properties such as chemical stability, low toxicity, and ease of functionalization. Compared to nanoparticles like SiO₂ and Fe₃O₄, CQDs possess structural compatibility with asphaltene molecules, rendering them a potential material for addressing asphaltene deposition issues during CO₂ flooding [26–28].

Addressing the aforementioned research gaps, this study elucidates the mechanisms and impact levels of asphaltene deposition under different displacement conditions by

modulating the factors of CO₂-induced asphaltene deposition. CQDs were synthesized, and their performance in inhibiting the aggregation and precipitation of asphaltene driven by CO₂ was investigated. This work introduces a novel solution for mitigating asphaltene deposition issues during CO₂ flooding.

2. Materials and Methods

2.1. Materials

The crude oil used in the experiments was obtained from the Xinjiang oil field, and the fractional compositions are tabulated in Table 1. An amount of 99.99 mol% of CO₂ was purchased from the Beijing Haipu Gas Co., Ltd. (Hefei, China). The trimethyl chloromethane and o-phenylenediamine used in the experiments were procured from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Anhydrous ethanol, dichloromethane, n-heptane, and toluene were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). All chemicals were used directly in the experimental procedures without further purification.

Table 1. Four components of Xinjiang crude oil.

Oil Sample	Asphaltenes m%	Resins m%	Saturates m%	Aromatics m%
JHW10036	9.57	25.14	14.84	50.46
JHW07121	15.58	20.58	16.47	47.37
JHW151	21.11	22.32	16.26	40.31

2.2. Methods

2.2.1. The Core Flooding Experiment

(1) To thoroughly remove internal moisture, the synthetic core was subjected to vacuum drying at 80 °C and −0.1 MPa for 2 h in a desiccator. Subsequently, the core was affixed in a core holder and subjected to a 2 h vacuum pumping process using a vacuum pump. Then, a 12 h simulation of saturation in formation water was conducted.

(2) The core was placed within a core holder, connected to a plunger pump for water flooding, and its permeability was measured. Subsequently, the core was saturated with crude oil for 12 h under a pressure of 18 MPa.

(3) CO₂ was injected into the core to conduct the CO₂ flooding experiment, maintaining a constant injection rate of 0.1 mL/min. The oil samples were collected and analyzed for asphaltene content. During the CO₂ flooding process, the injection volume of CO₂, core pressure variations, and other relevant parameters were continuously recorded.

(4) The core was subjected to multiple washes with petroleum ether, followed by the repetition of steps 1–3. After cleaning, the core's physical parameters, such as permeability, were remeasured. The core was then saturated with water and crude oil. Following this, CO₂ flooding experiments were conducted under varying conditions.

2.2.2. Synthesis of Carbon Quantum Dots

Oil-soluble CQDs were prepared using a solvent–thermal method. Specifically, 100 mg of o-phenylenediamine was dissolved in 40 mL of anhydrous ethanol via 10 min of ultrasonication. Then, the solution was heated to 200 °C for 10 h in a high-pressure, polytetrafluoroethylene-lined reactor. After the reaction, the mixture was cooled to room temperature, centrifuged at a speed of 10,000 rpm for 30 min, and filtered through a 0.22 µm membrane. Subsequently, the filtrate was transferred to a 100 mL round-bottom flask, to which 50 mL of dichloromethane and 100 mg of triethylamine were added.

The mixture was stirred in an ice bath for 1 h. Following this, 700 mg of triphenylmethyl chloroformate was added, and the ice bath stirring was continued for 10 h. After the reaction, the crude product of the synthesized carbon dots was purified through multiple column chromatography steps for further use [29].

2.2.3. Extraction of Asphaltene

Since asphaltene is insoluble in N-alkanes, n-heptane was used as the extracting agent for asphaltene from the crude oil. An amount of 10 g of crude oil sample was weighed and mixed with 400 mL of n-heptane. After thorough mixing, the mixture was subjected to ultrasonication for 2 h at room temperature, followed by magnetic stirring for 24 h to achieve dissolution equilibrium. The solution was then filtered through filter paper, and the filter paper was then extracted with toluene and n-heptane. Finally, the obtained asphaltene precipitate was dried.

2.2.4. Inhibition of Asphaltene Precipitation by Carbon Quantum Dots

In this experimental section, we describe how a static experimental approach was employed to investigate the inhibitory performance of CQDs on asphaltene deposition. n-heptane was selected as the asphaltene precipitant and added to the simulated oil solutions containing asphaltene to induce asphaltene deposition instead of directly employing direct CO₂ flooding for investigation. This is because supercritical CO₂ is a non-polar solvent, suitable for dissolving non-polar substances, and its dissolution performance is similar to that of n-heptane. As the asphaltene in the simulated oil begins to aggregate and subsequently deposit, the transmittance of the solution system changes. By determining the absorbance at various asphaltene concentrations, an asphaltene standard curve can be established, which allowing us to infer the asphaltene concentration corresponding to different absorbance values. Therefore, the extent of asphaltene deposition can be assessed by measuring the change in absorbance of the solution.

Asphaltene-toluene solution was used as the simulated oil system. n-heptane was introduced as an asphaltene precipitant into asphaltene-toluene solutions, both with and without the presence of CQDs, to assess the influence of CQDs on asphaltene aggregation and deposition. First, a solution of asphaltene in toluene with a concentration of 500 mg/L was prepared. This solution was then diluted to prepare several solutions with different concentrations, each containing 100 mg/L of asphaltene in a mixture of toluene, n-heptane, and CQDs. The concentrations of CQDs in these solutions were varied, ranging from 0 mg/L to 25 mg/L. The solutions were subjected to centrifugation for separation, and the supernatant's absorbance at a fixed wavelength was measured using a UV-Visible spectrophotometer (UNICO Instrument Co., Ltd., Shanghai, China). When asphaltene begins to deposit, the absorbance of the solution gradually decreases. Therefore, the volume of n-heptane at the onset of asphaltene deposition is defined as the asphaltene deposition onset point [30]. It reflected the ease of asphaltene deposition, while higher values indicated that it was more difficult for asphaltene to deposit.

By measuring the absorbance of solutions with different asphaltene concentrations, a standard curve for asphaltene concentration was established, enabling the determination of asphaltene concentrations corresponding to different absorbance values. Therefore, changes in the solution's absorbance can be correlated with asphaltene deposition. The asphaltene deposition inhibition rate was determined according to Equation (1).

$$R(\%) = \frac{W_{a0} - W}{W_{a0}} \times 100\% = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

where R is the asphaltene deposition inhibition rate; W_{a0} is the deposition amount without CQDs, mg; W is the deposition amount with CQDs, mg; C_0 is the concentration of deposited asphaltene caused by the addition of n-heptane without CQDs, mg/L; and C is the concentration of deposited asphaltene caused by the addition of n-heptane with CQDs, mg/L.

3. Results and Discussion

3.1. Influence of Injection Pressure on Asphaltene Deposition

Figure 1 shows the deposition rates of asphaltene in the core after CO₂ flooding at different experimental pressures and with oil samples containing varying levels of

asphaltene content. It could be observed that, under identical experimental pressure conditions, the asphaltene deposition rates driven by CO₂ increased with the level of asphaltene content in the oil sample. Additionally, with a constant level of asphaltene content in the crude oil, the asphaltene deposition rate initially increased and then decreased with the rise in experimental pressure. For instance, when the level of asphaltene content in the crude oil is 21.11% and the experimental pressure is 25 MPa, the maximum deposition rate of asphaltene could exceed 70%.

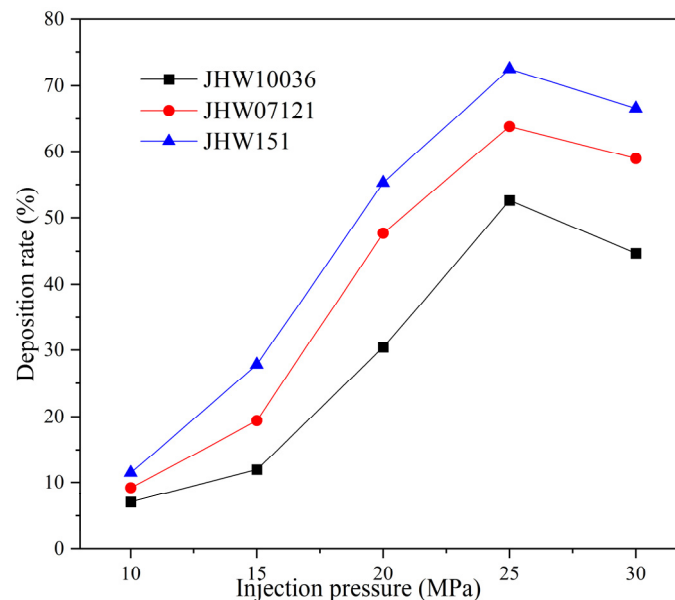


Figure 1. Asphaltene deposition rates at different experimental pressures and crude oil asphaltene content levels.

During the experimental process, the alterations in component content were highly intricate as pressure varied, and asphaltene deposition relied on the combined effects of numerous factors. In the dispersed phase, saturates played a promoting role in asphaltene deposition, while aromatics played an inhibitory role. At lower pressure, injected CO₂ primarily interacted with the lighter components in the crude oil, predominantly inducing dissolution. This led to an increase in saturates and a relative decrease in aromatics. The changes in these two components in the crude oil system disrupted the original dynamic equilibrium. Although it was not enough to directly cause asphaltene precipitation, it could influence the solubility, content, and gelation effect of resins on asphaltenes. As the pressure gradually increased, the extraction effect strengthened, leading to continued changes in saturates and aromatics, thereby enhancing the asphaltene deposition [31,32].

The solubility of CO₂ in crude oil increased with experimental pressure, gradually occupying the space outside the asphaltene originally encapsulated by resin, making it easier for asphaltene particles to coagulate and aggregate, leading to an increase in asphaltene deposition. However, upon reaching a certain pressure level and further increasing, the density of CO₂ molecules in the multiphase system with crude oil escalated, rendering asphaltene more susceptible to dissolution, eventually resulting in a decrease in asphaltene deposition [33].

3.2. Influence of CO₂ Injection Ratio on Asphaltene Deposition

After CO₂ injection, a proliferation of small CO₂ molecules occupied the surface space of asphaltene molecular clusters, resulting in a relative reduction in resin concentration. This reduction prevented the formation of micelles or led to insufficient solvent layers around the micelles, consequently promoting further asphaltene flocculation and deposition. As illustrated in Figure 2, the asphaltene deposition was highly sensitive to CO₂

concentration. With an increase in CO₂ injection ratio, the asphaltene deposition amount rapidly increased. This phenomenon was attributed to the enhanced diffusion of CO₂ molecules into the crude oil as CO₂ concentration rose, disrupting the stable dispersion of asphaltenes in the crude oil [34].

In the dispersed system of crude oil, the asphaltene molecules aggregated into micelle cores through hydrogen bonding and acid–base interactions, enveloped by the maltene, resulting in a homogeneous dispersion of micelles in the crude oil system. After CO₂ was injected, external pressure caused CO₂ to dissolve in the oil. Due to its small molecular size, CO₂ competed for space with resin dispersed around the asphaltene after entering the crude oil, leading to the disruption of the micellar equilibrium and the precipitation of asphaltene particles. With an increase in the proportion and pressure of CO₂ injection, more CO₂ dissolved in the crude oil, causing the precipitated asphaltene particles to gradually aggregate and coalesce, eventually leading to deposition [35]. Furthermore, experimental results indicated that as pressure increased, the trend of asphaltene deposition became more pronounced. At around 25 MPa, the relative asphaltene deposition reached its maximum, and beyond a certain pressure threshold (25 MPa), the deposition started to decrease, indicating a weakening trend. This could be attributed to the fact that, after the CO₂/oil system reached a two-phase equilibrium, further increasing the pressure enhanced the density of the system, reinforcing the solubility of asphaltene and reducing the precipitation of asphaltene.

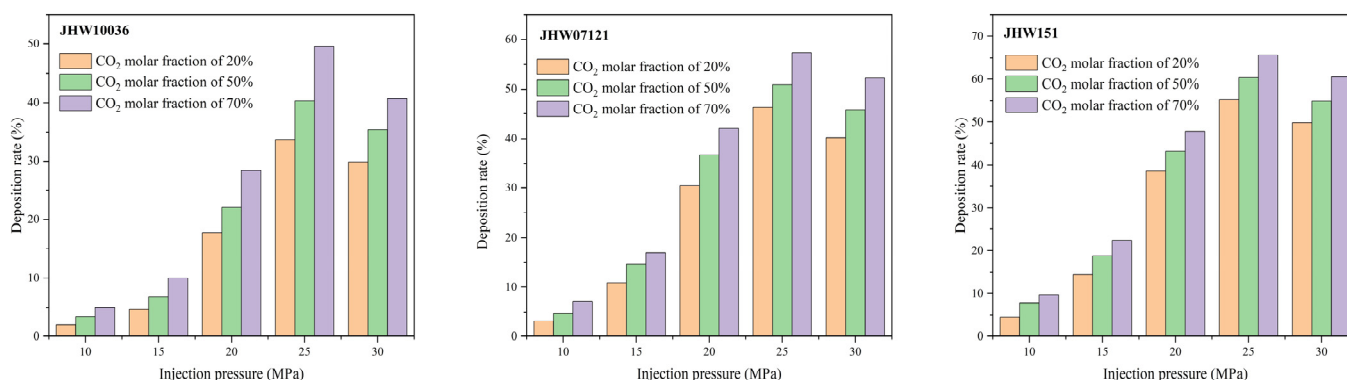


Figure 2. Asphaltene deposition rates under varying CO₂ injection ratios and pressure conditions.

3.3. Influence of Temperature on Asphaltene Deposition

Elevated temperatures accelerated molecular thermal motion within the crude oil system, disrupting the initial equilibrium state, which promoted asphaltene precipitation and caused reservoir damage. The asphaltene deposition rates under different temperature conditions (with controlled experimental pressure at 15 MPa and 100% CO₂ injection ratio) are illustrated in Figure 3. The findings revealed that increasing temperature led to an escalation in asphaltene deposition rates, establishing a positive correlation between temperature and asphaltene precipitation. This phenomenon may be attributed to the intensified thermal motion of CO₂ molecules with rising temperatures, expediting their dissolution in crude oil. This acceleration prompted the gradual occupation of asphaltene surfaces by CO₂ molecules, displacing the colloids that originally covered the asphaltene surfaces. Consequently, asphaltene molecules became exposed, undergoing mutual attraction and aggregation, ultimately forming large particle precipitates that progressively separate and deposit from the crude oil [6].

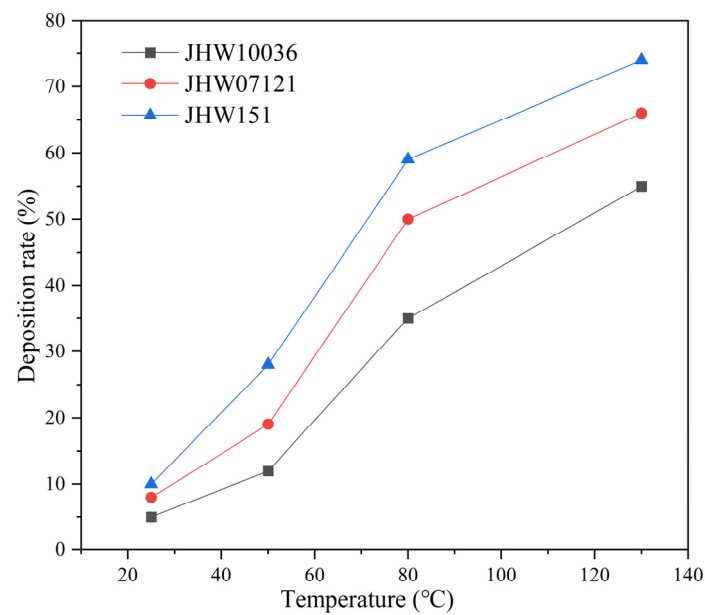


Figure 3. Asphaltene deposition rates at various experimental temperatures.

3.4. Influence of CQDs on the Asphaltene Deposition Onset Point

To investigate the inhibitory effect of CQDs on asphaltene aggregation, the absorbance of asphaltene-toluene-n-heptane-CQD solutions at different concentrations was measured. The influence of CQDs on the asphaltene deposition onset point is shown in Figure 4. When the volume fraction of n-heptane increased, the absorbance of the measured solution initially stabilized and then decreased. This trend arose from the disruption of the original solution equilibrium upon the introduction of the deposition agent, n-heptane. Consequently, asphaltene particles gradually precipitate from the solution, progressively aggregating into larger asphaltene clusters, ultimately leading to deposition and separation from the solution system, thereby reducing the solution's absorbance.

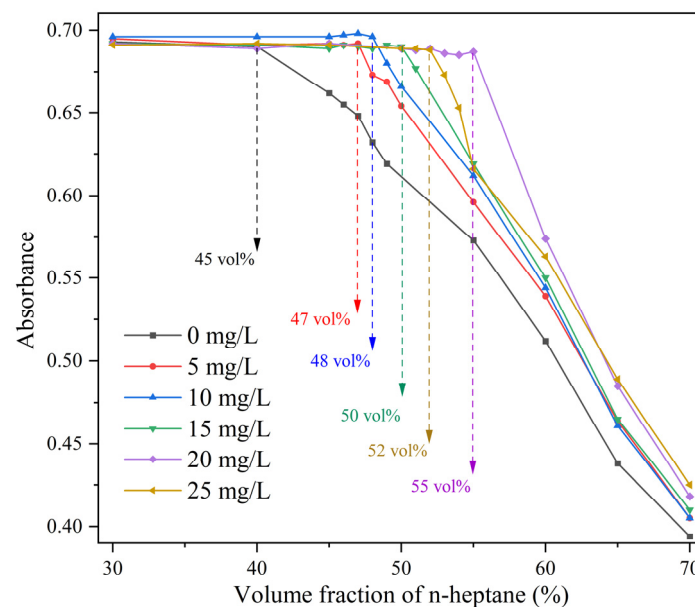


Figure 4. Influence of CQDs on the asphaltene deposition onset point.

The introduction of CQDs caused a delay in the onset of asphaltene precipitation, with the threshold increasing from a maximum of 45 V% (0 mg/L) to 55 V% (20 mg/L). This delay suggested that, during the CO₂ flooding progresses, the deposition of asphaltene

was likely to be postponed, potentially offering a new approach to control and manage asphaltene deposition in oil reservoirs. The aggregation behavior of asphaltene was significantly inhibited by the presence of CQDs, especially within a specific concentration range. Higher concentrations of CQDs exhibited a more pronounced inhibitory effect, indicating a concentration-dependent relationship. The mechanism behind this inhibition can be elucidated by considering the interactions between CQDs and asphaltene. At lower concentrations, CQDs formed strong interactions with asphaltene molecules, leading to the formation of CQD-asphaltene aggregates. These aggregates acted to stabilize asphaltene in the original system, preventing its aggregation and precipitation. However, as the concentration of CQDs increased beyond a certain threshold, isolated CQD particles started interacting with the existing CQD-asphaltene aggregates. This interaction led to the formation of excessively large aggregates, which could promote counterproductive coagulation and settling of asphaltene.

This complex interplay between CQDs and asphaltene aggregation highlights the importance of understanding the concentration-dependent mechanisms involved in the inhibition of asphaltene deposition. Further studies are required to explore the optimal concentration ranges of CQDs for effective inhibition of asphaltene deposition, as well as to elucidate the underlying molecular interactions between CQDs and asphaltene. Such studies could potentially lead to the development of novel strategies for controlling asphaltene deposition in oil reservoirs in order to improve efficiency and enhance oil recovery.

3.5. Influence of CQDs on the Inhibition Rate of Asphaltene Deposition

Figure 5 depicts the impact of CQDs' addition on the inhibition rate of asphaltene deposition in the sample solution with a n-heptane volume fraction of 60%. It is evident that increasing the amount of CQDs could initially cause the inhibition rate of asphaltene deposition to rise and subsequently decline, aligning with the observed trend in the onset of asphaltene precipitation. At a concentration of 20 mg/L, the asphaltene deposition inhibition rate reached a peak of approximately 36%, significantly enhancing the stability of asphaltene and consequently mitigating the risks associated with pore plugging resulting from deposition.

This phenomenon may be attributed to the structural similarity between CQDs and the surface functional groups of asphaltene, which both contain hydroxyl, carboxyl, and benzene ring structures. Their compatibility was enhanced due to the presence of these similar functional groups, facilitating strong hydrogen bonding interactions between the functional groups of CQDs and the active centers of the asphaltene. Additionally, a substantial π - π interaction was observed between the electron clouds on the aromatic rings of the CQDs and asphaltene. These combined interactions contributed to the effective adsorption of asphaltene on the surface of the CQDs.

To further elucidate the mechanisms underlying the inhibitory effect of CQDs on asphaltene deposition, future research should focus on studying CQDs' performance under the more extreme conditions typical of various reservoir environments. This includes investigating the effectiveness and stability of CQDs in inhibiting asphaltene deposition under conditions of high pressure, high temperature, and varying salinity. Additionally, the long-term effectiveness and stability of CQDs in inhibiting asphaltene deposition should be explored to assess their practical applicability in oil recovery operations over extended periods. Moreover, the impact of CQD concentration on the inhibitory performance should be thoroughly investigated to identify the optimal concentration range for effective inhibition of asphaltene deposition. Understanding the concentration-dependent mechanisms involved in the inhibition of asphaltene deposition will be crucial for optimizing the use of CQDs as inhibitors in oil recovery processes. Furthermore, the environmental and economic implications of using CQDs as asphaltene inhibitors should be assessed to evaluate their overall feasibility and sustainability in oil recovery operations, so that informed decisions regarding their deployment can be made.

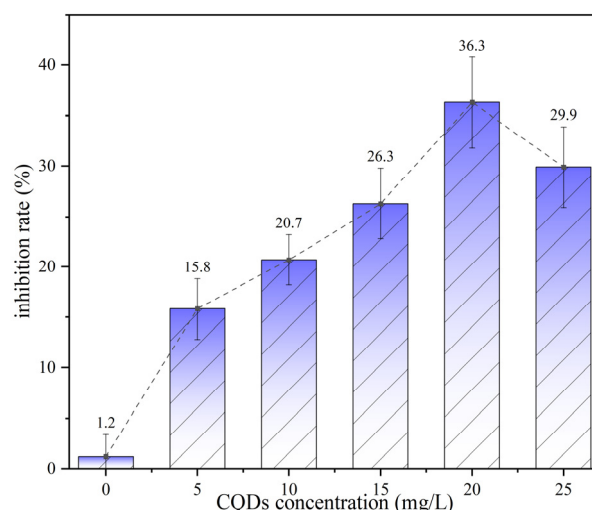


Figure 5. Influence of CQDs on the inhibition rate of asphaltene deposition.

4. Conclusions

This study is grounded in addressing the challenge of asphaltene deposition during CO₂-EOR. By manipulating the inducing factors of CO₂-induced asphaltene deposition, the research elucidated the mechanisms and extent of asphaltene deposition under different experimental conditions. The investigation into the inhibitory effect of carbon quantum dots on asphaltene deposition provided a novel approach to addressing asphaltene deposition issues during CO₂ flooding.

The injection of CO₂ into crude oil resulted in severe asphaltene precipitation and deposition, leading to pore plugging and alterations in pore-wetting characteristics. Core flooding experiments indicated that factors such as level of asphaltene content, injection pressure, CO₂ ratio, and temperature exert influence on asphaltene deposition during CO₂ flooding. The quantity of asphaltene deposition demonstrated a positive correlation with the level of asphaltene content in crude oil, CO₂ concentration (injection ratio), and temperature. However, with the increase in the injection pressure, the asphaltene deposition rate showed an initial increase followed by a subsequent decrease.

CQDs effectively inhibited the aggregation behavior of asphaltene. In the presence of CQDs, the onset of asphaltene precipitation was delayed, with the highest delay being observed from 45 V% to 55 V%, and the optimal CQDs' addition concentration was 20 mg/L. Furthermore, as the quantity of added CQDs increased, the inhibition rate of asphaltene deposition initially rose and then declined, reaching a peak of around 36%. This is attributed to the similarity between the functional groups on the surface of CQDs and asphaltene. CQDs promoted the dispersion of asphaltene through electrostatic, hydrogen bonding, and π - π interactions, thereby alleviating its deposition.

The next step of research should focus on the inhibitory performance of CQDs on asphaltene under the more extreme conditions typical of various reservoir environments, as well as the long-term effectiveness and stability of CQDs. Furthermore, it is essential to investigate the mechanisms of interaction between CQDs and asphaltene at the molecular level. These studies will help optimize the application of CQDs as asphaltene inhibitors, improving the efficiency and sustainability of oil field development.

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Data Availability Statement: The raw/processed data required to reproduce these findings cannot be shared at this time as the data also form part of an ongoing study.

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