CO₂ introduced the coagulation-flocculation of oil acidized wastewater: pollutant removal and cost analysis

Jinyi Qin, Yifan Gong, Chuan Qin, Hailong Meng, Yiwen He, Qingyang Qin and Junfa Gao

ABSTRACT

It is difficult to adjust the pH of oil acidized wastewater rich in Ca²⁺, thus hindering the polyacrylamide (PAM) flocculation. This study aims at accelerating the flocculation process by introducing CO₂ into the water to induce the formation of CaCO₃ nuclei. The order in which CO₂ and NaOH were added affected the floc structures. Compared with CO₂-NaOH-PAM, the flocs of NaOH-CO₂-PAM were more compact and more CaCO₃ crystals were formed. The aqueous Ca²⁺ involved in the reaction reached 20%, and CO₂ utilization was enhanced. The settling time was shortened by half (from 20 to 3 min), and NaOH consumption was reduced by one-tenth (from 0.03 to 0.003 mol), hence significantly reducing the costs. Due to the higher settling rate and shorter contact time, the NaOH-CO₂-PAM flocs adsorbed less so that the residual oil was 124 mg·L⁻¹, while in the case of CO₂-NaOH-PAM it was 88 mg·L⁻¹.

As a promising coagulation aid, CO₂ can also be used to mineralize pollutants in wastewater.

Key words | Ca²⁺, CO₂, floc core, oil acidized wastewater, polyacrylamide

HIGHLIGHTS

● The introduction of CO₂ formed CaCO₃ flocculation nuclei in oil acidification wastewater.
● NaOH-CO₂-PAM required 800 g less NaOH to treat 1 ton of wastewater.
● NaOH-CO₂-PAM reacted with more Ca²⁺, which was 61 times that of CO₂-NaOH-PAM.
● The flocs produced by NaOH-CO₂-PAM were compact and settled fast.
INTRODUCTION

Oil acidized wastewater contains a large amount of Ca\(^{2+}\); hence, its pH value cannot be readily adjusted by adding NaOH. This severely restricts polyacrylamide (PAM) flocculation (Qin et al. 2018). Adding Na\(_2\)CO\(_3\) consumes Ca\(^{2+}\) and solves the bottleneck of pH adjustment. The CaCO\(_3\) flocculation nucleus formed can promote the flocculation of PAM (Qin et al. 2018). However, the high cost of Na\(_2\)CO\(_3\) makes it unsuitable for large-scale industrial wastewater treatment. In this study, CO\(_2\) greenhouse gas was introduced into the oil acidized wastewater for the first time to generate CaCO\(_3\) instead of expensive Na\(_2\)CO\(_3\) additives, thereby not only improving the oil removal efficiency but also being cost-effective.

Rapid industrial development and significant energy demand have led to concomitantly large CO\(_2\) emissions in recent decades (Veetil & Hitch 2020). To reduce CO\(_2\)-induced changes in the environment and ensure the long-term storage of gases, mineral carbonation (in which metal ions can react to form carbonates) has been proposed as a more permanent solution to address these issues (Lackner 2002). The aqueous route seems to be the most effective for carbonate conversion (Gerdemann et al. 2007). Gaseous CO\(_2\) reacts with calcium to form CaCO\(_3\), which is stable and harmless to the environment (Azdarpour et al. 2014; Rashid et al. 2019). However, mineral carbonation has rarely been studied for wastewater treatment.

Under acidic conditions, the CO\(_2\) introduced into the water cannot react with Ca\(^{2+}\). When the pH is neutral, CO\(_2\) dissolves in water to generate H\(_2\)CO\(_3\) or HCO\(_3^-\) (Mun & Cho 2013); only when the pH is $\geq$9, the CO\(_3^{2-}\) required for mineral carbonate can be formed. After introducing sufficient CO\(_2\), NaOH can be used to adjust the pH to above 9, which can then promote reaction between Ca\(^{2+}\) and CO\(_3^{2-}\), leading to the formation of stable CaCO\(_3\) precipitates (Mun & Cho 2013). High Ca\(^{2+}\) concentrations or high CO\(_3^{2-}\) concentrations in strongly alkaline wastewater can improve carbonation efficiency (Azdarpour et al. 2015).

Coagulation-flocculation was widely used for handling dye/textile, pulp/paper, food processing, agricultural, tannery wastewater and landfill leachate (Teh et al. 2016). Coagulation-flocculation treatments were done by adding a coagulant and an auxiliary coagulant. Ferrum chloride, aluminum sulphate and polychlorinated aluminum were commonly used as coagulants (Rui et al., 2012). Macromolecule metal flocculant is a new type of flocculant that is able to remove both turbidity (by electrical neutralization plus bridging effect between particles) and soluble metal ions (coordination and chelation) (Chang et al. 2009; Naushad 2014; Naushad et al. 2016). Ca\(^{2+}\) is common in oil acidized wastewater. Although cationic polyacrylamide (CPAM) modifies the surface of CaCO\(_3\) significantly, improving pollutant removal rate, it requires the environment pH to be 9.5 (Mustafa Bob 2001). However, our aim is to introduce CO\(_2\) to generate metal flocculants, which will not cause significant changes to the pH and will reduce excessive consumption of NaOH. Therefore, the key to regulate flocculation using CO\(_2\) is to accurately produce carbonate nuclei.
The sequence of pH control and CO₂ introduction has been known to affect pollutant removal efficiency and operating costs, determining whether the method is environmentally friendly and economical (Kandji et al. 2017).

Two experiments of CO₂-NaOH-PAM and NaOH-CO₂-PAM were designed. Conductometric titration was used to record the production of CO₃²⁻ during the flocculation process, and paraffin-embedded sediment was used to analyze the floc structure. The residual oil and methyl tert-butyl ether (MTBE) in the supernatant was measured to determine the efficiency of CaCO₃-flocculation. The purpose of using CO₂ gas in oil acidized wastewater was to promote the mineralization of pollutants, affect the flocculation rate of PAM and help reduce atmospheric emissions.

**MATERIAL AND METHODS**

**Materials**

In this investigation, oil acidized wastewater was collected from the Changqing Oil Recovery Station located in Inner Mongolia and was stored at 4 °C before use. Ethylenediaminetetraacetic acid (EDTA), calcium red indicator, petroleum ether, xylene, methanol, benzene, ethylbenzene, hard paraffin with a melting point of 56–59 °C (Leica, Germany), and gelatin were purchased from Sigma-Aldrich (MO, USA). All reagents were of analytical grade. The purity of CO₂ gas was approximately 99.9%, which is suitable for laboratory experiments. The solution was prepared using a deionizing-distilling apparatus and MilliQ apparatus (Millipore, USA).

**Coagulation-flocculation experimental procedures**

Experiments were carried out in a coagulation test mixer (Zhongrun ZR4–6, China), equipped with six 500-mL beakers. A total of 150 mL of wastewater was poured into a 500-mL beaker and aerated using an aeration tray. The optimal carbonation was achieved by controlling the carbonation time and CO₂ flow. The maximum CaCO₃ production was determined by the gravimetric method (see Tables S1, S2, S3).

After determining the optimal CO₂ flow and carbonation time, 150 mL of oil acidized wastewater was used for comparative experiments: (1) 40 mg·L⁻¹ PAM was added as a flocculant for direct flocculation; (2) 1 mol·L⁻¹ NaOH was added to the wastewater to adjust the pH to 12 and then 40 mg·L⁻¹ PAM was added for the coagulation-flocculation experiment; (3) it was first aerated with CO₂ for approximately 30 min, and then 1 mol·L⁻¹ NaOH was added until the pH reached 12. Then 40 mg·L⁻¹ PAM was added for the coagulation-flocculation experiment; (4) CO₂ aeration in the water lasted approximately 1 min, then 1 mol·L⁻¹ NaOH was added until pH reached 12, and finally 40 mg·L⁻¹ PAM was added for the coagulation-flocculation experiment; (5) additional CO₂ aeration in the water lasted approximately 1 min, then 1 mol·L⁻¹ NaOH was added until the pH reached 10, and finally 40 mg·L⁻¹ PAM was added for the coagulation-flocculation experiment; (6) 1 mol·L⁻¹ NaOH was added to the wastewater until the pH reached 10, then CO₂ was added to the wastewater for 1 min, and finally 40 mg·L⁻¹ PAM was added for coagulation-flocculation experiments.

After PAM was added, the stirring speed was increased to 150 rpm for 10 s to allow rapid mixing, then reduced to 30 rpm for 5 min, and the liquid was clarified by allowing it to stand for 10 min at about 25 °C (Amuda & Amoo 2007; Qin et al. 2018). A total of 40 mL of supernatant was taken for ultraviolet (UV) analysis of the oil content (Mao & Han 2013; Qin et al. 2018). 20 mL of supernatant was used for conductometric titration; 5 mL supernatant from coagulation-flocculation was placed in a 10-mL centrifuge tube and 2 g sodium chloride was added to it. After sonication (15 min) and centrifugation (10 min), with the help of a syringe the mixture was passed through a 0.45 μm organic filter membrane and analyzed to determine the benzene series content (benzene, ethylbenzene) using high-performance liquid chromatography (HPLC) (Hanbang NS4201, China) (Na et al. 2011). Flocs (100 μL) were taken out and were embedded in paraffin. The samples were sectioned and floc structure was observed. The remaining flocs were taken out and dried for FTIR analysis (Nicolet6700, Thermo, America) and SEM (Hitachi S-4800, Japan). The concentration of Ca²⁺ in the original wastewater was determined by EDTA titration (Metrom-888 Titrando, Switzerland). All experiments were performed in triplicate and sampled after 10 min (see Supporting Information for detailed methods).

**RESULTS AND DISCUSSION**

**Effect of adding NaOH and CO₂ in different order on oil removal**

As shown in Figure 1(a), when NaOH-CO₂-PAM was used, the oil removal efficiency after 1 min of CO₂ aeration was up to 77%. When the CO₂ aeration was extended to 5 min, the oil removal efficiency dropped to 71% and the residual oil
was 159 mgL⁻¹. This was due to excessive CO₂ gas reacting with the CaCO₃ precipitate and forming soluble Ca(HCO₃)₂. However, continuous CO₂ aeration for over 10 min could slightly improve the oil removal to 74%. This may be due to a large amount of CO₂ gas aeration, resulting in air flotation. Due to the effect of surface tension, the rising bubbles gather dispersed oil droplets, which was beneficial for PAM to effectively trap large oil droplets, which resulted in increased oil removal efficiency.

As shown in Figure 1(b), CO₂-NaOH-PAM was used when the pH was adjusted to 12, CO₂ aeration was controlled for 30 min, and CO₂ flow was 500 mL min⁻¹. The oil removal under these conditions was higher than 400 mL min⁻¹ and 600 mL min⁻¹ CO₂ flow, and the residual oil in the wastewater was reduced to 88 mg L⁻¹. The CO₂ flow of 400 mL min⁻¹ was insufficient, achieving a low efficiency of carbonation (Kandji et al. 2017), resulting in poor oil removal. However, when the CO₂ flow was 600 mL min⁻¹, excessive CO₂ was introduced into the wastewater and the pH value was negatively affected (Rahmani 2018), reaching 5.76, which weakened the effectiveness of PAM flocculation (Qin et al. 2018). When the order of CO₂ and NaOH addition were reversed, wastewater pH was adjusted to 10 and CO₂ aeration was carried out for 1 min, then the pH of the wastewater dropped back to 6.63, and then PAM was added. In the case of NaOH-CO₂-PAM, the highest oil removal efficiency was observed at the CO₂ flow at 500 mL min⁻¹; suggesting that CO₂ flow at this rate for 1 min may result in saturation of the aqueous solution with CO₂. The remaining oil in the wastewater was 124 mg L⁻¹, which was 7% lower than that in the case of CO₂-NaOH-PAM.

As shown in Figure 1(b), when only PAM was used to treat raw wastewater at a pH of 6.54, an oil removal efficiency of 56% was obtained. In the original wastewater, the oil content and suspended solids (SS) were 540 mg L⁻¹ and 564 mg L⁻¹, respectively. As Ca²⁺ was very high, the pH was difficult to adjust. When NaOH was added (and pH increased to 10), PAM showed better molecular chain stretch ability and net capture performance, compared to at pH 6.54 (Besra et al. 2004; Qin et al. 2018); moreover, its oil removal efficiency increased to 66%. Compared with NaOH-PAM, although the pH value of CO₂-NaOH-PAM approached 12, it formed a CaCO₃ flocculation core, thus improving PAM flocculation. The oil removal efficiency improved to 84%, which was 18% higher than that in the case of NaOH-PAM. There was 88 mg L⁻¹ residual oil and the NaOH consumption was 0.03 mol. When the wastewater was aerated with CO₂ for 1 min, the pH of the wastewater was not sufficiently low and the consumption of a large amount of NaOH adjusted the pH to 12; hence, the oil removal efficiency was 78% and the residual oil value was 114 mg L⁻¹. In addition, when CO₂ aeration was carried out for 1 min and pH was adjusted to 10, the NaOH consumption reduced to 0.003 mol. After PAM flocculation, the oil removal efficiency was 74% and the residual oil was 142 mg L⁻¹. When the same amounts of NaOH and CO₂ were consumed, by only changing the addition order of NaOH and CO₂, the oil removal efficiency of NaOH-CO₂-PAM was 77% and the residual oil was 124 mg L⁻¹. Thus, the removal effect of NaOH-CO₂-PAM was better than that of CO₂-NaOH-PAM. Considering consumption of NaOH and CO₂ in series, NaOH-CO₂-PAM was found to be more economical and efficient for oil removal.

**Conversion efficiency of CO₂ gas in oil acidized wastewater**

Oil acidized wastewater contains various metal ions, such as Ca, Fe and Mg²⁺ (see Table S8). The Ksp of CaCO₃ was
3.36 \times 10^{-9} \text{ which is easy to precipitate (Bjørnstad \\ Stamatakis 2006). The content of Mg and Fe in the \text{waste-}\
\text{water only accounts for } 1\% \text{ of } \text{Ca}^{2+}, \text{so the interference}\
effects of other metals are minimal.}

As the pH of the original wastewater was 6.54, CO₂ gas \text{introduced into the \text{wastewater existed in the form of } H_2CO₃}\
\text{in the water. The steps of the carbonation reaction are}\
\text{shown in Figure 2(c) (Rahmani 2018). Figure 2(a) shows}\
\text{wastewater titration with NaOH after introducing 500}\
\text{mL·min}^{-1} \text{ CO}_2 \text{ for 30 min. Before titration, the value}\
of pH \text{ decreased to 5.76. The concentration of } \text{Ca}^{2+} \text{was as}\
\text{high as 6,412.8 mg·L}^{-1} \text{ in the raw wastewater. After}\
\text{adding 0.55 mL of NaOH dropwise, the area of the titration}\
\text{curve with a pH less than 7 was termed the neutralization}\
\text{reaction zone. } HCO_3^- \text{ can only exist when the pH is neutral}\
\text{(Rahmani 2018), and generates unstable } \text{Ca(HCO}_3)_2\text{. There-}\
\text{fore, when NaOH was added dropwise to a total volume}\
of 1 \text{ mL, the pH of the wastewater increased from 7 to 9}\
\text{and increasing amounts of } \text{Ca(OH}_2) \text{ and } \text{Ca(HCO}_3)_2 \text{were}\
\text{gradually formed. Stable } CO_3^{2-} \text{ was formed when the pH}\
exceeded 9 (Figure 2(c)); \text{ therefore, stable calcium com-}\
\text{pounds, } CaCO_3 \text{ and } Ca(OH)_2, \text{ were generated. To obtain}\
\text{stable } CaCO_3, \text{ the pH of the wastewater must be adjusted}\
to >9; \text{ however, hydroxide precipitation is also promoted}\
\text{under these pH conditions, which is undesirable for coagu-}\
\text{lation-flocculation (Kandji et al. 2017). At pH > 12, the slope}\
of the } \text{Ca}^{2+} \text{ curve caused by the dropwise addition of NaOH}\
tended to be stable. It can be speculated that the CO₂ gas}\
dissolved in the wastewater completely formed a precipitate,\text{so the } OH^- \text{ and } \text{Ca}^{2+} \text{ in the water reacted with each other to}\
\text{form stable } \text{Ca(OH}_2).}

When the pH was greater than 12, the Ca(OH)_2 generation \text{could be expressed as } y = -0.45x - 167.82, \text{ and the slope was 0.5, indicating that two molecules of } OH^- \text{ reacted}\
\text{with one molecule of } \text{Ca}^{2+} \text{ to form stable Ca(OH)_2. By}\
\text{extending the slope in the opposite direction, it was deter-}\
m\text{mined that Ca(OH)_2 should be generated in the grid area}\
\text{with a pH of 9–12. Therefore, the generated } CaCO_3 \text{ was}\
\text{formed in the upper right diagonal area above the slope. By}\
\text{integrating the upper right diagonal area, it can be seen}\
\text{that the amount of } CaCO_3 \text{ generated accounts for only}\
\text{0.33% of the total amount of } \text{Ca}^{2+} \text{ in the wastewater. This}\
\text{indicates that little } \text{Ca}^{2+} \text{ is involved in the formation of}\
\text{CaCO}_3 \text{ during the CO}_2\text{-NaOH treatment.}

For the NaOH-CO₂-PAM, 3 mL of NaOH was added \text{to the wastewater to generate Ca(OH)_2 and then}\
\text{500 mL·min}^{-1} \text{ CO}_2 \text{ was introduced for 1 min, so that}\
\text{Ca(OH)_2 could be effectively converted into CaCO}_3 \text{ precipi-}\
tate. The reaction processes likely involved are shown in}\
\text{Figure 2(d) (Praneeth et al. 2020). Figure 2(b) shows the}\
\text{change process of } \text{Ca}^{2+} \text{ in the supernatant (pH = 6.72)}\
titrated by OH^- \text{ after NaOH-CO}_2\text{-PAM treatment. The } Ca^{2+} \text{ content was determined to be 5, 130 mg·L}^{-1} \text{ by area}\
\text{integration. After titrating 6 mL with 1 mol·L}^{-1} \text{ NaOH, the}\
\text{amount of } Ca^{2+} \text{ stabilized, indicating that the residual}\
\text{Ca}^{2+} \text{ in the water was completely consumed. Thus, CO}_2 \text{ gas}\
\text{entering the wastewater could react with } Ca^{2+}, \text{ accounting for 20% of the total amount of } Ca^{2+} \text{ in the wastewater.}

Floc structure formed in CO₂-NaOH-PAM and NaOH-CO₂-PAM

Na₂CO₃ was added to the CaCl₂ solution, and the resulting \text{precipitate is shown in Figure 3(a). The precipitate structure}\
\text{had cubic characteristics and uniform brightness; hence, it}\
\text{was proposed to be CaCO}_3 \text{ crystals. Figure 3(b) shows the}\
\text{precipitate morphology formed after } CO_2, \text{ NaOH and}\
PAM \text{ were added serially; a large and wide white network}
structure was observed. The settlement speed of the produced flocs was higher in the case of CO₂-NaOH-PAM than in the case of NaOH-PAM. The flocs were found to have large gaps and a fluffy structure (when observed at a magnification of ×10; Figure 3(c)), and rare CaCO₃ crystals were noted in the gaps. The wastewater environment was alkaline, and the added PAM molecular chain could be stretched. However, the Ca²⁺ utilized by CO₂-NaOH-PAM only accounted for 0.33%; thus, the generated CaCO₃ floculation core was limited.

The flocs produced by NaOH-CO₂-PAM were compact (Figure 3(d)), and visual observations revealed that they
settled completely within 3 min. CO2 gas entered the wastewater and formed stable CO3^-2. Compared with OH^-2, it preferentially combined with Ca2^+ and produced CaCO3 flocculent cores. After PAM was added, curled flocs wrapped around CaCO3, leading to an increase in floc volume and weight; this facilitated a more rapid settlement of the flocs (Qin et al. 2018). As observed from Figure 3(e) (×10 magnification), these flocculent precipitates were characterized by poor light transmittance and small gaps, indicating that the structure was compact and readily captured CaCO3 crystals. CO2 reacted with 20% Ca2^+ and more CaCO3 flocculation cores were formed. However, the increased amount of CO2 gas in the wastewater lowered its pH and caused the flocs to appear dark. This was mainly because of the poor extension of the PAM molecular chain at low pH.

The structure and morphology of the CO2-NaOH-PAM (Figure S4A) and NaOH-CO2-PAM flocs (Figure S4B) were characterized by scanning electron microscope (SEM). It can be seen from Figure S4A that the surface of CO2-NaOH-PAM floc was smooth and had rare crystals. Compared with Figure S4A, the floc surface of NaOH-CO2-PAM had a lot of crystal particles, and the floc structure was more compact. Hence, this proved the interpretation of Figure 3(d) and 3(e) made earlier.

FTIR was performed to characterize the main functional groups of oil acidized wastewater and two different flocs. As shown in Figure 4, the flocs produced by CO2-NaOH-PAM and NaOH-CO2-PAM have a peak between 1,400 and 1,600 cm^-1, and the Abs of the flocs produced by NaOH-CO2-PAM in this waveband is higher. This is because the CO3^-2 formed by CO2 binds to the surface of the floc, producing C-O bond extension and vibration. The surface functional groups of NaOH-CO2-PAM flocs peak between 3,200 and 3,400 cm^-1, which is caused by free O-H, which means that adding NaOH makes a large amount of OH^- on the surface of the flocs, but CO2 does not consume all OH- to generate CO3^-2 (Awual et al. 2015).

BTEX removal from oil acidized wastewater by CO2-induced PAM flocculation

Oil removal efficiency in the case of NaOH-CO2-PAM was 77%, which was lower than that in the case of CO2-NaOH-PAM (84%). Therefore, in case of the former, it was speculated that some hydrophobic compounds remained in the wastewater. This indicated that the CO2 and NaOH addition sequence indeed affected the removal of benzene and ethylbenzene in coagulation-flocculation.

As seen in Figure 5, the content of benzene in the original wastewater was high, reaching 7.67 mg·L^-1, while the concentration of ethylbenzene was as high as 0.97 mg·L^-1. The concept based on the soil-water partition coefficient, normalized to organic carbon content (Koc), has been widely used to assess the fate of compounds in soil-water compartments (Andrić et al. 2016). The Koc of benzene is 97, which is lower than that of ethylbenzene (622) (Mitra & Roy 1993), due to the dissolution of benzene in water being higher than that of ethylbenzene in water. The octanol-water partition coefficient (Kow) is a simple thermodynamic measurement, which has been extremely useful in estimating the effects of chemical pollutants on aquatic environments. It is an extremely important quantity because it describes the
hydrophobicity or hydrophilicity of a compound, as well as the sorption of the compound to sediments (Ropel et al. 2005). Benzene and ethylbenzene have moderate hydrophobicity (Zytner 1994) and easily adsorb onto solid particles such as PAM. As the log (K_{ow}) of benzene is 2.13 and that of ethylbenzene is 3.15, the adsorption affinity of ethylbenzene is greater than that of benzene (Kenaga 1980; Zytner 1994). Therefore, the removal of ethylbenzene is greater than benzene regardless of sequence of CO_{2} and NaOH addition in the coagulation-flocculation experiments.

When using NaOH-PAM to treat wastewater, the removal efficiencies of benzene and ethylbenzene were 86.3% and 97.4%, respectively. In the control experiment with pH = 12, CO_{2}-NaOH-PAM had a better removal efficiency for benzene and ethylbenzene, up to 92.7 and 99%, respectively. Compared with NaOH-PAM, CO_{2}-NaOH-PAM combined floc adsorption and CaCO_{3} sedimentation, improving the removal effect. The fate of benzene entered the water, making the content of benzene in water higher than that of ethylbenzene. In addition, as the flocs contained few CaCO_{3} crystals, the precipitation speed was slow. This was conducive for PAM and benzene in water coming into contact with each other for a longer duration, resulting in more benzene being captured.

When NaOH-CO_{2}-PAM was used to treat wastewater, the pH was 6.63 and the removal values of benzene and ethylbenzene after treatment were 74 and 97%, respectively. Under the same pH conditions, benzene and ethylbenzene removed by PAM flocculation were 55.7% and 57.2%, respectively, showing that CaCO_{3} formation can effectively remove these compounds in PAM flocculation. The flocs produced by CO_{2}-NaOH-PAM had large gaps, loose structures, and a slow precipitation speed. Compared to the flocs produced by CO_{2}-NaOH-PAM, the flocs formed by NaOH-CO_{2}-PAM were compact, had small gaps, and more CaCO_{3} crystals were produced. Hence, in the case of the latter, the flocs settled more rapidly, reducing the contact time between PAM and benzene; consequently, less amount of benzene was captured from the surrounding water. Therefore, the removal of benzene by NaOH-CO_{2}-PAM was lower than that by CO_{2}-NaOH-PAM.

### Economic evaluation of CO_{2}- induced PAM flocculation

Differences in the order of CO_{2} introduction led to changes in processing and investment costs (Table 1). When CO_{2}-NaOH-PAM was used to remove oil from 1 ton of wastewater, 10^{5} L of CO_{2} gas had to be introduced and 200 L of 1 M NaOH was added. Therefore, the processing cost caused by the introduction of CO_{2} was ¥8,420. However, when NaOH-CO_{2}-PAM was used, only 3.3 \times 10^{3} L of CO_{2} and 20 L of NaOH were required to generate a larger amount of CaCO_{3}. Here, 20% of Ca^{2+} reacted with CO_{3}^{2-} to form CaCO_{3} (Figure 2(b)). As shown in Figure 3(d) and (e), flocs precipitated faster, completing the coagulation-flocculation process. Therefore, the processing cost was reduced to ¥289.

As the amount of PAM used in the two treatment processes was comparable, it was more economical to choose NaOH-CO_{2}-PAM based on the calculation of investment cost. The processing flow rate was set to 13.89 m^{3}·min^{-1}. In the case of CO_{2}-NaOH-PAM treatment, the settling time was 120 min. This required the construction of a 1,667 m^{3} flocculation tank with an investment of ¥16.67 million. In contrast, the settling time was shortened to 60 min in the case of NaOH-CO_{2}-PAM, the required flocculation tank volume was 833 m^{3}, and the investment was only ¥8.33 million, which was half of the former. Overall, NaOH-CO_{2}-PAM greatly reduced the investment and

### Table 1 | Economic comparison of CO_{2}-NaOH-polyacrylamide (PAM) and NaOH-CO_{2}-PAM

<table>
<thead>
<tr>
<th>1 ton of wastewater</th>
<th>CO_{2}-NaOH-PAM</th>
<th>Processing cost</th>
<th>Settling time (min)</th>
<th>Flocculation tank (m^{3})</th>
<th>Investment cost</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amount consumed</td>
<td>Price (¥ L^{-1})</td>
<td>1 M NaOH (L)</td>
<td>Flow: 13.89 m^{3}·min^{-1}</td>
<td>price: ¥10,000 m^{-3}</td>
</tr>
<tr>
<td>CO_{2} demand (L)</td>
<td>1.0 \times 10^{5}</td>
<td>0.083</td>
<td>200</td>
<td>1,667</td>
<td>¥10,000 m^{-3}</td>
</tr>
<tr>
<td>NaOH (L)</td>
<td>8.3 \times 10^{3}</td>
<td>0.6</td>
<td>120</td>
<td>833</td>
<td>¥10,000 m^{-3}</td>
</tr>
<tr>
<td>Processing cost</td>
<td>¥8.42 \times 10^{3}</td>
<td>0.6</td>
<td>120</td>
<td>833</td>
<td>¥10,000 m^{-3}</td>
</tr>
<tr>
<td>Settling time (min)</td>
<td>¥289</td>
<td>120</td>
<td>833</td>
<td>¥10,000 m^{-3}</td>
<td>¥10,000 m^{-3}</td>
</tr>
<tr>
<td>Flocculation tank (m^{3})</td>
<td>1,667</td>
<td>833</td>
<td>833</td>
<td>¥10,000 m^{-3}</td>
<td>¥10,000 m^{-3}</td>
</tr>
<tr>
<td>Investment cost</td>
<td>¥16.67 million</td>
<td>¥8.33 million</td>
<td>¥8.33 million</td>
<td>¥10,000 m^{-3}</td>
<td>¥10,000 m^{-3}</td>
</tr>
</tbody>
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operating costs and hence, is more conducive to the on-site treatment of industrial wastewater.

CO₂ gas of 99.9% purity, as used in the laboratory, is expensive and its mass production is difficult (Zhang et al. 2017; Zhang et al. 2019). Therefore, from an economic perspective, it is more practical and environmentally friendly to use industrial flue gas in actual operation (Zhang et al. 2017). Factories can build trapping devices to collect the flue gas to replace pure CO₂ gas. Direct introduction of the flue gas comprises approximately 20% CO₂, the carbonization efficiency is lower than that of pure CO₂ (Zhang et al. 2017; Zhang et al. 2019). Therefore, in actual wastewater treatment, either the gas pressure can be increased (Azdarpour et al. 2014, 2015) or the carbonation time can be extended (Zhang et al. 2019) to increase the CO₂ concentration, leading to a higher amount of CO₃²⁻ reacting with Ca²⁺ to form the precipitate, improving carbonation efficiency and strengthening flocculation, thereby increasing the efficiency of oil removal from oil acidized wastewater.

**CONCLUSIONS**

The pH of oil acidized wastewater was 6.54, and the concentration of Ca²⁺ was as high as 6,412.8 mg·L⁻¹. Hence, introducing CO₂ into wastewater to form CaCO₃ was proposed as a novel and effective wastewater treatment technology. After the CO₂ gas entered the wastewater, it quickly formed CO₃²⁻ and combined with Ca²⁺ to form a CaCO₃ precipitate, which acted as a nucleus and promoted the flocculation of PAM for oil removal. The reactive Ca²⁺ in CO₂-NaOH-PAM only accounted for 0.33%, while that involved in NaOH-CO₂-PAM reached 20%. The cost of NaOH-CO₂-PAM treatment per ton of wastewater was ¥289, and the investment was only ¥8.33 million. Based on the results, the addition of NaOH, CO₂, and PAM to the wastewater, in the given sequence (i.e. NaOH-CO₂-PAM), is recommended.

NaOH-CO₂-PAM has a good effect in treating oil acidized wastewater because its flocs are compact and form a large amount of CaCO₃ flocculation nuclei, prompting the flocs to settle quickly. The settling time of NaOH-CO₂-PAM was reduced by half, and the consumption of NaOH was reduced by one-tenth. However, it is not as effective as CO₂-NaOH-PAM in removing oil, benzene and ethylbenzene because the flocs produced by NaOH-CO₂-PAM settle too fast, making insufficient contact time between flocs and pollutants. In order to improve the removal of various pollutants in wastewater while maintaining a faster settling speed of flocs, CO₂ aeration can be reduced on the basis of NaOH-CO₂-PAM. It can not only reduce the amount of CaCO₃ produced, slow down settling speed of flocs, but also slightly lower the pH of wastewater and promote better extension of the PAM molecular chain.

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**DECLARATION OF INTERESTS**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

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