The role of sodium carbonate in PAM coagulation-flocculation for oil acidized wastewater treatment

Jinyi Qin, Hainan Wang, Chuan Qin, Hailong Meng, Wengang Qu and Hui Qian

ABSTRACT

The pH value of oil acidized wastewater is relatively low (pH = 6.1), which seriously affects the flocculation of polyacrylamide (PAM). NaOH was used to adjust the pH value, but the maximum was only 7.5. The regulation was limited as the Ca^{2+} in aqueous phase up to 1,350 mg L^{-1} consumed OH^-. A novel formulation of Na_2CO_3 + PAM was proposed to form $CaCO_3$ floc core to facilitate PAM coagulation. When the concentration was above 400 mg L^{-1}, the PAM precipitation tended to be maximum, followed by NaOH adjustment of pH to 8.0 that could enhance PAM flocculation successively. The sewage sludge (SS) remained and residue oil reduced to 25 mg L^{-1} and 34 mg L^{-1} respectively. The analysis of the species and composition of fatty acids indicated that the coagulation-flocculation selectively effected the sedimentation of saturated fatty acids (SAT). This provides a new idea for recovery of high value-added residual oil. The optimal additive of Na_2CO_3 is expected as promising coagulant aid to improve the PAM coagulation-flocculation of oil acidized wastewater.

Key words | Ca^{2+}, floc core, oil acidized wastewater, PAM

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INTRODUCTION

The operation of acid fracturing, which is used to boost yield, is common in oil and gas wells, so oil extraction wastewater possesses high acidity and strong corrosion. As reported in literatures, the wastewater contains large amounts of calcium chloride up to 3×10^3 to 2.8×10^4 mg L^{-1} (Wang *et al.* 2004). The Ca^{2+} in aqueous phase consumes OH^- resulting in difficulty in pH adjustment and water treatment. The conventional treatments so far are composed of flocculation, neutralization, oxidation and AC sorption (Wang *et al.* 2016). But the problem was still not settled perfectly on account of the wastewater characteristic of low pH. In this study, a new approach to increase the PAM flocculation during the Na_2CO_3 addition is investigated. The addition of Na_2CO_3 is not only as an alkaline additive to improve the pH of wastewater slightly, but also coagulates calcium ions

to form insoluble calcium carbonate, the fine precipitates absorbing suspended solids effectively (Hassani *et al.* 2008).

A novel formulation of coagulation-flocculation process was anticipated in wastewater treatment (Hassani *et al.* 2008). Under the high pH conditions, the negative surfaces of calcium carbonate were modified by cationic PAM significantly and increased the adsorption of humic acid (Bob & Walker 2001). However, there has been a long time argument with the role of calcium carbonate in coagulation-flocculation. Apparently, the $CaCO_3$ can easily form a floc core. The precipitates acted by the sweep coagulation mechanism affecting the sewage sludge (SS) removal, separating from water to introduce precipitation of heavy metals, phenolic compounds and long chain fatty acids efficiently (Lee *et al.* 2007; Greenberg *et al.* 2005). The electrical

double layer (EDL) between colloid particles was compressed by the dissolved calcium ion, which made the colloid size bigger and forming flocs easier (Sudoh et al. 2015). When low lime is used in drinking water treatment, the calcium carbonate contributes to PAM coagulation and settlement (Leentvaar & Rebhun 1982). Conversely, the improper way of adding PAM will impede the precipitation of calcium carbonate. The higher concentration induced more convex and concave shapes presented on the surface of calcium carbonate crystals (Peronno et al. 2015).

The lower pH value of oil acidized wastewater weakens the effectiveness of PAM flocculation. To elucidate whether adding Na_2CO_3 assists the formation of $CaCO_3$ floc core and improves the PAM flocculation, the removal of SS and residue oil in supernatant were examined. Comparing the effects of adding PAM and Na_2CO_3-PAM, there is a new insight into the role of Na_2CO_3 in coagulation-flocculation. Moreover, the Na_2CO_3 possibly selectively recycles the high value-added residual oil from wastewater.

MATERIALS AND METHODS

Materials

In this investigation, wastewater was collected from Changqing Oil Recovery Station located in Inner Mongolia, which was stored at 4 °C prior to use. The reagent of EDTA, calcium red indicator, methanol, n-hexane, methyl tert-butyl ether and petroleum ether were purchased from Sigma-Aldrich (MO, USA), respectively. A novel formulation of Na_2CO_3 coagulant (Merck, Germany) PAM flocculants (Cationic C-100, SNF Co., China) was used for SS and oil removal. All the reagents were of analytical reagent grade, and were dissolved in water purified with both a deionizing-distilling apparatus and a MilliQ apparatus (Millipore, USA). The solution pH was measured with a pH meter (TOA DKK, Japan). The concentration of calcium ions was determined by EDTA titration.

Methods

Coagulation-flocculation experimental procedures

Experiments were carried out in a jar-test apparatus, equipped with beakers of 500 mL volume. At the beginning, 200 ml of oil acidized wastewater was taken, coupled with pH adjustment, six strategies of NaOH-Na_2CO_3-PAM

addition were adopted: in the absence of NaOH and PAM, Na_2CO_3 was added with concentrations of 0, 400, 800, 1,600 and 2,000 mg L^{-1} (i.e. 0, 4, 8, 15 and 19 mmolL^{-1}) respectively, to obtain the $CaCO_3$ coagulants. Since the oily wastewater had high polymer residue, 200 mg L^{-1} PAM was used as flocculant, the dosage selection being based on practical application in the oil field (Zhao et al. 2008). Apart from PAM, 0, 30, 60, 120 and 150 mg L^{-1} (i.e. 0, 0.8, 1.5, 3.0 and 3.8 mmolL^{-1}) of NaOH was blended with wastewater in the control. Instead of NaOH, 0, 400, 800, 1,600 and 2,000 mg L^{-1} of Na_2CO_3 were added respectively for each coagulation-flocculation experiments. In the case of NaOH at 120 mg L^{-1}, the experiment was carried out by addition of 0, 400, 800, 1,600 and 2,000 mg L^{-1} Na_2CO_3 separately. Last, when the Na_2CO_3 was maintained at 800 mg L^{-1}, the experiment was conducted by adding NaOH at 0, 30, 60, 120 and 150 mg L^{-1} respectively.

After rapidly mixing for 10 s at 150 rpm and slowly mixing for 1 min at 30 rpm, the liquid was clarified for 10 mins (Amuda & Amoo 2007). 50 ml of supernatant was taken for SS (in mg L^{-1}) gravimetric determination, 40 ml of supernatant was taken for oil content UV analysis, 50 ml of supernatant was taken for fatty acid analysis, 100 μl of flocculate was picked out and diluted with MilliQ water to observe the precipitate by 40× microscope (BX61, Olympus, Japan). Unless otherwise stated, all experiments were performed in triplicate and sampled after 10 mins.

The analysis of oil content

The 40 ml of supernatant from coagulation-flocculation was blended with 10 ml of petroleum ether in 50 ml of centrifuge tube. Sample extraction was conducted with a reciprocate shaker (incubator personal Lt, TAI TEC, Japan) for 2 h; afterwards, the mixture was centrifuged at 10,000 rpm for 10 mins to break the emulsion. The supernatant was withdrawn to measure the UV absorbance (UV 2450 PC, Shimadzu, Japan) at 235 nm (Mao & Han 2013).

The analysis of fatty acid

After saponification and methylation of 0.5 g precipitate, 1 ml of premixed solvent (n-hexane: methyl tert-butyl ether = 1: 1) was added for extraction, and the upper organic phase was taken for the GC-MS analysis.

RESULTS AND DISCUSSION

The formulations of NaOH and Na_2CO_3 effects on the pH value and Ca^{2+} removal

As shown in Figure 1(a), with the increased concentration of NaOH, the pH value of the wastewater rose to 7.9. A plateau was observed at high equilibrium concentrations, suggesting the limited capacity of NaOH to adjust pH. Meanwhile, the discrepancy of pH regulated by NaOH between 1 and 10 mins implied that a weak acid buffer system may consume OH^- as time increases. The original calcium in wastewater was up to 1,350 mg L^{-1} based on the titration of EDTA in the solution. Addition of NaOH from 0.75 mmol to 3.75 mmol resulted in the consumption of Ca^{2+} from 0.4 mmol to 2 mmol, which demonstrated the consumption ratio of $OH^-:Ca^{2+} \approx 2:1$. The Ca^{2+} in the oil wastewater neutralized most of the OH^- to form Ca(OH)2. Although 30 mg L^{-1} NaOH theoretically provided 7.5×10^{-4} mol L^{-1} OH^-, only 6×10^{-7} mol L^{-1}, 0.8 ‰ OH^- was used to adjust the pH value within 1 min. Similarly, there were 4×10^{-7} mol L − 1 and 0.5 ‰ OH^- for the regulation of pH within 10 mins. It is demonstrated that Ca^{2+} and H^+ compete to bind with OH^- and there is greater reactivity of Ca^{2+} than the reaction of H^+.

Figure 1(b) presents the effect of sodium carbonate on the pH value of oil acidized wastewater. The consumption of Na_2CO_3 and Ca^{2+} was 1:1. As the content of Na_2CO_3 increased more than 15 molL^{-1}, the pH value of the solution reached 7.4. Na_2CO_3 was inherently a weak alkaline reagent; the dissolved CO_3^{2-} in the wastewater was rapidly captured by Ca^{2+} to form precipitated nuclei, and the rest of the Na_2CO_3 reacted with H^+ in liquid to present a partial capability for pH adjustment. As shown in Figure 1(a), 4 molL^{-1} Na_2CO_3 cooperated with 0.75 mol L^{-1} NaOH significantly increased the aqueous pH to 8. Here, the ratio of $CO_3^{2-}:Ca^{2+} = 1:1$ and the $CaCO_3$ coagulation was preferentially formed, the reaction of CO_3^{2-} to Ca^{2+} was stronger than that between OH^- and Ca^{2+}. Conversely, 1 ‰ OH^- was used to regulate the pH value and the utilization of NaOH was tripled.

The effect of precipitated $CaCO_3$ on the coagulation and flocculation

It can be seen from Figure 2(a) that the PAM produced floc is a loose group and light grey. The lower adsorption of PAM contributed to the acidic pH of 6. Either the pollutant was in a highly ionized state, where the surface was close to the point of zero charge, or the expanded form of the PAM
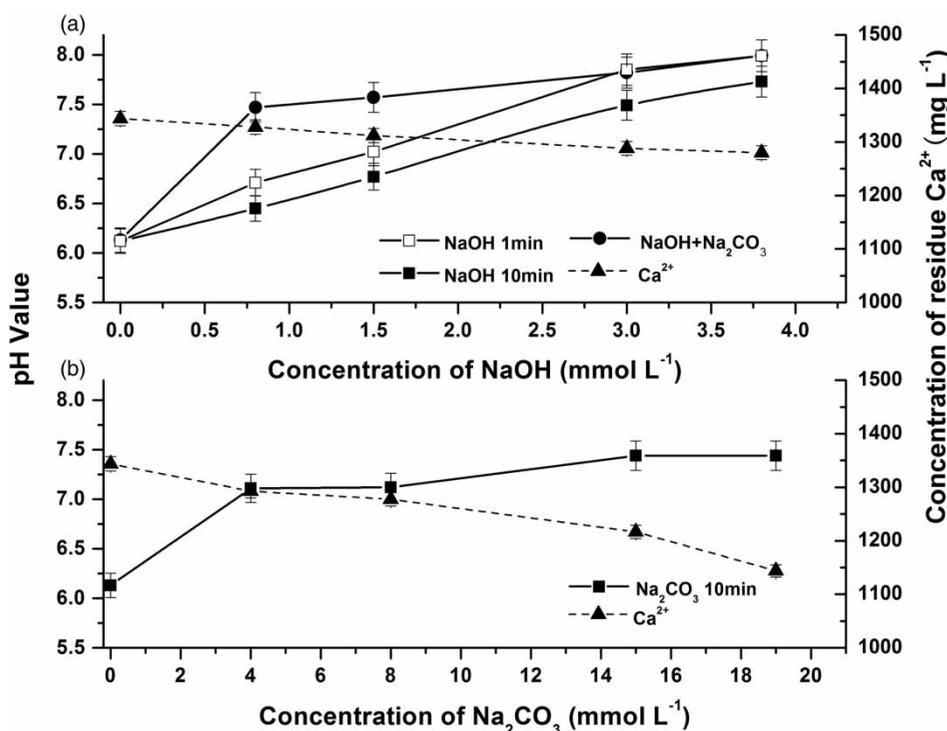

Figure 1 │ The effect of NaOH (a) and Na_2CO_3 (b) on the pH value (solid line) and Ca^{2+} (dashed line) depletion of oil acidized wastewater.
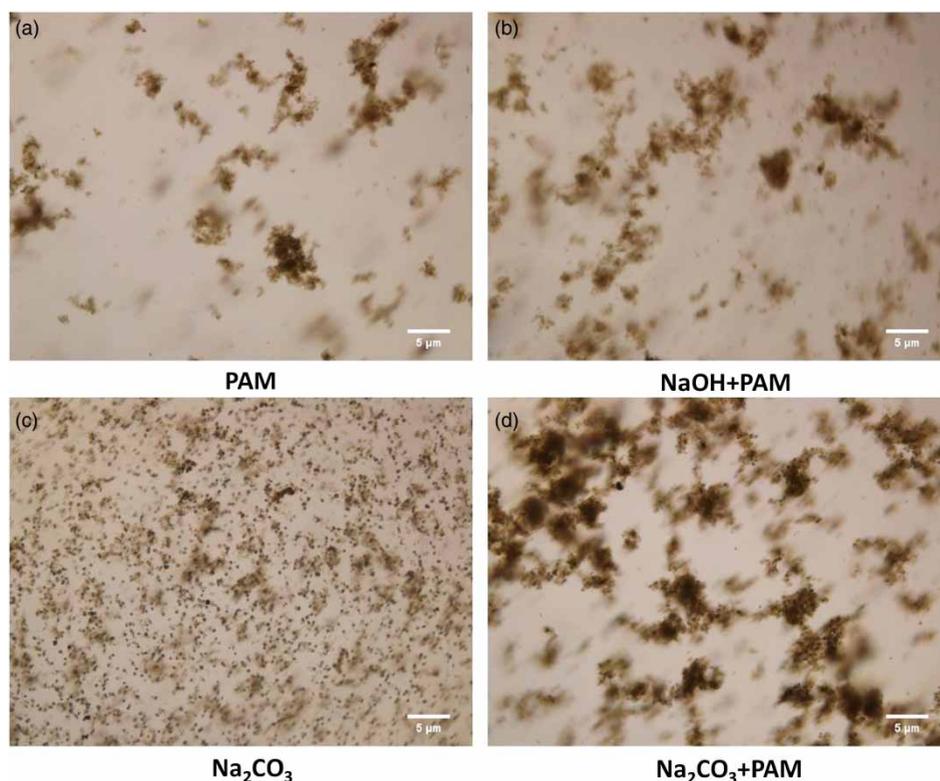
Figure 2 | The coagulation-flocculation precipitates by the addition of 200 mg L^{-1} PAM (a), 120 mg L^{-1} NaOH + 200 mg L^{-1} PAM (b), 800 mg L^{-1} Na$_2$CO$_3$ (c) and 800 mg L^{-1} Na$_2$CO$_3$ + 200 mg L^{-1} PAM (d) to the oil acidized wastewater.

polymer coil, which covered more surface area on adsorption (Besra *et al.* 2004). Additionally, in Figure 2(b), when the pH adjustment was done by NaOH, the number of clusters increased, and the PAM floc became bigger and the settling speed was accelerated. The colloidal particles from long distance came through the bridge to form loose flocs with much internal water (Wu *et al.* 2000). But this looser structure was susceptible to the exterior environment and easily broken up (Jarvis *et al.* 2005).

Figure 2(c) shows the prominent coagulation of Na$_2$CO$_3$ in the wastewater. The CO$_3^{2-}$ is preferentially bound with calcium ions and produces a CaCO$_3$ floc core ($\phi = 1$–2 μm). The coagulated nuclei adsorb contaminants from the wastewater to form fine pellet precipitates and shorten the settling time (Sudoh *et al.* 2015). At a neutral pH of 7.4, CaCO$_3$ particles were neutral or slightly positively charged. Thus, a high adsorption affinity of the negatively charged pollutant was observed. In Figure 2(d), PAM as bridge and CaCO$_3$ as coagulant aid were applied to the wastewater. The flocs coiled around the CaCO$_3$ were supposed to increase the volume and weight of the settling sludge, showing a dark black core. The CaCO$_3$ as the porous adsorbent (Sudoh *et al.* 2015)

improved the cohesive force and made a faster liquid-solid separation, consequently it was no longer vulnerable under the action of hydrodynamic shear force (Gray & Ritchie 2006). Comparing the results of Figure 2(d) to Figure 2(a)–2(c), CaCO$_3$ as the coagulant aid and nuclei was wrapped with coiled floc, which made the biggest clusters, easier settled and harder to break up. As a consequence, the supernatant was clearer and the handling result was more stable.

The effect of sole Na$_2$CO$_3$ on coagulation-flocculation

As shown in Figure 3(a), with the increase in time, the removal of SS and residue oil were improved. The maximal clarifications were 37% and 84% respectively. Comparing the processing effect between 40 and 10 mins, the removal of SS was increased by 19% for 40 mins, while the difference in oil removal was negligible.

Figure 3(b) experiments show that the high concentration of Na$_2$CO$_3$ increased the flocculation and raised the corresponding pH value. As the concentration was 400 mg L^{-1}, Na$_2$CO$_3$ adjusted the pH value to 6, and the removal efficiency of SS was up to 22%. As the
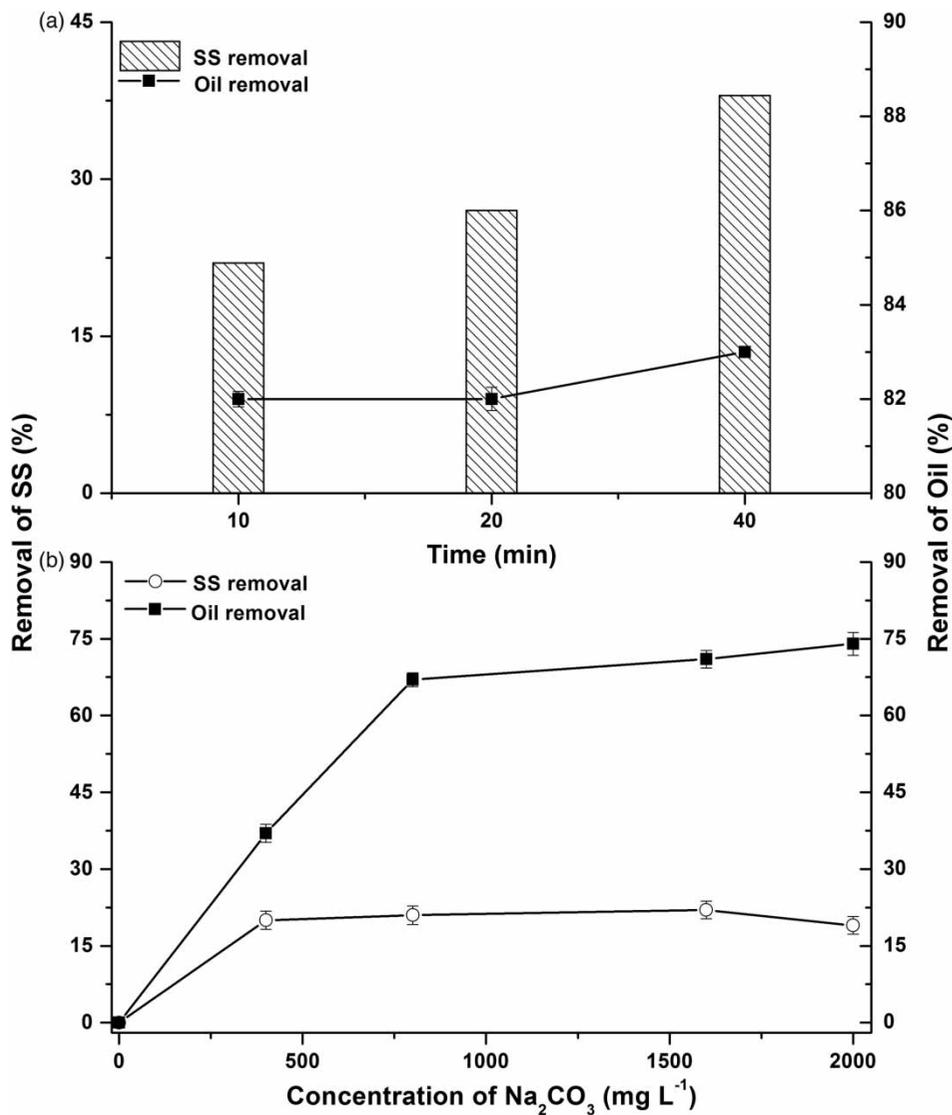
Figure 3 │ The effect of settling time (a) at 800 mg L^{-1} Na$_2$CO$_3$ and varying Na$_2$CO$_3$ concentrations (b) on the removal of SS (square) and residue oil (circle).

concentration was 800 mg L^{-1}, the adjustment of pH value was up to 7, the removal of residue oil attained the maximum of 68%. A plateau was observed at high equilibrium concentrations, suggesting monolayer coverage on the calcium carbonate surface (Bob & Walker 2001). The isoelectric point (IEP) for CaCO$_3$ particles was around pH 8.1 (Thompson & Pownall 1989). When the pH of the solution equaled 6 or 7, the calcium carbonate particles were positively charged or uncharged, and obtained highly adsorptive affinity to the negatively charged pollutant. It can be seen that the increase of the processing time and the amount of sodium carbonate can promote the precipitation, so as to further purify the water quality.

The effect of NaOH on the coagulation-flocculation of Na$_2$CO$_3$-PAM

The result of Figure 4 demonstrates the influence of NaOH on removal of SS and residue oil solely by PAM and combined Na$_2$CO$_3$-PAM respectively. In the absence of NaOH, the SS residue after adsorption of PAM was 293 mg g^{-1}. In contrast, an equivalent of PAM and 800 mg L^{-1} of Na$_2$CO$_3$ were used to remove SS, and SS residue declined to 256 mg g^{-1}.

The adjustment of pH done by NaOH influenced the PAM flocculation and affected the PAM molecular chain stretch (Besra *et al.* 2004). The higher pH gave rise to higher efficiency flocculation. When the concentration of
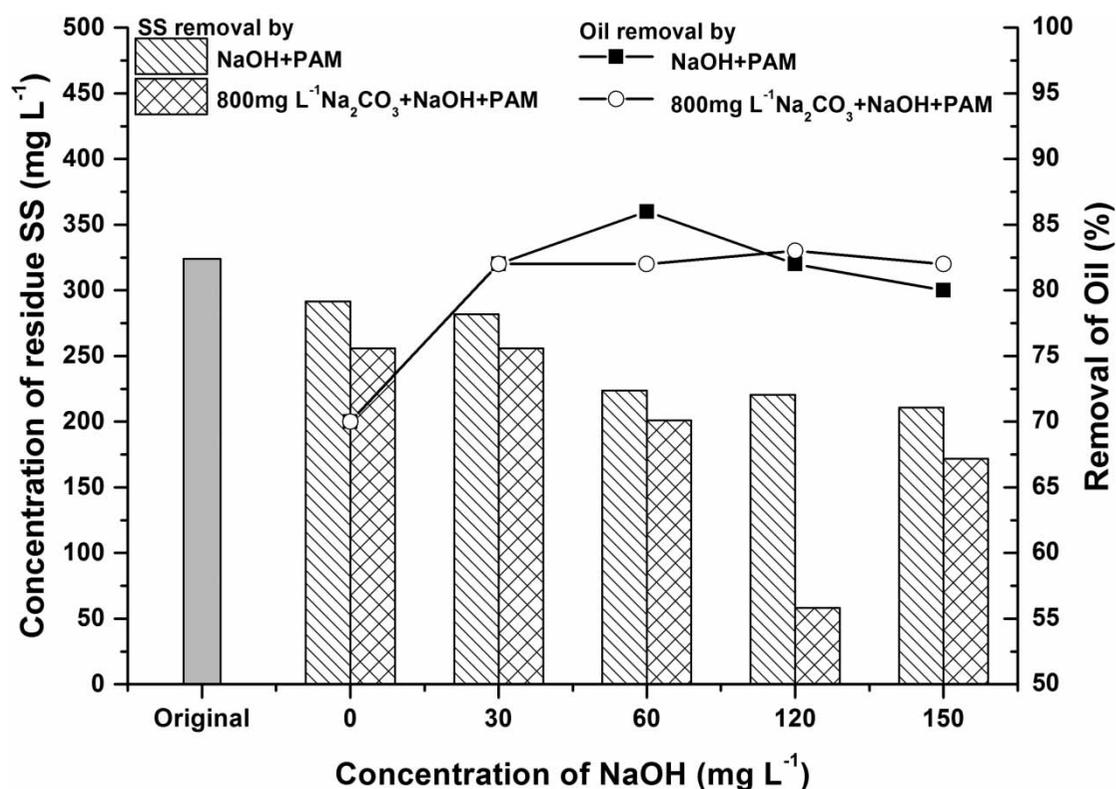
Figure 4 | Effect of PAM cooperated with 0 mg L^{-1} and 800 mg L^{-1} of Na_2CO_3 on the removal of SS (histogram) and residue oil (linear) as a function of NaOH.

NaOH approached 60 mg L^{-1}, the PAM flocculation attained its maximum. The SS residue was lowest at 217 mg L^{-1} and the removal ratio of oil was highest at 88%. However, a plateau was observed at high equilibrium concentrations of NaOH, suggesting pH in a certain range can promote PAM flocculation.

As can be seen, the removal of residue oil and SS by PAM-CaCO$_3$ was better than the sole function of PAM. Specifically, when the Na$_2$CO$_3$ and NaOH were added at 400 mg L^{-1} and 120 mg L^{-1} respectively. The SS declined to 10 mg L^{-1} and 97% of the removal ratio, while the reduction of residue oil was around 85%. This was consistent with the values in the literature (Bob & Walker 2001); cationic polyacrylamide cooperated with calcium carbonate particles to promote the adsorption, and so on to increase of the flocculation effect. However, the removal was influenced both by electrostatic interactions and chemical interactions between contaminant particles and PAM-CaCO$_3$. Petrovic et al. pointed out that the ligand exchange played a role in adsorption of calcium (Petrović et al. 1999). In this work, the experimental environment was carried out at pH about 7.5, the net electrophoretic mobility of PAM-CaCO$_3$ particles was positive (Bob & Walker 2001), and

facilitated the attachment of SS and oil to PAM-CaCO$_3$. However, it cannot interpret an increasing removal of SS and oil corresponding with the increase in NaOH. We assumed that the higher pH had a more significant effect on the negative charge of the contaminant colloidal, which resulted in the higher amount of adsorption by PAM-CaCO$_3$.

The effect of Na$_2$CO$_3$ on the PAM coagulation

As Na$_2$CO$_3$ increased, the pH value rose to 7.4 and 7.7 in the absence and presence of 120 mg L^{-1} NaOH respectively (shown in Figure 1(a)). A steady stream of porous CaCO$_3$ was generated to attach more contaminants (Sudoh et al. 2015). Figure 5 demonstrates the performance of coagulation-flocculation as a function of Na$_2$CO$_3$. Calcium ions were homogeneously blended with SS and residue oil beforehand in wastewater, which blocked the negatively colloidal particles and acted as bridges between functional groups of the two adjacent molecules (Duan et al. 2003). CaCO$_3$, acting as a coagulant aid by forming larger flocs, shortened the settling time for the removal of DOC (Sudoh et al. 2015). The removal efficiency of SS and residue oil by adding Na$_2$CO$_3$ and PAM simultaneously was better
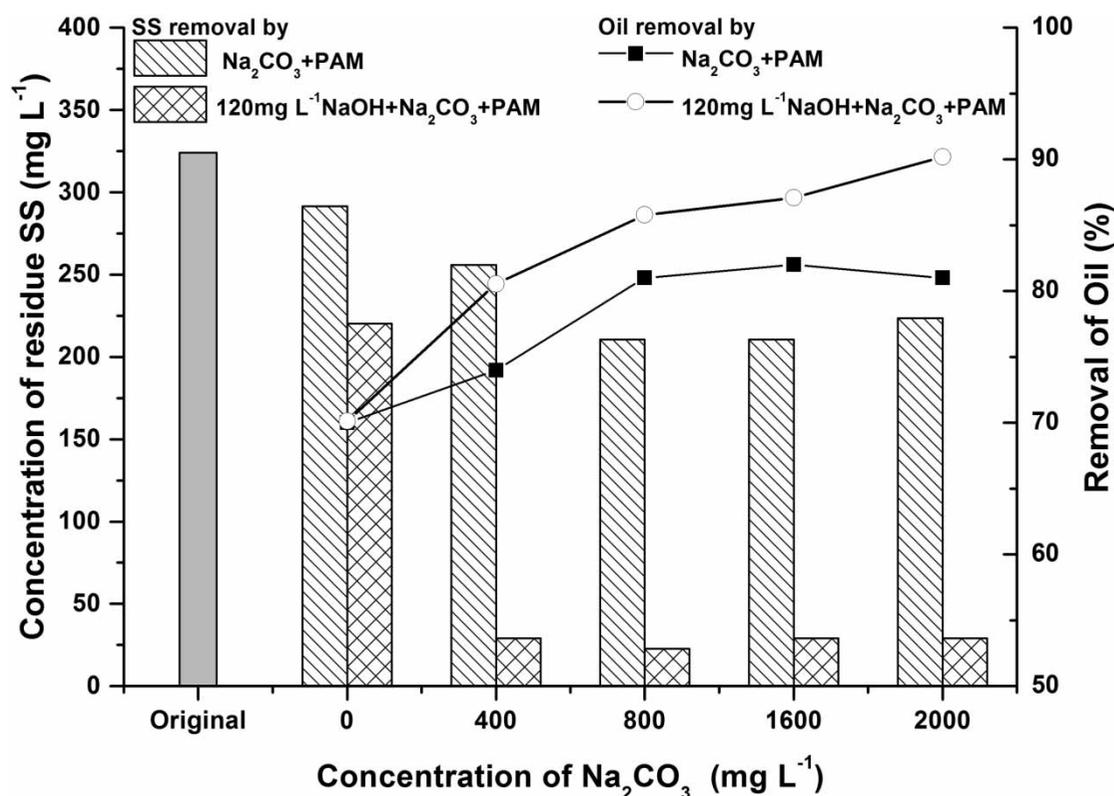
Figure 5 | Effect of PAM cooperated with 0 mg L^{-1} and 120 mg L^{-1} of NaOH on the removal of SS (histogram) and residue oil (linear) as a function of Na$_2$CO$_3$.

than successively (Figure S1, available with the online version of this paper), which once again proved that the CaCO$_3$ as condensed nuclei coagulated with PAM flocs facilitated the coagulation-flocculation.

In the presence of NaOH at 120 mg L^{-1}, the PAM flocculation enhanced the increase of Na$_2$CO$_3$ to 2,000 mg L^{-1}, the removal of residue oil approached the maximum of 90% and the residue SS declined to the minimum of 25 mg L^{-1}. The dissolved Ca^{2+}, compressing the EDL between colloids at higher pH, made SS and residue oil cohesive and easy to sink (Iakovides *et al.* 2016). Consequently, the effect of coagulation-flocculation was cumulatively enhanced by adding NaOH to the Na$_2$CO$_3$-PAM system.

Effects of Na$_2$CO$_3$ on selective deposition of fatty acids for oil recovery

Only a few reports so far have focused on the species of fatty acids in oil-containing wastewater. A complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids in wastewater is named naphthenic acids (NAs). NAs can be divided into saturated fatty acids (SAT) and unsaturated fatty acids (UFA). Acyclic carboxylic acid as

the major part of naphthenic acid in the Changqing oil accounted for 48.08%, followed by cycloaliphatic carboxylic acids at 34.11%, the low content of phenylalkanoic acid was 17.79% (Liu *et al.* 2015). SAT contained more energy than UFA, and thus the ubiquitous NAs in oil wastewater required to be removed and recovered efficiently. In raw oil acidized wastewater (Figure 6), the fatty acids were mainly composed of SAT and mono-UFA, accounting for 95% and 5% respectively, but the content of polyunsaturated fatty acids was small and negligible.

As shown in Figure 6, adding Na$_2$CO$_3$ to the oil wastewater, the UFA content decreased from 65% to 35% with the increase of Na$_2$CO$_3$. Most of the UFA entered the supernatant, indicating that CaCO$_3$ was selectively combined with SAT in wastewater. The selective sedimentation of SAT was conducive to the recovery of residue oil. Similarly, a significant loss of C20:5 was detected in sludge when the fatty acid was separated by flocculation. Borges *et al.* also found that addition of PAM led to high levels of C14:0 and low content of C20:5 trapped by the flocculants (Borges *et al.* 2011). The positive part of the flocculent adhered to the fatty acid and the negative formed bridges with medium components, causing the UFA crawling to
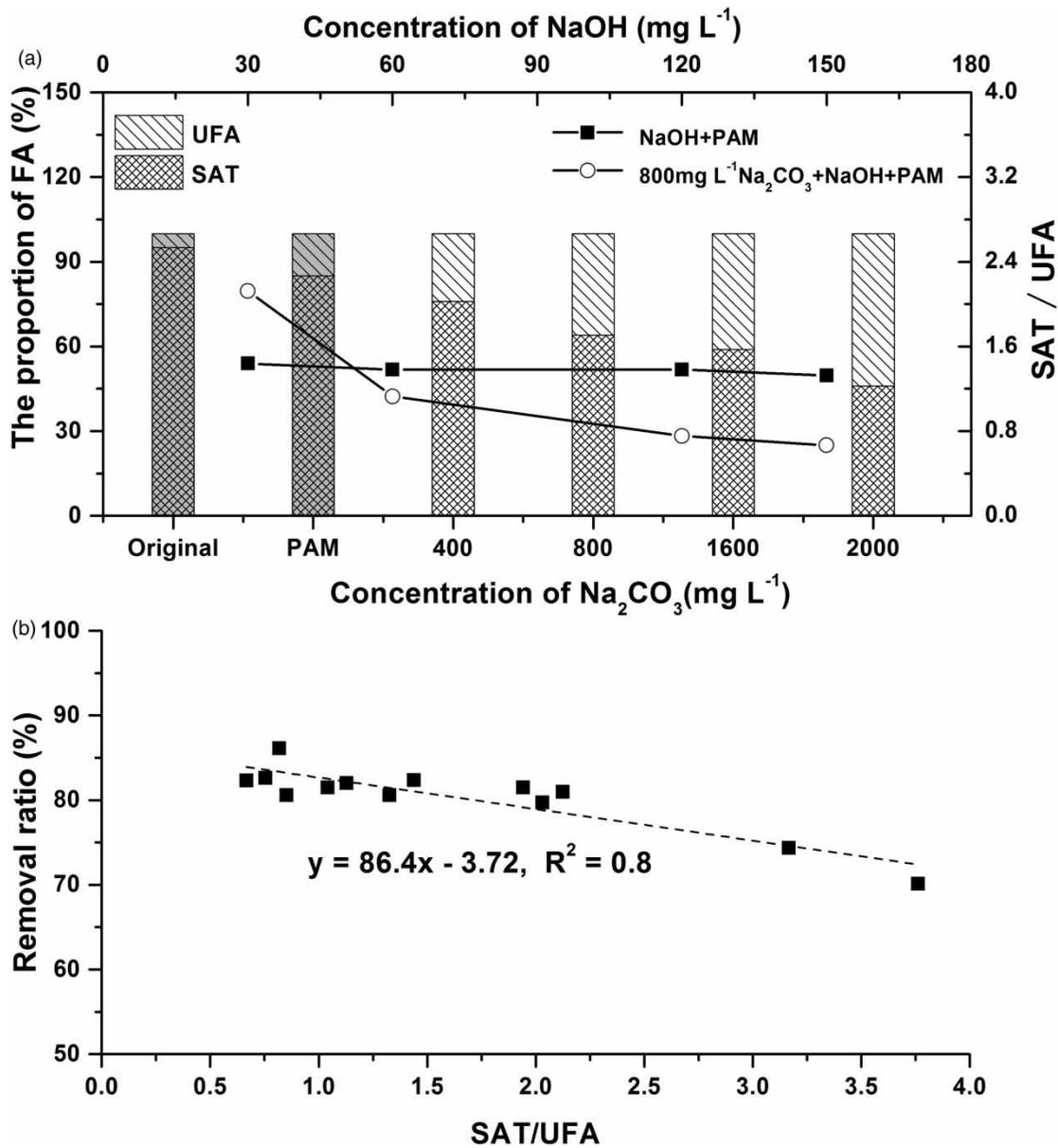
Figure 6 | Effect of PAM (grey histogram), Na_2CO_3 + PAM (white histogram), NaOH + PAM (square) and 800 mg L^{-1} Na_2CO_3 + NaOH + PAM (circle) on the removal of SAT (grids) and UFA (diagonal) in oil acidized wastewater (a), and the removal ratio related to the varieties of SAT/UFA which derived from experimental data of Na_2CO_3 + PAM, NaOH + PAM and 800 mg L^{-1} Na_2CO_3 + NaOH + PAM (b).

the culture medium. Thus, the difference in the percentage of fatty acids may be due to the remaining UFA in the supernatant, not the entry into sedimentation during the flocculation (Martínez *et al.* 2014).

Compared with the distribution of fatty acids in the original wastewater, the percentage of UFA in the supernatant gave rise to 15% solely by PAM flocculation. This rose to 54% in the presence of Na_2CO_3 + PAM, indicating that both PAM and Na_2CO_3 had a selective sedimentation on SAT. Na_2CO_3 and PAM interacted with each other to

promote the coagulation-flocculation, both together had a stronger settling effect on the species of fatty acids. The equivalent PAM along with different concentrations of NaOH was used in Figure 6, the ratio of SAT/UFA basically remaining at 1.3. The ambiguous effect was possibly due to the excessive calcium ions disabling the impact of NaOH on pH value. However, at the addition of 800 mg L^{-1} Na_2CO_3, the ratio of SAT/UFA decreased gradually with the increase in NaOH; the equilibrium state was at 0.5. The residual concentration of SAT being 14 mg L^{-1} in the

supernatant confirmed that $CaCO_3$ precipitates promoted the selective sedimentation of fatty acid species. In high pH-induced flocculation-sedimentation researched in the productivity of bio-diesel, therein more UFA than SAT were found, the increase of fatty acid unsaturation might be a mechanism of adaption to environmental conditions (Castrillo *et al.* 2013). Although an increase of UFA was detected in supernatant at pH values below 8, the reason for this was unclear. Consequently, the association of removal ratio to the SAT/UFA was investigated in Figure 6(b). As can be seen, the relationship is presented as $y = 86.4x - 3.72$ with correlation coefficient R^2 of 0.8, the selective deposition of FA was considered to follow a uniform mechanism. Based on the tendency line, we suspected that the distribution of fatty acids is highly related to the degree of removal ratio in coagulation-flocculation.

CONCLUSIONS

The data presented in this research propose one way to improve the PAM flocculation of SS and residue oil by the addition of Na_2CO_3. Oil acidized wastewater obtained a pH value at 6.1, herein the calcium ion was up to 1,350 mg L^{-1} and consumed NaOH at 99%. The released CO_3^{2-} binding with Ca^{2+} faster than OH^- suggested that $Na_2CO_3 + NaOH$ enhanced the utilization of OH^- to neutralize. In the presence of pH 6.1–7.5, $CaCO_3$ particles expressed positive charges under the IEP of 8.1, the electrostatic attraction was primarily at the interface of particles and contaminates, facilitating the SS and residue oil to attach to PAM-$CaCO_3$. The increase of NaOH was beneficial to PAM flocculation because of the stretch of the PAM molecular chain. Under the premise of Ca^{2+} homogeneously blending with contaminants, the Na_2CO_3 collected Ca^{2+} together to generate a $CaCO_3$ floc core, as a coagulant aid to improve coagulation-flocculation. Besides, the $CaCO_3$ and PAM selectively combined with SAT to settle down in favor of high-value oil recovery. The optimal formulation was suggested as 200 mg L^{-1} PAM, 120 mg L^{-1} NaOH and 400 mg L^{-1} Na_2CO_3. In this case, the content of SS and oil was reduced to 25 mg L^{-1} and 34 mg L^{-1} respectively, which almost met the requirements of MCLs and maximized the recycling of SAT. A novel hybrid technology combing with Na_2CO_3 coagulation and PAM flocculation is highly recommended to effectively remove contaminants in oil acidized wastewater. Future work is needed to explore the size effect of precipitated $CaCO_3$ on coagulation-flocculation. In addition, this study could expand to other different coagulants as the floc core to decontaminate in acidized environments.

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