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Coagulation treatment of SDS by hydrolyzed Al species: effects of pH and substrate concentration

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ABSTRACT

In this paper, the removal of the anionic surfactant sodium dodecyl sulfate (SDS) by coagulation using aluminum sulfate as a coagulant is reported. The effects of factors including pH, SDS concentration, and coagulant dosage on the SDS removal performance were investigated through batch experiments. The dried flocs were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, and X-ray diffraction. The results indicate that the redissolution of SDS occurred as the aluminum salt concentration increased and the SDS concentration exceeded the critical micelle concentration. At pH values of 3.0, 4.5, and 6.5, the least effective dosages of coagulant were found to be at C_{Al}/C_{SDS} ratios of 0.33, 1, and 2, respectively. The lowest amount of residual SDS was observed in a pH range of 4.0 to 5.0, and the SDS removal was due to neutralization, complexation, and absorption bridging effects. The SDS removal rate increased with an increase in initial SDS concentration, and the highest removal rate of 99% was obtained with an initial SDS concentration of 0.05 mol L^{-1} at pH 4.5. These findings reveal that better coagulation performance for SDS with aluminum sulfate can be achieved in a wide pH range by optimizing the reaction stoichiometry.

Keywords: Coagulation; Sodium dodecyl sulfate; Aluminum sulfate; pH

1. Introduction

Surfactants, organic compounds containing hydrophilic and hydrophobic groups in the same molecule, are soluble in both water and organic solvents because of their amphipathic nature [1,2]. Anionic surfactants, such as linear alkylbenzene sulfonate, alkyl sulfate, and alkyl epoxy sulfate, are the most widely used surfactant products worldwide [3]. The wide application of anionic surfactants in industrial products, such as personal toiletries and domestic and industrial detergents, inevitably means that they are released into the environment in large quantities, which has resulted in concerns about their potential ecotoxicity [4,5].

To date, a series of techniques has been developed to treat wastewater containing surfactants, including coagulation, membrane separation, adsorption, catalytic oxidation, and bio-treatment [6,7]. For instance, the ultrafiltration of sodium dodecyl sulfate (SDS) solutions using polymeric membranes is an effective and efficient method to remove SDS from wastewater [8]. However, the high cost of the membrane material is a barrier to its wide application. In addition, the anaerobic biodegradation of SDS is an environmentally friendly technique for the removal of low concentrations of SDS [9]. For industrial wastewater containing high concentrations of surfactants, coagulation has been demonstrated to be an efficient and economic pretreatment technique [4,10]. During coagulation, high valence electrolytes, polyelectrolytes, and macromolecules act as coagulants. Moreover, the addition of multivalent cations into the coagulation system

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can neutralize the surface charges of anionic surfactants [11,12]. For example, aluminum and ferric salt compounds are often used as cationic coagulants to treat wastewater containing anionic surfactants [13]. Previous reports have indicated that, for SDS, the coagulation efficiency of aluminum salts is higher than that for ferric salt compounds [14,15]. In the presence of aluminum salts, the zeta potential of SDS micelles drops to zero. Thus, with changes in the concentration of metal ions, SDS aggregates with a liquid crystal structure form [12].

The coagulation performance is influenced by several key factors such as surfactant concentration, coagulant dosage, pH, and temperature. Among these factors, pH plays a particularly important role in coagulation when aluminum salt compounds are utilized as coagulants because these compounds change form with pH [6,16]. Paton and Talens-Alesson [17] studied the coagulation of SDS using aluminum salts at pH values ranging from 1 to 13 and demonstrated that the SDS removal performance decreased significantly when the pH was greater than 8. The morphology and molecular aggregation number of the surfactants are strongly concentration dependent, which might further affect the coagulation of surfactants by aluminum salts [18]. In addition, the molar ratio of Al to SDS in the flocs is dosage related. Thus, optimizing the coagulant dosages and reaction conditions has been suggested to be an effective method for improving the use of coagulants for the treatment of surfactant-containing wastewater.

Therefore, in this study, we aimed to investigate the effects of the pH, surfactants, and coagulant concentration on Al–SDS coagulation. The coagulation process was investigated by changing the concentrations of SDS and aluminum sulfate under acidic and neutral conditions. The variations in the zeta potential and pH of the mixture and the residual concentration of SDS and aluminum sulfate were determined during the operation. In addition, the flocs were also characterized using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and X-ray diffraction (XRD) techniques. By optimizing the reaction conditions, we achieved good coagulation performance toward SDS using aluminum sulfate as a coagulant in a wide pH range.

2. Materials and methods

2.1. Coagulation with different concentrations of SDS and aluminum sulfate

Three different concentrations of SDS (≥99%, J&K, China) were selected based on a comparison with the critical micelle concentration (CMC) of 0.008 mol L^{-1} (Table 1). Certain dosages of SDS were added to vitreous reactors with deionized water to a total volume of 100 mL. Then, a quantity of $Al_2(SO_4)_3 \cdot 18H_2O$ (99%, Tianjin Kermel Chemical Reagent Co., China) was injected into each reactor and completely mixed with SDS by rapid stirring for 3 min. Subsequently, the reactors were placed in a 25 ± 1°C water bath for 1 h to ensure that equilibrium was reached. A volume of 5 mL was taken from each reactor using a syringe for the pH (Mettler Toledo, FE28-Standard, Switzerland) and zeta potential (Malvern Nano-ZS90, UK) analyses. The filtrate (20 mL) obtained after solid–liquid separation using a 0.45 μm polyethersulfone membrane was analyzed to measure the residual concentrations of Al and SDS. In addition, the dried floc precipitate was obtained after vacuum filtration and freeze-drying for 36 h.

Table 1
Different concentrations of SDS and aluminum sulfate

Comparison with CMC	SDS (mol L^{-1})	Aluminum sulfate (mol L^{-1})
<CMC	0.004	0.0005–0.06
>CMC	0.01	0.00125–0.15
>>CMC	0.05	0.00625–0.3

2.2. Coagulation at different pH values

The same concentrations of SDS (0.004, 0.01, and 0.05 mol L^{-1}) were selected, having C_{Al}/C_{SDS} ratios of 1/3, 1, 2, and 3, respectively, to demonstrate the coagulation performance under different pH conditions. Certain concentrations of the SDS–Al mixture were stored in 100 mL reactors and the initial pH was adjusted with NaOH or HCl to 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, and 6.5 (±0.03). Afterward, the reactors were placed in a 25 ± 1°C water bath for 1 h to ensure the attainment of equilibrium. Then, analysis was carried out according to the methods outlined above.

2.3. Coagulation settling tests

To test the SDS removal efficiency during the coagulation settling period, experiments were carried out with C_{Al}/C_{SDS} ratios of 1/2, 1, and 3 (initial SDS concentration of 0.01 mol L^{-1}) at uncontrolled pH, pH 4.5, and 6.5, respectively. The coagulation process was conducted at 25 ± 1°C for 1 h, and samples of the mixture and filtrate were collected at 4, 6, 8, 10, 15, 20, 25, 30, 40, 50, and 60 min. The turbidity of the mixture was measured using a turbidimeter (WGZ-B, Shanghai Xinrui Instrument & Meter Co., Ltd.), and the residual SDS concentration of the filtrate was also determined.

2.4. Effects of ionic strength on the SDS removal efficiency

Na^+ and Ca^{2+}, which are common cations in wastewater, were chosen to investigate the effect of their ionic strength on the SDS removal efficiency. Mixtures of 0.01 mol L^{-1} of SDS and a series of Na^+ and Ca^{2+} solutions with ionic strengths of 0, 0.01, 0.05, 0.1, 0.25, and 0.5 mol L^{-1} were prepared. The coagulation process was conducted by adding 0.0025 and 0.005 mol L^{-1} of aluminum sulfate to the mixture of SDS and Na^+ and adding 0.0025 mol L^{-1} of aluminum sulfate to the mixture of SDS and Ca^{2+}. The mixtures were then placed in a 25 ± 1°C water bath for 1 h to ensure the attainment of equilibrium, followed by the determination of the residual SDS concentrations of the filtrate as described above.

2.5. Analytical methods

The residual Al and SDS concentrations in the filtrate were determined using ethylenediaminetetraacetic acid titration and methylene blue spectrophotometry (756PC, Shanghai Spectrum, China), respectively. The characterization of the dried flocs was achieved via SEM (Quanta 450, FEI, USA), XRD (Empyrean, PANalytical, Netherlands), and FT-IR (Equinox 55, Bruker, Germany) analysis. The XRD measurements were carried out using Cu Kα radiation generated at 40 kV and 30 mA in the 2θ range of 2°–70° (λ = 1.541 A) at a scanning rate of 10 min^{-1}. FT-IR spectra were obtained using the KBr disk method, and the spectra were obtained between 400 and 4,000 cm^{-1} at a resolution of 1 cm^{-1}.

3. Results and discussion

3.1. Coagulation with different concentrations of SDS and aluminum sulfate

Fig. 1(a) shows that the pH of the SDS–Al mixture decreased sharply with an increase in initial C_{Al}/C_{SDS} ratio until the ratio reached 1, then showing a slow decrease as the initial C_{Al}/C_{SDS} ratio increased to 15. At an initial SDS concentration of 0.004 mol L^{-1}, the increase in the initial C_{Al}/C_{SDS} ratio from 1/8 to 15 resulted in a decrease in the pH from 4.33 to 3.43. For an initial SDS concentration of 0.01 mol L^{-1}, the increases in the initial C_{Al}/C_{SDS} ratio from 1/8 to 15 led to a pH drop from 4.74 to 3.41. For an initial SDS concentration of 0.05 mol L^{-1}, a decrease in the pH from 4.45 to 3.41 was observed on the increase in the initial C_{Al}/C_{SDS} ratio from 1/8 to 6. The Al ions in the solution were mostly in the hydrated state, that is, $Al(H_2O)_6^{3+}$, rather than free Al^{3+}. These hydrated Al ions, for instance, $Al(H_2O)_6^{3+}$ can produce H^+ by hydrolysis, resulting in an acidic solution. Thus, the pH showed a decreasing trend as the initial concentration of Al salts increased. In the SDS–Al mixture, DS^- can bind with Al^{3+} to form $Al(DS)_3$, which might inhibit the hydrolysis of Al salts. As a result, at high SDS concentrations, the pH of the mixture was higher than that of a pure aluminum sulfate solution. As the initial C_{Al}/C_{SDS} ratio increased, the neutralization reaction was expected to be almost complete. Under such conditions, because of the hydrolysis of Al salts, further increases in the concentration of Al salts would induce a continuous decrease in the pH to less than 4.0, much closer to the pH of a pure aluminum sulfate solution. At initial C_{Al}/C_{SDS} ratios between 1/8 and 1/4 (pH > 4.0), no precipitates were observed in the SDS solution. At a ratio of C_{Al}/C_{SDS} over 1/3 and a pH below 4.0, white flocs were formed in the mixture. This was caused by the presence of aluminum salts in the form of Al^{3+} and $Al(OH)(H_2O)^{2+}$ when the pH was less than 4.0 [19].

The variation in the zeta potential of the SDS–Al mixture with an increase in initial C_{Al}/C_{SDS} ratio was affected by the SDS concentration (Fig. 1(b)). At an initial SDS concentration of 0.004 mol L^{-1}, increasing the initial C_{Al}/C_{SDS} ratio resulted in an increase in the zeta potential from −25 to 0 mV. Meanwhile, the destabilization of the colloid was observed, suggesting that favorable coagulation performance could be obtained with an initial C_{Al}/C_{SDS} ratio higher than 0.375. For an initial SDS concentration of 0.01 mol L^{-1}, the zeta potential of the mixture first increased from −35 to 0 mV and, then, dropped to −8.98 mV. Meanwhile, the formation and redissolution of flocs was observed because of the destabilization of the colloid, indicating better coagulation performance with an initial C_{Al}/C_{SDS} ratio of 0.375–6. At an initial SDS concentration of 0.05 mol L^{-1}, increasing the initial ratio of C_{Al}/C_{SDS} led to an increase in the zeta potential from −30 to 0 mV, followed by a decrease to −13 mV. A similar formation and redissolution of flocs was observed, which, again, demonstrates that good coagulation performance can be achieved with an initial C_{Al}/C_{SDS} ratio of 0.25–1.

With initial SDS concentrations of 0.01 and 0.05 mol L^{-1}, the zeta potential of the mixture first increased gradually from negative values to near zero as the concentration of Al salts increased. This result suggests the destabilization and coagulation of micelles caused by the neutralization of the surface charge. However, a further increase in the concentration of Al salts resulted in a continuing decrease in the zeta potential to negative values, which indicates that the dissolution of flocs was not triggered by the excess adsorption of Al salts that might lead to the reversal of the surface charge of the particles. Based on these results, we inferred that the

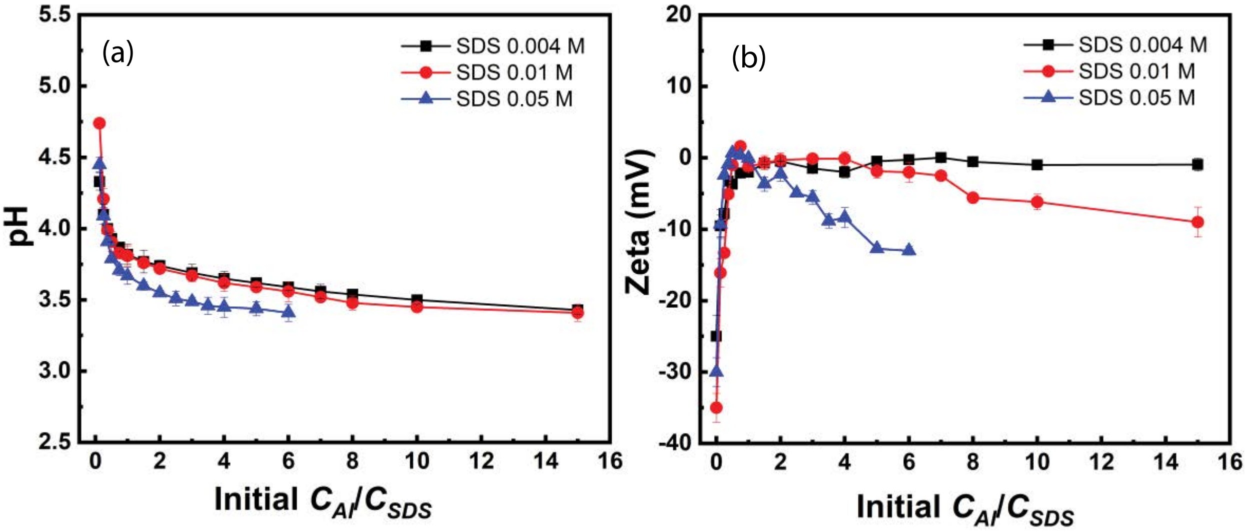

Fig. 1. pH (a) and zeta potential (b) at different initial concentrations of SDS and C_{Al}/C_{SDS} ratio.

formation of dissolved complexes by surfactants and Al ions resulted in the redissolution of the flocs in the presence of high concentrations of Al salts. When the initial concentration of SDS was 0.004 mol L^{-1}, no such redissolution of flocs was detected, which might be attributed to the concentration of SDS being lower than its CMC, making it unable to form a soluble complex with Al ions.

Fig. 2(a) shows the variation in the residual SDS concentration with an increase in C_{Al}/C_{SDS} ratio. In the presence of 0.004 mol L^{-1} SDS, as the C_{Al}/C_{SDS} ratio increased, the concentration of residual SDS dropped rapidly to 0.0008 mol L^{-1} and, subsequently, decreased at a slow rate to a concentration below the detection limit (0.017 mmol L^{-1}). For an initial SDS concentration of 0.01 mol L^{-1}, the concentration of residual SDS also rapidly decreased to approximately 0.0008 mol L^{-1} with an increase in C_{Al}/C_{SDS} ratio, and it further dropped below the detection limit when the ratio of C_{Al}/C_{SDS} reached 6. However, further increasing the C_{Al}/C_{SDS} ratio resulted in the redissolution of the flocs, and the residual concentration of SDS increased gradually to 0.01 mol L^{-1}.

In the presence of 0.05 mol L^{-1} SDS, increasing the initial C_{Al}/C_{SDS} ratio resulted in a two-stage variation in the residual SDS, which first decreased to 0.00132 mol L^{-1} and then increased further to 0.045 mol L^{-1}. These results showed that the increase in the additional aluminum salts could result in the redissolution of the flocs when the initial concentration of SDS was higher than the CMC. Thus, the additional dosage of aluminum salts should be controlled during the coagulation reaction. From the above results, we found that the concentration of residual SDS showed a slight difference in the optimal coagulation range, about 0.0008 mol L^{-1}, and this is consistent with the findings of Paton and Talens-Alesson [17]. These results show that under such conditions, micellar SDS was totally precipitated and the residual SDS was present as monomers.

Fig. 2(b) shows the changes of the C_{Al}/C_{SDS} ratio in the flocs. The ratio of C_{Al}/C_{SDS} in the flocs was calculated using Eq. (1):

$$\left[\frac{C_{Al}}{C_{SDS}}\right]_{flocs} = \frac{C_{Al1} - C_{Al2}}{C_{SDS1} - C_{SDS2}} \tag{1}$$

where C_{SDS1} and C_{Al1} are the initial concentrations of SDS and aluminum salts, respectively, and C_{SDS2} and C_{Al2} are the residual concentrations of SDS and aluminum salts, respectively.

At an initial SDS concentration of 0.004 mol L^{-1}, favorable coagulation performance was obtained when the initial C_{Al}/C_{SDS} ratio was greater than or equal to 0.375. Under such conditions, the C_{Al}/C_{SDS} ratio of the flocs gradually increased from 0.33 to 1.2. At an initial SDS concentration of 0.01 mol L^{-1}, similar coagulation performance was achieved between an initial C_{Al}/C_{SDS} ratio of 0.375 and 6, and the C_{Al}/C_{SDS} ratio of the flocs increased from 0.31 to 0.604. When the initial C_{Al}/C_{SDS} ratio was higher than 6, the C_{Al}/C_{SDS} ratio of the flocs further increased to 8.8. At an initial SDS concentration of 0.05 mol L^{-1}, at an initial C_{Al}/C_{SDS} ratio between 0.25 and 1.5, favorable coagulation performance was observed as the C_{Al}/C_{SDS} ratio of the flocs increasing from 0.298 to 0.37. With a further increase in the initial C_{Al}/C_{SDS} ratio beyond 2, the C_{Al}/C_{SDS} ratio of the flocs increased to 5.14. Therefore, the C_{Al}/C_{SDS} ratio of the flocs ranged between 0.298 and 0.33 under favorable coagulation conditions with moderate addition of aluminum salts. Because the aluminum salts were mostly present in the form of Al^{3+} and $Al(OH)(H_2O)^{2+}$ under these conditions (pH < 4.0), the aluminum salts in the flocs could exist in the form of $Al(DS)_3$, which is charge neutral and could further induce the destabilization, aggregation, and precipitation of the colloids [17].

3.2. Effect of pH on SDS–Al coagulation

At an initial C_{Al}/C_{SDS} ratio of 1/3, the zeta potential of the SDS–Al mixture decreased from −7.96 to −51.7 mV with an increase in pH (Fig. 3(A)). This result demonstrates the conversion of colloids from an unstable state to a restabilized state, based on the observed coagulation phenomena. The variation in the zeta potential for initial C_{Al}/C_{SDS} ratios of 1 and 3 are consistent with that obtained from the initial C_{Al}/C_{SDS} ratio of 1/3. The zeta potential was enhanced on increasing the amount of added aluminum salt. At an initial C_{Al}/C_{SDS} ratio of 2, the zeta potential was distributed around 0 mV within the acidic pH range, the absolute value of which was

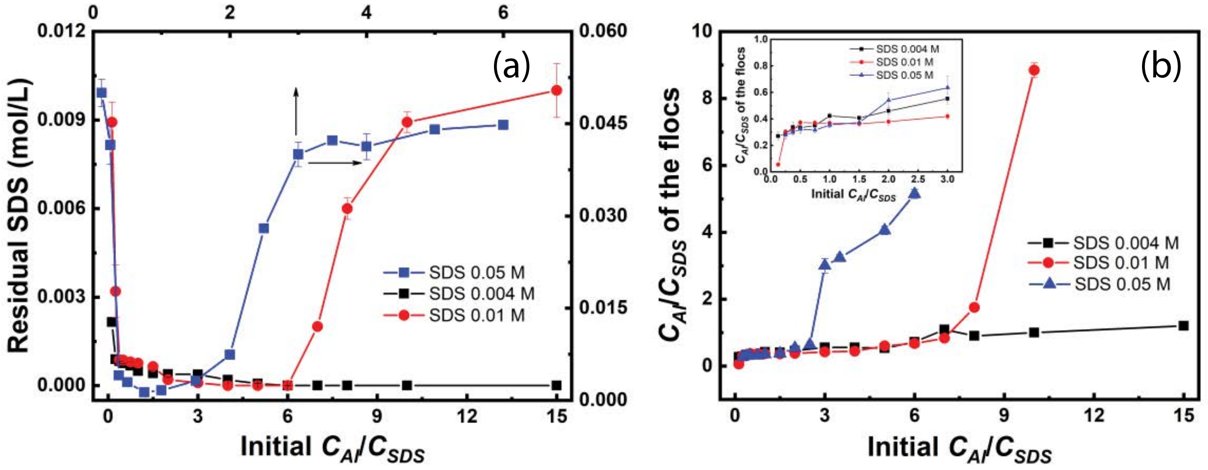

Fig. 2. Residual SDS (a) and C_{Al}/C_{SDS} ratio of the flocs (b) with different initial concentrations of SDS and C_{Al}/C_{SDS} ratios.

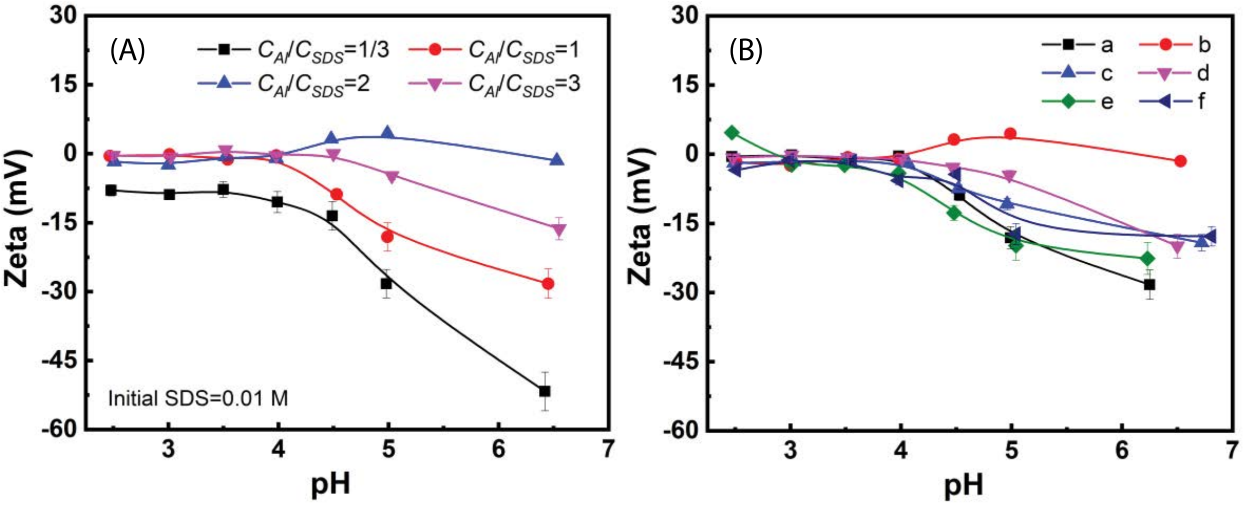

Fig. 3. Effects of pH on the zeta potential with different initial C_{SDS} and C_{Al}/C_{SDS} ratios: (A) C_{SDS} = 0.01 mol L^{-1} and (B) a,b: C_{SDS} = 0.01 mol L^{-1}; c,d: C_{SDS} = 0.004 mol L^{-1}; and e,f: C_{SDS} = 0.05 mol L^{-1}. a,c,e: C_{Al}/C_{SDS} = 1 and b,d,f: C_{Al}/C_{SDS} = 2.

the lowest of all the C_{Al}/C_{SDS} ratios. These results demonstrate that different dosages of aluminum salts are required for SDS coagulation under different pH conditions. When the pH ranged from 2.5 to 4.0, an initial C_{Al}/C_{SDS} ratio of 1/3 could satisfy the charge neutralization with SDS, resulting in the destabilization and coagulation of the SDS colloids. At pH 4.5, the destabilization and coagulation of the SDS colloids could be achieved with an initial C_{Al}/C_{SDS} ratio greater than 1. When the pH was controlled between 5.0 and 6.5, the zeta potential of the mixture reached 0 mV only when the C_{Al}/C_{SDS} ratio was 2. Although the zeta potential was measured as −16.3 mV when the initial ratio of C_{Al}/C_{SDS} was 3, favorable coagulation with the formation of a layered solution was observed. These results suggest that the coagulation reaction at pH 5.0–6.5 was not only induced by the neutralization mechanism. Considering that the aluminum salts within this pH range are mostly present in a highly polymeric state, such as Al_{13}, the coagulation could also be controlled by absorption bridging effect or by the formation of complexes with SDS [20].

Fig. 3(B) shows the variations in the zeta potential of the SDS–Al mixture with different initial concentrations of SDS (initial C_{Al}/C_{SDS} ratio of 1 and 2, pH = 2.5–6.5). As shown in Fig. 3(B), the absolute values of the zeta potential with an initial C_{Al}/C_{SDS} ratio of 2 were always lower than those obtained with an initial C_{Al}/C_{SDS} ratio of 1 under different initial SDS concentrations. The zeta potential remained relatively stable at pH values lower than 4.0. However, when the pH value exceeded 4.0, the zeta potential declined sharply as the pH rose. The zeta potential remained around 0 mV only under the conditions of an initial SDS concentration of 0.01 mol L^{-1} and C_{Al}/C_{SDS} ratio of 2. This result reveals that the coagulation reaction between SDS and aluminum salts differed with different initial SDS concentrations. At an initial SDS concentration of 0.004 mol L^{-1}, as the C_{Al}/C_{SDS} ratio increased to 3, the zeta potential remained around 0 mV under acidic conditions. This is mainly because of the neutralization-mechanism-controlled coagulation of the SDS (which is mostly in an ionic state) and aluminum salts. However, globular micelles were formed with an initial SDS concentration of 0.01 mol L^{-1} because the main coagulation mechanism changed from neutralization to absorption bridging as the C_{Al}/C_{SDS} ratio and pH increased [15,16]. At an initial SDS concentration of 0.05 mol L^{-1}, the aggregation number of the micelles increased, and, simultaneously, the globular micelles changed to clubbed micelles [18].

The absorption bridging effect and complexation between aluminum salts and SDS contributed most to this conversion at pH 5.0 to 6.5. Moreover, the zeta poetical was measured to be −20 mV, which also confirms the main coagulation mechanism. At pH < 4.0, redissolution of the SDS micelles was observed as the C_{Al}/C_{SDS} ratio increased to 1.5, which occurred because of the formation of Al–SDS complexes [6]. Therefore, the main coagulation mechanism at high concentrations of SDS and aluminum salts is a combination of neutralization and complexation at pH < 4.0.

The C_{Al}/C_{SDS} ratio of the flocs is shown in Fig. 4. For the initial C_{Al}/C_{SDS} ratio of 1/3 at pH ≤ 4.0, the C_{Al}/C_{SDS} ratio of the flocs increased from 0.29 to 0.32, suggesting that every three anion head groups combined with one Al^{3+}, which is consistent with the conditions required for neutralization. The C_{Al}/C_{SDS} ratio of the flocs increased with an increase in aluminum salt concentration and pH at an initial C_{Al}/C_{SDS} ratio of 1 to 3. At pH ≤ 4.0, the C_{Al}/C_{SDS} ratio of the flocs increased from 0.38 to 0.55, suggesting that the least effective dosage of coagulant was at a C_{Al}/C_{SDS} ratio of 0.33. Successive increases in the aluminum salt concentration might further compress the thickness of the diffusion layer by increasing the counterion concentration, which could facilitate the coagulation of the micelles.

At pH 4.5, the C_{Al}/C_{SDS} ratio of the flocs increased from 0.90 to 2.14, and the least effective dosage of coagulant was at a C_{Al}/C_{SDS} ratio of 1. Under these conditions, each Al ion has one positive charge, such as $Al(OH)_2(H_2O)_4^+$, $Al_2(OH)_2(H_2O)_8^{4+}$, and $Al_3(OH)_5(H_2O)_9^{4+}$ [21]. The C_{Al}/C_{SDS} ratio of the flocs increased from 1.10 to 3.39 from pH 5.0 to 6.5. Within this pH range, the aluminum salts were present mainly in highly polymeric form, such as $Al_{13}(OH)_4(H_2O)_{24}^{7+}$ and $Al(OH)_3$

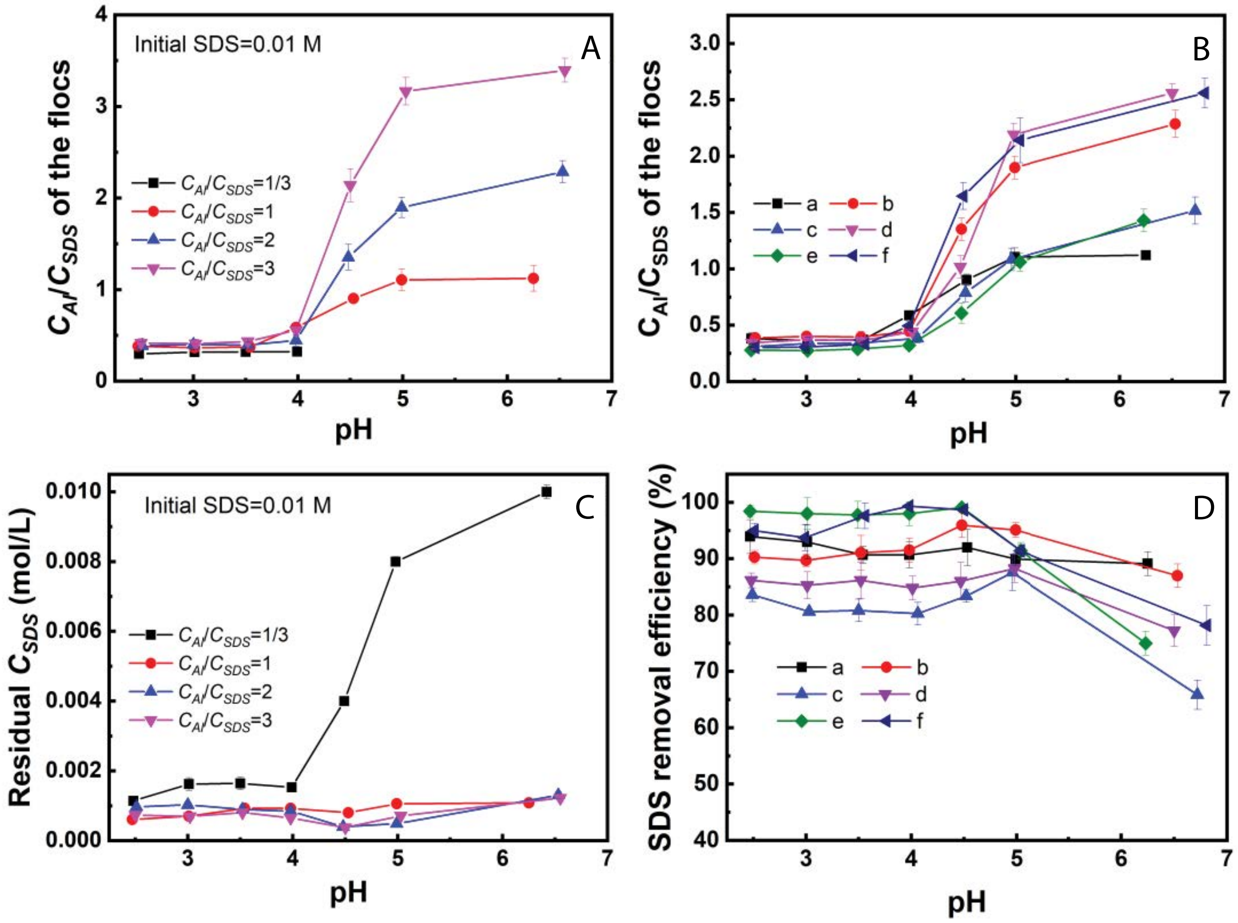

Fig. 4. Effects of the pH on the SDS removal efficiency and the C_{Al}/C_{SDS} ratio of the flocs at different initial C_{SDS} and C_{Al}/C_{SDS}: ((A) and (C)) C_{SDS} = 0.01 mol L^{-1} and ((B) and (D)) a,b: C_{SDS} = 0.01 mol L^{-1}; c,d: C_{SDS} = 0.004 mol L^{-1}; and e,f: C_{SDS} = 0.05 mol L^{-1}. a,c,e: C_{Al}/C_{SDS} = 1 and b,d,f: C_{Al}/C_{SDS} = 2.

[20,22], which are insoluble in water. The least effective dosage of coagulant was at a C_{Al}/C_{SDS} ratio of 2, and each Al ion had a half-positive charge.

Fig. 4(B) shows the C_{Al}/C_{SDS} ratio of the flocs with different initial SDS concentrations under conditions of initial C_{Al}/C_{SDS} ratios of 1 and 2 and pH 2.5–6.5. At each SDS concentration, the C_{Al}/C_{SDS} ratio of the flocs increased with an increase in aluminum salt concentration and pH. With initial C_{Al}/C_{SDS} ratios of 1 and 2, the C_{Al}/C_{SDS} ratio of the flocs showed similar trends at different initial SDS concentrations. This is mainly because the form of aluminum salts is controlled by the pH rather than the initial SDS concentrations.

Fig. 4(C) shows the residual SDS concentration in the filtrate at an initial SDS concentration of 0.01 mol L^{-1}, C_{Al}/C_{SDS} ratio from 1/3 to 3, and pH from 2.5 to 6.5. At a C_{Al}/C_{SDS} ratio of 1/3, favorable coagulation performance, yielding a residual SDS concentration from 0.0011 to 0.0015 mol L^{-1} and a removal rate of 88%, was observed at pH ≤ 4.0. However, when the pH was 4.5 to 6.5, the residual SDS concentration increased to 0.01 mol L^{-1} because of the shortage of aluminum salts. For initial C_{Al}/C_{SDS} ratios of 1–3, the residual SDS concentration further dropped to 0.0006–0.00085 mol L^{-1} with a total removal rate of 93% at pH ≤ 4.0. The lowest residual SDS concentration was measured as 0.0004 mol L^{-1} with a removal rate of 96% at a pH range from 4.0 to 5.0. In contrast, the residual SDS concentration at pH 6.5 increased to 0.00125 mol L^{-1} with a removal rate of 87.5%. Thus, the optimal pH range for removing SDS was 4.0–5.0 in this study, and the removal efficiency of SDS was assumed to be related to the coagulation mechanism.

The removal efficiency of SDS with different initial SDS concentrations and initial C_{Al}/C_{SDS} ratios of 1 and 2 at pH 2.5–6.5 is shown in Fig. 4(D). As shown in this figure, the removal efficiency of SDS increased with an increase in aluminum salt and initial SDS concentrations. A reasonable explanation for these results is that the residual SDS concentration, namely, the critical aggregation concentration, is controlled by the concentration of aluminum salts and the pH rather than the initial SDS concentration [11]. At different initial concentrations of SDS, the highest removal rates were all obtained in a pH range from 4.0 to 5.0. The highest SDS removal rate was 99%, which was obtained at pH 4.5 with an initial SDS concentration of 0.05 mol L^{-1}.

3.3. Coagulation settling tests

To monitor the coagulation settling period to ascertain if a settling time of 1 h is enough to achieve a relatively high coagulation efficiency, tests were carried out to measure the variation in the turbidity and SDS removal efficiency under different pH conditions (uncontrolled pH and pH 4.5, and pH 6.5). As shown in Fig. 5(a), with an increase in reaction time, the SDS removal efficiency increased significantly and a plateau in performance was reached at 15, 10, and 20 min at an uncontrolled pH, pH 4.5, and pH 6.5, respectively. Furthermore, floc settling occurred rapidly once the stirring was stopped. Fig. 5(b) shows that the turbidity of the solution rapidly decreased to 18.4, 5.7, and 6.5 nephelometric turbidity unit (NTU) within 10, 8, and 20 min at uncontrolled pH, pH 4.5, and pH 6.5, respectively. At 60 min, the turbidity further dropped to 3.8, 1.8, and 3.5 NTU, suggesting good coagulation performance. The variation in the turbidity and SDS removal efficiency indicate that the coagulation rate differed under different pH conditions but that the coagulation was almost complete within 20 min.

3.4. Effects of ionic strength on coagulation

Considering that the coagulation process using aluminum sulfate as a coagulant might be affected by other cations present in real wastewater, the effects of the ionic strength on coagulation were investigated with Na^+ and Ca^{2+}. Fig. 6 illustrates the effects of different ionic strengths on the SDS removal efficiency after coagulation using Al salts. When the initial concentration of Al salts was 0.0025 mol L^{-1}, the SDS removal efficiency dropped from 73.2% to 10.4% with an increase in Na^+ concentration, and almost no flocs were produced with 0.05 mol L^{-1} Na^+. When the initial concentration of Al salts increased to 0.005 mol L^{-1}, the SDS removal efficiency declined from 93.1% to 25.8%, and no flocs were observed until the concentration of Na^+ increased to 0.25 mol L^{-1}. These results suggest that the competition with Na^+ prevented the effective shielding of the micelles by Al^{3+}, which led to the de-coagulation of the surfactants at lower Al^{3+} concentrations. In the case of coagulation of SDS with aluminum sulfate, the effects of Na^+ might be attributed to the change in the CMC of the surfactants in the presence of Na^+ and the decrease in the chemical activity because of the higher ionic strength. However, the presence of Ca^{2+} significantly improved the SDS removal efficiency during coagulation. The promotion effect might result from the formation of Ca^{2+} and SDS precipitates.

3.5. Characterization of flocs

Fig. 7 shows the SEM images of the flocs obtained at different pH values after coagulation with 0.01 mol L^{-1} SDS and 0.02 mol L^{-1} aluminum salt. Fig. 7(a) shows the SEM image of the precipitates obtained at pH 3.0. Semitransparent flocs without individual particles were observed. Moreover, after drying, interlayer water seemed to be stored in the precipitates, which is consistent with our observations. Thus, we believe that $Al(DS)_3$ is formed at pH 3.0. The continuous production of $Al(DS)_3$ could further trap the colloidal particles in the liquid, producing thick precipitates.

Fig. 7(b) shows images of the precipitates obtained at pH 4.2, in which slightly white solids can be seen with

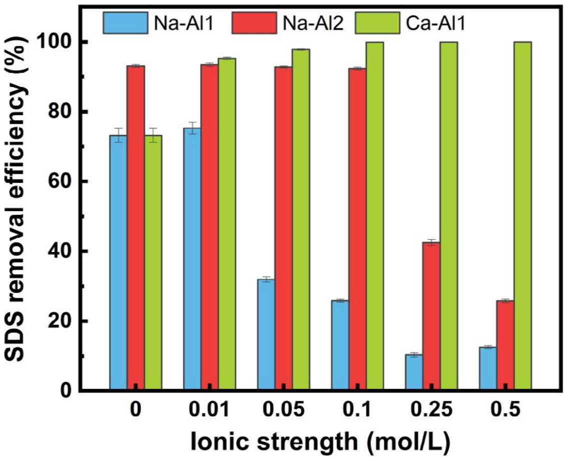

Fig. 6. Effects of ionic strength on coagulation performance.

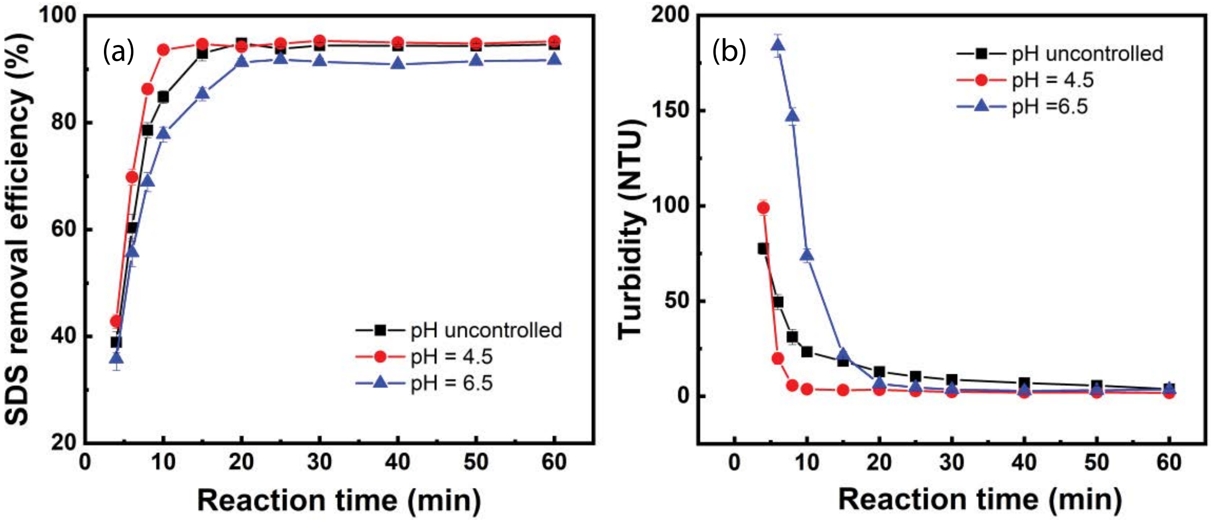

Fig. 5. Variation in SDS removal efficiency (a) and turbidity (b) during coagulation.

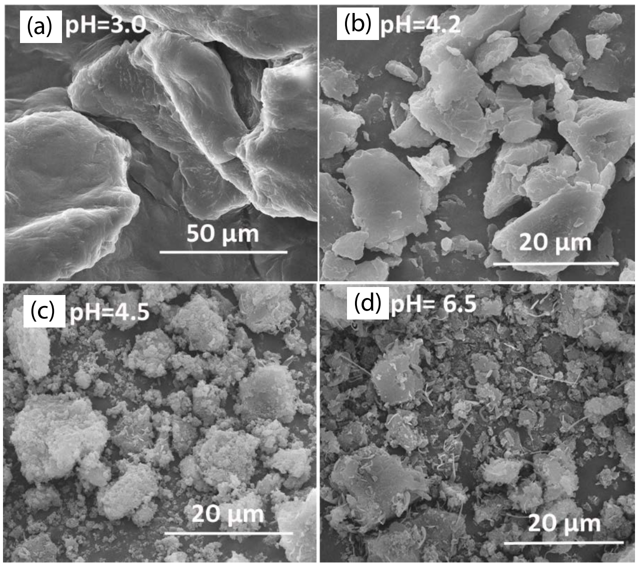

Fig. 7. SEM images of flocs formed by SDS–Al coagulation at different pH values ((a)–(d)). Initial C_{SDS} = 0.01 mol L^{-1} and C_{Al} = 0.02 mol L^{-1}.

different sizes, smooth surfaces, and layered structures. It was assumed that, at pH 4.2, the aluminum salts were present in a small polymeric form, and the formation of precipitates was induced by the combined effects of neutralization and complexation between the SDS colloids and aluminum hydroxide. Figs. 7(c) and (d) show the SEM images of precipitates at pH 4.5 and 6.5, respectively. Unevenly distributed opaque flocs with rough surfaces can be seen. In addition, there are many filaments on the surfaces of the precipitates, particularly for the samples obtained at pH = 6.5. It could be assumed that a combination of hydroxyl bridging effects and complexation between the aluminum salts and SDS played the key role at pH 4.5 and 6.5. However, the absorption bridging effects dominated at pH 6.5.

Fig. 8 shows the FT-IR spectra of flocs formed by SDS–Al coagulation at different pH values. The FT-IR spectra of pure SDS is shown as curve a, and curves b to e are the FT-IR spectra of the flocs obtained at pH 3.0, 4.5, 5.5, and 6.5, respectively. Compared with those of pure SDS, the spectra of the flocs contain two absorption peaks at 3,450–3,550 and 1,650 cm^{-1}. The broad absorption peak at 3,450–3,550 cm^{-1} belongs to the O–H stretching vibration of the interlayer water in the liquid crystals and aluminum hydroxide [23]. In addition, the peak area at 3,450–3,550 cm^{-1} increased with an increase in pH. The peak at 1,650 cm^{-1} corresponds to the O–H bending vibration absorption of the absorbed interlayer water of the liquid crystals [24]. In addition, the FT-IR spectra of SDS–Al flocs showed an obvious change at 400–1,000 cm^{-1} compared with those of the pure SDS. The above characteristics demonstrate the formation of SDS–Al complexes, where the binding sites are located at the sulfate ions of SDS [25].

Fig. 9 shows the XRD patterns of pure SDS and SDS–Al flocs obtained at different pH values. Clearly, multiple peaks are present in the diffraction patterns of pure SDS and the SDS–Al flocs at pH values of 3.0 and 3.5. However, at pH values of 4.2 and 4.5, one amorphous peak was found, which is consistent with the SEM results. The XRD patterns of the pure SDS contain six obvious peaks. Among them, three relatively strong peaks were d_{001} = 1.236 nm, d_{002} = 0.997 nm, and d_{003} = 0.842 nm. The XRD pattern of the SDS–Al flocs formed at pH 3.0 contained five more obvious peaks, (001), (-202), and

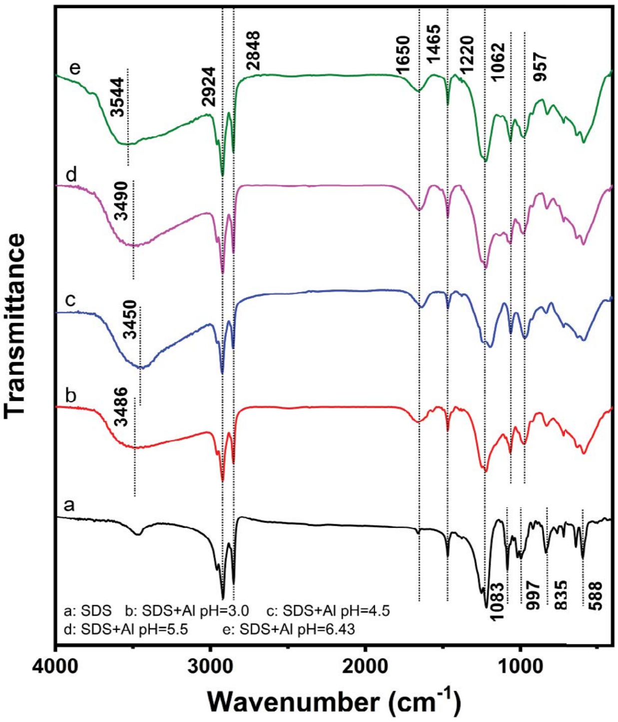

Fig. 8. FT-IR spectra of flocs formed by SDS–Al coagulation at different pHs. Curve a: pure SDS, curve b: pH 3.0, curve c: pH 4.5, curve d: pH 5.5, and curve e: pH 6.5. Initial C_{SDS} = 0.01 mol L^{-1} and C_{Al} = 0.02 mol L^{-1}.

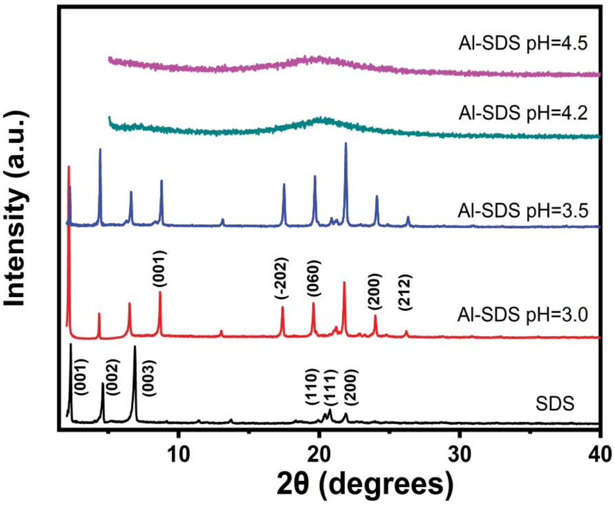

Fig. 9. XRD patterns of flocs formed by SDS–Al coagulation at different pH. Initial C_{SDS} = 0.01 mol L^{-1} and C_{Al} = 0.02 mol L^{-1}.

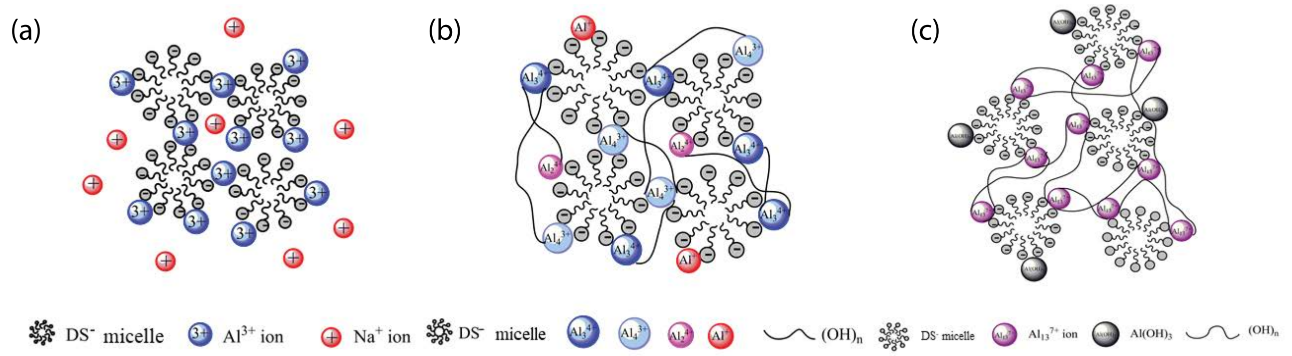

Fig. 10. Proposed mechanism of SDS–Al coagulation at different pH values: (a) 3.0, (b) 4.5, and (c) 6.5.

(212) (JCPDS: 10-0538) and (060) and (200) (JCPDS: 22-0022), compared with that of the pure SDS. No significant changes in the characteristic peaks of SDS were observed, except for the d_{001}, d_{002}, and d_{003} values of SDS–Al, which increased to 1.989, 1.993, and 1.096 nm. These results reveal the formation of $Al(DS)_3$ and the potential existence of interlayer water, which enhanced the sizes of the crystals. Meanwhile, some of the SDS was hydrolyzed under acidic conditions. The XRD spectra of SDS–Al flocs at pH 3.5 showed no significant changes compared with those obtained at pH 3.0. The peak height of (001) reduced obviously and d_{001} = 3.119 nm was promoted. The main peaks of the crystals formed of SDS–Al were related to the (001) reflection, suggesting that the crystal had a layered arrangement [11].

3.5. Coagulation mechanism

The above results indicate that the pH significantly influenced the coagulation of aluminum salts and SDS, and the highest SDS removal efficiency was obtained in the pH range from 4.0 to 5.0. Fig. 10 shows the three potential mechanisms controlling the coagulation reaction at different pH values.

Fig. 10(a) shows the potential mechanisms of coagulation at pH 3.0. Under these conditions, Al^{3+} is the main aluminum species. Because of electrical neutralization, the SDS is destabilized and coagulates with the aluminum salts to form liquid crystal aggregates of $Al(DS)_3$ with a layered structure. Fig. 10(b) reveals the coagulation at pH 4.5. At this pH, the aluminum salts were mainly in small polymeric aluminum hydroxides, such as $Al(OH)_2(H_2O)_4^+$, $Al_2(OH)_2\ (H_2O)_8^{4+}$, and $Al_3(OH)_5(H_2O)_9^{4+}$. The coagulation reaction was complex at pH = 4.5 and mainly controlled by neutralization, complexation, and absorption bridging effects. The optimal SDS removal efficiency was achieved by a combined mechanism at pH 4.5. Fig. 10(c) illustrates the coagulation mechanism at pH 6.5. Because the aluminum salts were present as $Al_{13}(OH)_4(H_2O)_{24}^{7+}$ and $Al(OH)_3$, the multi-hydroxyl absorption bridging effect became the main mechanism, which drove the formation of amorphous white flocs.

4. Conclusions

In summary, this study demonstrates the coagulation of SDS using aluminum sulfate as an inorganic coagulant under different conditions. The least effective dosage of coagulant was determined to be at a C_{Al}/C_{SDS} ratio of 0.375 under uncontrolled pH conditions. The SDS removal efficiency was mainly controlled by the concentration of Al salts and the pH rather than the initial concentration of SDS. Although the coagulation rate differed at different pH values, the coagulation was almost complete within 20 min. The presence of Na^+ in the mixture weakened the coagulation performance, but Ca^{2+} promoted it. The dominant coagulation mechanism depended on the formation of Al ions at different pH values. Neutralization, absorption bridging effects, and a combination of these mechanisms are suggested as the dominant functional mechanisms at pH 3.0, 6.5, and 4.5, respectively. Based on the results obtained in this study, the effective and efficient coagulation of SDS with aluminum sulfate over a wide pH range can be achieved, which could justify the wider use of aluminum sulfate in the treatment of wastewater containing surfactants.

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