



Performance on calcium scales inhibition in the presence of a novel double-hydrophilic block terpolymer

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ABSTRACT

An effective method for controlling scale formation in circulating cooling water system is the use of scale inhibitors. A novel multi-functional scale inhibitor AA-APES- H_3PO_3 terpolymer, was prepared by acrylic acid (AA), ammonium allylpolyethoxy sulfate (APES), and phosphorous acid (H_3PO_3) and the structural properties were identified by Fourier transform infrared and 1H -NMR. The inhibitory power of the terpolymer was determined by using a static scale inhibition method. The polymer's effectiveness on calcium scales was assessed by using X-ray diffractometer, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It is shown that AA-APES- H_3PO_3 terpolymer exhibited an excellent ability to control the formation of $CaCO_3$ scale at a mole ratio of 2/1 (AA/APES) with an inhibition efficiency of 92.6% at a level of 8 mg L^{-1} , and at the same time, it maintained a superior efficiency even at increasing solution temperature, pH value, and Ca^{2+} concentration. Compared with commercial inhibitors, the order of preventing the precipitation of calcium carbonate was AA-APES- H_3PO_3 > EDTMP > HEDP > PESA > PAA. Also the terpolymer displayed a superior ability to prevent calcium phosphate with approximately 100% inhibition efficiency at the dosage of 6 mg L^{-1} .

Keywords: Double-hydrophilic block terpolymer; Scale inhibition; Calcium carbonate; Calcium phosphate

1. Introduction

Recently, one of the major problems in circulating cooling water system is scale deposition. The commonly occurring scales include calcium carbonate, calcium sulfate, magnesium hydroxide, barium sulfate, calcium phosphate, calcium oxalate, etc. Among them, it is worth noting that calcium scales are considered the most frequent with the use of water for cooling purposes which has high temperature and elevated concentration, such as calcium carbonate and calcium phosphate [1–4]. Once calcium scales adsorb onto the surface of the equipment, the heat transfer exchange of the systems

will be hindered seriously, the service lifetime of the equipment will be shortened and they will even increase the cost of production [5,6].

In circulating cooling water system, the most widely used and effective way to avoid the formation of calcium scales is the addition of scale inhibitors [7,8]. For example, poly (acrylic acid) (PAA), hydrolytic poly (maleic anhydride) (HPMA), 2-phosphomobutane-1,2,4-tricarboxylic acid (PBTCA), 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP), and polyaspartic acid (PASP) have been widespread concerns. However, PAA and HPMA, which can retard the scale deposition at low concentrations, have low calcium tolerance and will bring about the formation of salts with alkaline earth metal ions or the formation of micelles

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if the respective concentration in solution exceeds the critical micellization concentration [9–11]. Simultaneously, PBTCA and HEDP, inhibitors composed of phosphonate, tend to form insoluble salts with alkaline earth metal ions at the critical micellization concentration and can revert to orthophosphates, leading to the eutrophication in water, which will increase environmental concerns and discharge limitations [12–15]. PASP, a green degradable inhibitor, has attracted more and more attention due to its non-nitrogenous, non-phosphorus and non-toxicity. Nevertheless, its corrosion inhibition and inhibition performance for $\text{Ca}_3(\text{PO}_4)_2$ are not prominent, which limits the use of PASP [5,16]. Hence, with the increasing environmental awareness, the current trend for scale inhibitor usage is to develop low-phosphorous and phosphorus-free polymers, with higher calcium tolerance [17,18].

In the present work, a multi-functional scale inhibitor AA-APES- H_3PO_3 terpolymer, containing carboxylic, hydroxylic, sulfonic and amide groups and low-phosphorous, was prepared with water as solvent and redox system of hypophosphorous and ammonium persulfate as initiator by the free-radical polymerization. In the molecule, the carboxylic groups are the main functional groups inhibiting the formation of calcium carbonate and calcium sulfate scales, the hydroxylic groups are the main functional groups inhibiting the formation of calcium phosphate, while sulfonic groups can play a role in the inhibition and dispersion stability due to its high electron density of oxygen atoms and high polarity [19,20]. In order to measure the content of phosphorous in the synthesized terpolymer, the energy-dispersive X-ray (EDX) analysis was used, showing that the mass percentage of phosphorous was less than 1.5%, indicating that AA-APES- H_3PO_3 is the low-phosphorous terpolymer and a new environmentally safe cooling water treatment agent. The structure of AA-APES- H_3PO_3 was characterized by Fourier transform infrared spectroscopy (FT-IR) and $^1\text{H-NMR}$. The inhibition efficiency of the terpolymer toward CaCO_3 scale in the artificial cooling water was studied through static scale inhibition tests with different dosages, solution temperature, pH, and concentration of Ca^{2+} , while the antiscaling efficiency toward $\text{Ca}_3(\text{PO}_4)_2$ was studied at different dosages. The mechanism was investigated through determining the morphology and crystal structure by X-ray diffractometer (XRD), SEM, and TEM.

There are few reports of low-phosphorous terpolymer of AA-APES- H_3PO_3 used as a scale inhibitor in cooling water. Because of its simple synthesis procedure, multifunctional groups, low phosphorous and decreasing eutrophication, this new scale inhibitor is believed to represent a potentially new environmentally safe scale inhibitor suitable for cooling water systems. However, its stability and anti-corrosion performance are still low and the terpolymer has no excellently comprehensive performance.

2. Experimental methods

2.1. Materials and instruments

The chemicals were used as received without further purification and were of analytical reagent grade. Acrylic acid, phosphorous acid, calcium chloride, sodium bicarbonate, monopotassium phosphate, ammonium persulfate and ascorbic acid used were purchased from Zhongdong Chemical

Reagent Co., Ltd. (Nanjing, Jiangsu, People's Republic of China). Distilled water was used in the whole experiments.

A VECTOR-22 FT-IR (Bruker Co., Germany) and an AVANCE AV-500 Bruker NMR analyzer (Bruker, Switzerland) were utilized to explore the structure of APES and AA-APES- H_3PO_3 . About 1 mg dried samples were mixed with 100 mg dried KBr powder and then compressed into a disk for spectrum recording, while the NMR analyzer operated at 500 MHz [4].

The morphological changes of the CaCO_3 crystals on glass plates were examined through XRD and SEM, and $\text{Ca}_3(\text{PO}_4)_2$ crystals through XRD and TEM, with the addition of the terpolymer. Precipitated phases were identified by XRD on a Rigaku D/max 2400 X-ray powder diffractometer (Japan) with Cu Ka ($k51.5406$) radiation (40 kV, 120 mA). The samples were coated with a layer of gold and observed in a SEM (S-3400N, HITECH, Taiwan, China). A TEM (JEM-2100SX, Japan) was also used to observe the shape of calcium phosphate crystals.

2.2. Preparation of AA-APES- H_3PO_3 terpolymer

APES was synthesized from allyloxy polyethoxy ether (APEG) in our laboratory according to Du et al. [21,22]. The synthesis procedure of the terpolymer AA-APES- H_3PO_3 is given in Fig. 1. Under nitrogen atmosphere, a four-neck round bottom flask, equipped with a thermometer, a mechanical stirrer, and a reflux condenser, charged with 40 mL distilled water and a total of 0.5 mol AA, was heated to the reaction temperature 80°C over a period of time. Then, a mixture of the raw materials APES and H_3PO_3 were added with 25 mL distilled water. In mixed conditions, the initiator ammonium persulfate was dropped at a constant flow rate separately for about 1 h. After that, the reaction was heated to 90°C and maintained at this temperature for an additional 1.5 h, eventually obtaining an aqueous polymer solution containing approximately 21.6% solid.

2.3. Static scale inhibition tests against CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$

The inhibition performance of AA-APES- H_3PO_3 terpolymer for CaCO_3 is estimated according to the China National Standard (GB/T16632-2008) [23] by the static test method. The experimental conditions of CaCO_3 were $\rho(\text{Ca}^{2+}) = 240 \text{ mg L}^{-1}$, $\rho(\text{HCO}_3^-) = 736 \text{ mg L}^{-1}$ (as CaCO_3), and the solutions were maintained at 80°C for 10 h in water bath. The remaining Ca^{2+} in the supernatant was titrated by EDTA standard solution and compared with blank test. The inhibition efficiency η was defined as follows:

$$\eta = \frac{\rho_1(\text{Ca}^{2+}) - \rho_2(\text{Ca}^{2+})}{\rho_0(\text{Ca}^{2+}) + \rho_2(\text{Ca}^{2+})} \times 100\% \quad (1)$$

where $\rho_0(\text{Ca}^{2+})$ is the total concentrations of Ca^{2+} (mg L^{-1}), $\rho_1(\text{Ca}^{2+})$ is the concentrations of Ca^{2+} (mg L^{-1}) in the presence of the terpolymer inhibitor, $\rho_2(\text{Ca}^{2+})$ is the concentrations of Ca^{2+} (mg L^{-1}) in the absence of the terpolymer inhibitor.

The inhibition efficiency of AA-APES- H_3PO_3 against $\text{Ca}_3(\text{PO}_4)_2$ precipitation was determined according to the national standard of P. R. China concerning the code for

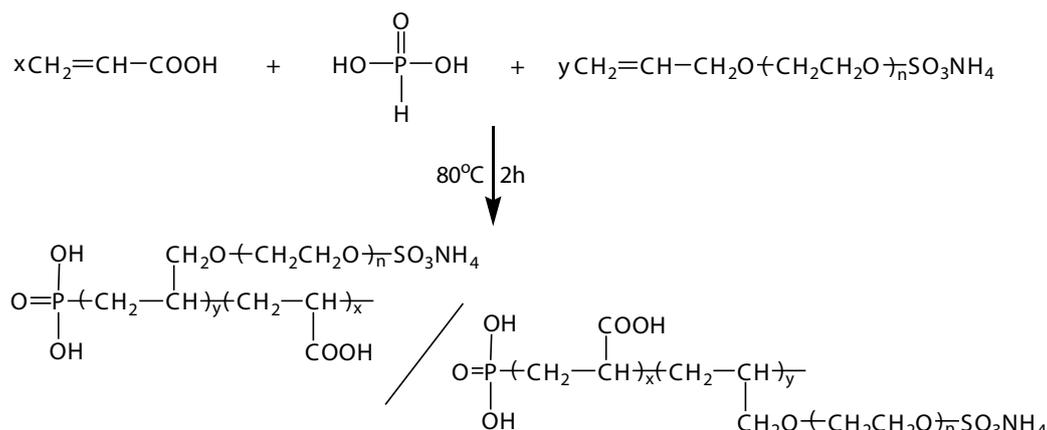


Fig. 1. Synthesis procedure of AA-APES-H₃PO₃.

the design of industrial circulating cooling-water treatment (GB 50050-95) [24]. A known volume of phosphate stock solution (the final PO₄³⁻ concentration would be 5 mg L⁻¹) was added to a glass bottle (250 mL) with a known volume of water, while the inhibitors were added before the calcium stock solution was added in such an amount that the final calcium concentration would be 250 mg L⁻¹ or the required values. After these solutions were heated 10 h at a temperature of 80°C, precipitation in these solutions was monitored by analyzing aliquots of the filtered (0.22 μm) solution for phosphate concentration by using the standard colorimetric method according to the international standard ISO 6878:2004 [25]. Investigation with and without inhibitors was all carried out. Anti-scalant efficiency as a calcium phosphate inhibitor was calculated by using the following equation:

$$\text{inhibition}(\%) = \frac{[\text{phosphate}]_{\text{final}} - [\text{phosphate}]_{\text{blank}}}{[\text{phosphate}]_{\text{initial}} - [\text{phosphate}]_{\text{blank}}} \times 100\% \quad (2)$$

where [phosphate]_{final} = concentration of phosphate in the filtrate in the presence of inhibitors at 10 h, [phosphate]_{blank} = concentration of phosphate in the filtrate in the absence of inhibitors at 10 h, and [phosphate]_{initial} = concentration of phosphate at the beginning of the experiment.

3. Results and discussion

3.1. Characterization of AA-APES-H₃PO₃ inhibitor

The FTIR spectra were taken for raw material APES (a) and the synthesized terpolymer (b), as shown in Fig. 2. vibration peak of C=C; the absorption peak at 1,352 cm⁻¹ is attributed to the asymmetric stretching vibration of S=O; and 1,100 cm⁻¹ is assigned to the asymmetric stretching vibration peak of C-O-C. As seen from curve (b), it is found that there are absorption peaks of 1,724, 1,402, 1,173, 1,027 and 942 cm⁻¹, among which 1,724 cm⁻¹ is assigned to the stretching vibration peak of C=O, the peak at 1,402 cm⁻¹ is attributed to the vibration of C-P, the peak at 1,173 cm⁻¹ is assigned to the stretching vibration of P=O and 1,027 and 942 cm⁻¹ are the stretching vibration peaks of P-O [26]. The existence of C-P absorption peak at 1,402 cm⁻¹ and the disappearance

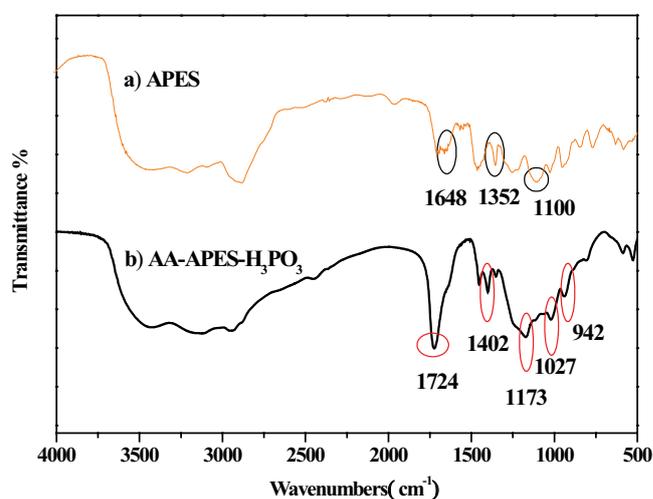


Fig. 2. FT-IR spectra of (a) APES and (b) AA-APES-H₃PO₃ terpolymer.

of C=C absorption at 1,648 cm⁻¹ clearly reveal that free radical polymerization among AA, APES and H₃PO₃ has occurred successfully.

Fig. 3 shows the ¹H NMR spectra of raw material APES (a) and the low phosphorous terpolymer AA-APES-H₃PO₃ (b). It can be seen that δ = 2.50 is assigned to the solvent residual peak of (CD₃)₂SO and δ in the region of 4–6 ppm are assigned to propenyl protons (CH₂=CH-CH₂-) in curve (a). As seen from curve (b), there are no peaks in this region, meaning that the double bond absorption peaks completely disappear, which confirmed the successful synthesis of AA-APES-H₃PO₃. This fact is consistent with the result of FT-IR analysis.

3.2. Relationship between AA/APES mole ratio and the calcium carbonate scale inhibition efficiency

According to literature and experimental data, mole ratio is an influential factor in the performance of anti-scalant. Therefore, the scale inhibition performance of AA-APES-H₃PO₃ toward calcium carbonate deposits at

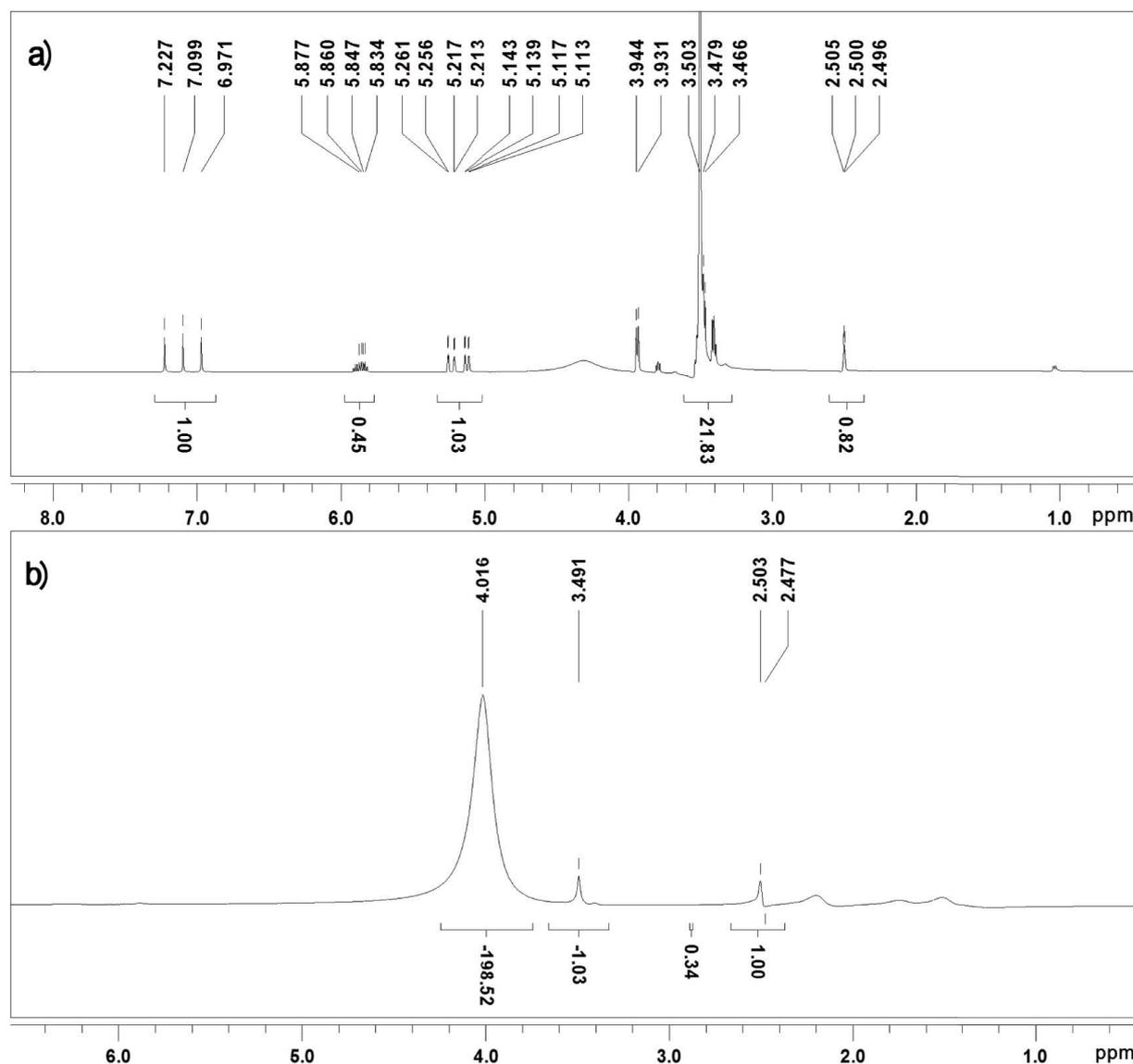


Fig. 3. $^1\text{H-NMR}$ spectra of (a) APES and (b) AA-APES- H_3PO_3 terpolymer.

different mole ratio of AA/APES was studied, as shown in Fig. 4. It is obvious that the inhibition efficiency obtained for AA/APES (2/1) is better than the other mole ratios, which exceeds 90% at a level of 8 mg L^{-1} polymer and the efficiency is tend to stabilize with the increasing concentrations of the inhibitor. While it is about 78.6%, 71.3%, 64.2%, and 60.4% at different mole ratio (3/1, 1/1, 1/2, and 1/3) under the same conditions.

The molar ratio (based on fixed molar quantity of H_3PO_3) of the scale inhibitor greatly influenced the performances of AA-APES- H_3PO_3 . Due to the special structure of APES, the side chain of the terpolymer was long. If the ratio of APES was high, there would be a lot of long chains in the molecule. The chains were easy to twine with each other and many functional groups ($-\text{COOH}$) would be wrapped, which would lead to the inhibition efficiency toward calcium scales declining as the carboxyl was the functional group inhibiting scale. Therefore, when the ratio of AA/APES changed

from 2/1 to 1/2 and 1/3, the inhibition efficiency of CaCO_3 declined. However, if the ratio of AA was too high, the uncovered functional groups ($-\text{COOH}$) were excessive and the intramolecular H-bonding of terpolymer formed, resulting in the inhibition efficiency toward CaCO_3 declining, as shown from 1/1 to 3/1. Therefore, the ratio of 2/1 is better than the other mole ratios.

3.3. Relationship between AA-APES- H_3PO_3 concentration and the calcium carbonate scale inhibition efficiency

During the last decades, researchers have paid much attention to calcium inhibitors, such as PAA, HEDP, PESA, and EDTMP, which are widely used in water treatment industry and synthesized from diverse monomers with different functional groups. The effect of AA-APES- H_3PO_3 concentration on scale inhibition efficiency against CaCO_3 was compared with common inhibitors in Fig. 5. It is

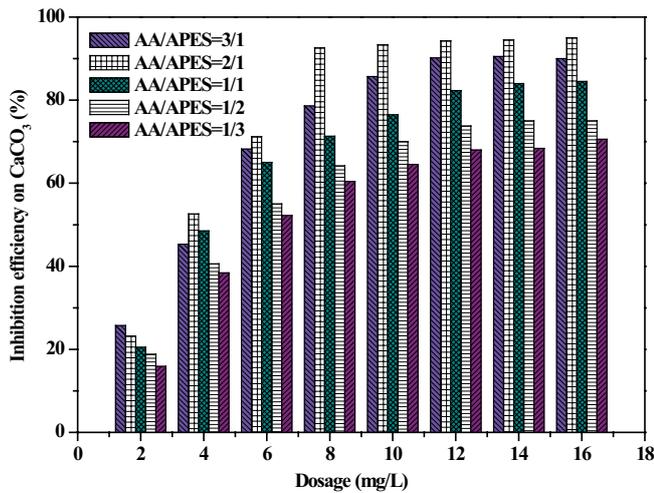


Fig. 4. Influence of dosage and mole ratio on CaCO_3 scale inhibition (Ca^{2+} : 240 mg L^{-1} , HCO_3^- : 732 mg L^{-1} , pH: 9, T : 80°C , t : 10 h).

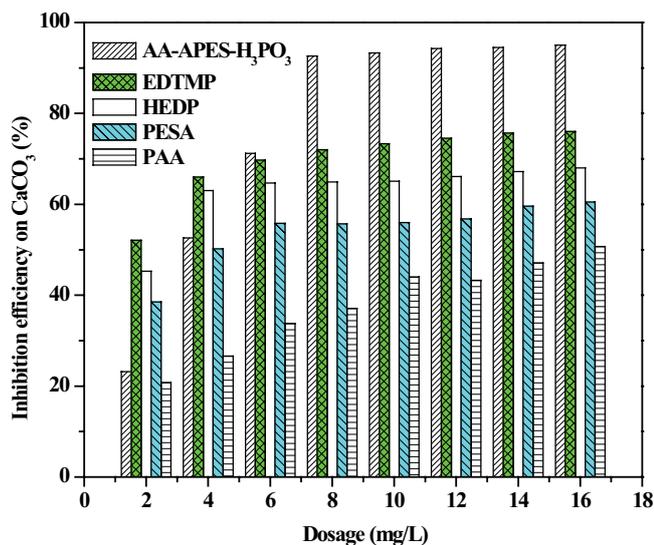


Fig. 5. Comparison of scale inhibition efficiency on CaCO_3 (Ca^{2+} : 240 mg L^{-1} , HCO_3^- : 732 mg L^{-1} , pH: 9, T : 80°C , t : 10 h).

apparent that the inhibition efficiency gradually increases with the increase in the concentration of inhibitors. The terpolymer AA-APES- H_3PO_3 exhibits the optimal inhibition performance, which is as high as 95% in the concentration of 16 mg L^{-1} . The inhibition efficiency of EDTMP and HEDP, phosphonate inhibitors, 76% and 68% at 16 mg L^{-1} , are better than PESA and PAA, which only contain the carboxyl groups. However, phosphonates contain high phosphorus, reverting to orthophosphates, which will be potential nutrients for algae. The above analysis illustrates that the capacity of the interaction between carboxyl group and Ca^{2+} is weaker than that between ether group and Ca^{2+} , or that between sulfonic group and Ca^{2+} , or that between $-\text{P}(\text{O})(\text{OH})_2$ and Ca^{2+} . Consequently, the kind of functional groups play a great role in preventing the growth of calcium deposits [27].

3.4. Relationship between conditions of circulating water and calcium carbonate scale inhibition efficiency

Parameters of the circulating water, such as temperature, pH and concentration of Ca^{2+} , affected the efficacy of the inhibitor and were displayed in Fig. 6.

As we can see from Fig. 6a, scale inhibition efficiency decreases as temperature rises from 70°C to 90°C (Ca^{2+} : 240 mg L^{-1} , HCO_3^- : 732 mg L^{-1} , pH: 9, t : 10 h, AA-APES- H_3PO_3 : 8 mg L^{-1}). The soluble calcium carbonate scale in solutions became fewer and the formation of scales was quickened with the increasing of temperature. Besides, the chelation between scale and terpolymer was exothermic, which would weaken the reactions and reduce the chelation quantity. Hereupon, the inhibition performance showed a declined trend.

The effect of pH value was another factor that affected the inhibition efficiency of AA-APES- H_3PO_3 as shown in Fig. 6b (Ca^{2+} : 240 mg L^{-1} , HCO_3^- : 732 mg L^{-1} , T : 80°C , t : 10 h, AA-APES- H_3PO_3 : 8 mg L^{-1}). Fig. 6b shows that the efficiency was lower when the pH value was higher. It could be seen from the chemical equilibrium equation below that dynamic equilibrium existed in the solution. As is well-known, with the increase of pH, the concentration of H^+ decreases and the equilibrium between H^+ and CO_3^{2-} breaks up, resulting in CO_3^{2-} becoming excessive. Accordingly, the first equilibrium equation goes toward the right, the formation of calcite and the scaling tendency is enhanced. Therefore, the scale inhibition declines with increasing pH.



Fig. 6c shows the results of the effect of Ca^{2+} concentration, an important factor of water's hardness affecting the performance of scale inhibition (HCO_3^- : 732 mg L^{-1} , pH: 9, T : 80°C , t : 10 h, AA-APES- H_3PO_3 : 8 mg L^{-1}). With the increase of Ca^{2+} concentration, the scale inhibition efficiency decreased. Obviously, increasing Ca^{2+} would promote the formation of calcium carbonate according to the equation above and result in declined inhibition efficiency.

3.5. Relationship between AA/APES mole ratio and the calcium phosphate scale inhibition efficiency

Based on fixed molar quantity of H_3PO_3 , the mole ratio of AA/APES has been investigated on inhibition of calcium phosphate scale, listed in Table 1. The results show that when the mole ratio (AA/APES) was 2/1, the inhibition efficiency was the best and the date was 98.2% at the dosage of 6 mg L^{-1} . In the molecule of terpolymer, the side chain, mainly in APES, was long and was apt to twine each other with the increasing amount of APES. Hence, when the ratio (AA/APES) raised from 1/1 to 1/3, the inhibition efficiency descended. On the other hand, if the quantity of AA was too many, the intramolecular H-bonding of copolymer formed and carboxyl groups could not play a part in scale inhibition, leading to declined efficiency of calcium phosphate.

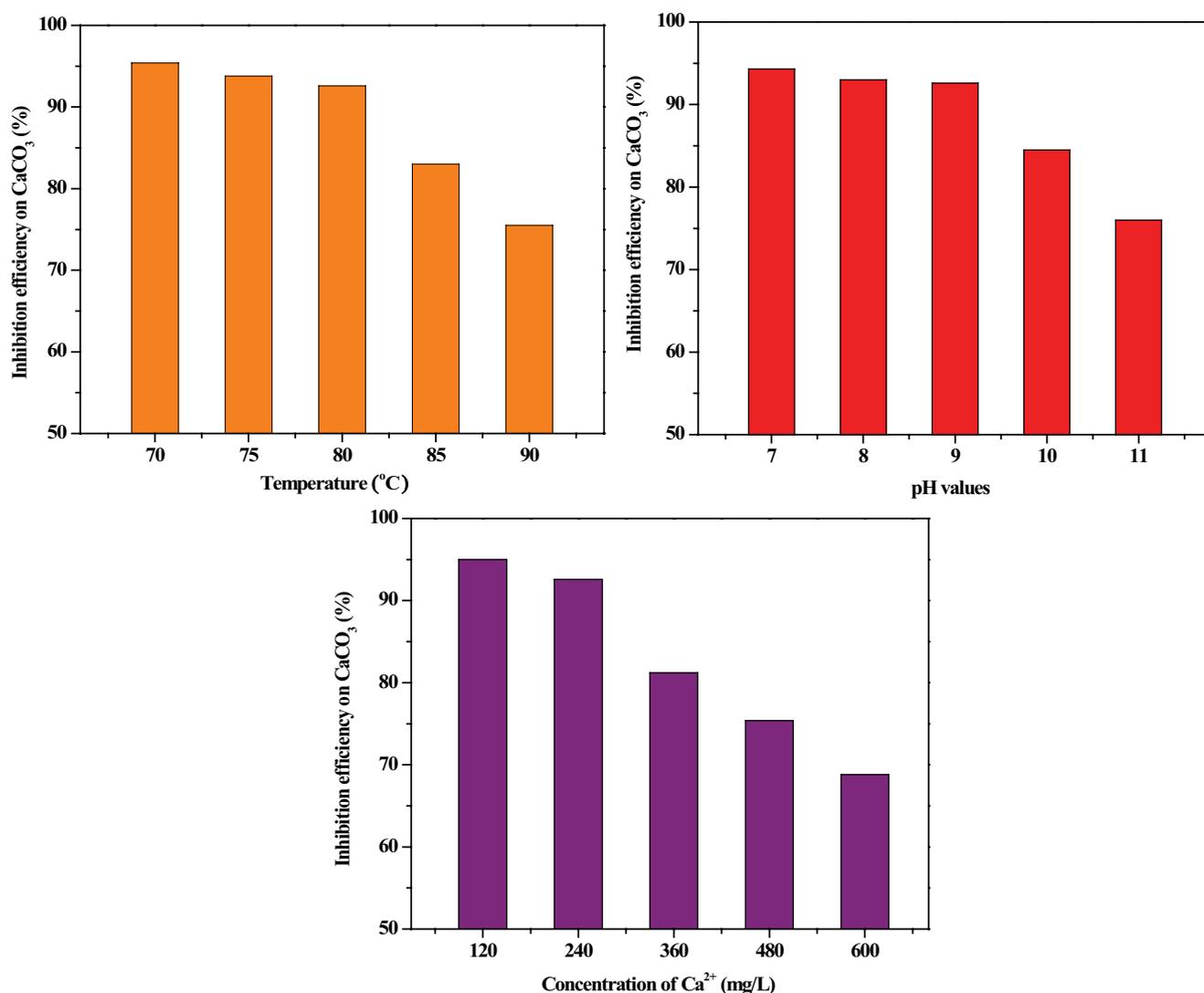


Fig. 6. Influence of conditions of circulating water on CaCO₃ scale inhibition.

Table 1
Influence of dosage and mole ratio on Ca₃(PO₄)₂ scale inhibition (%)

Dosage (mg L ⁻¹)	AA/APES = 1/1	AA/APES = 2/1	AA/APES = 3/1	AA/APES = 1/2	AA/APES = 1/3
2	28.4	25.8	29.6	30.2	24.5
4	65.3	71.5	64.8	62.2	55
6	90	98.2	86.7	83.4	80.5
8	98.9	99	96.2	95	86.8
10	100	99.9	99.6	98.8	92.3
12	100	100	100	99	95

3.6. Relationship between AA–APES–H₃PO₃ concentration and the calcium phosphate scale inhibition efficiency

Compared with commercial inhibitors, such as EDTMP, HEDP, PESA and PAA, AA–APES–H₃PO₃ had an absolute advantage for scale inhibition, as displayed in Fig. 7. EDTMP and HEDP are phosphonate with weak scale inhibition efficiency against Ca₃(PO₄)₂ and now high phosphorus

has limited their use. PESA and PAA, “green” inhibitors, contained carboxyl groups that had strong affinity to multivalent cations, such as Ca²⁺. Thus, the terpolymer, AA–APES–H₃PO₃, containing multi-functional groups, played an important role in inhibition of calcium phosphate scale.

When the mole ratio of AA/APES was 2/1, the inhibition efficiency against Ca₃(PO₄)₂ increased dramatically with the

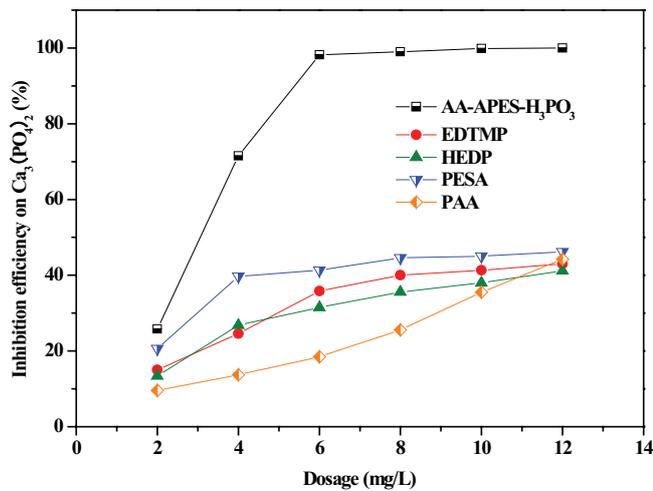


Fig. 7. Comparison of scale inhibition efficiency on $\text{Ca}_3(\text{PO}_4)_2$.

rising of terpolymer concentration from 2 to 6 mg L⁻¹ and then kept nearly unchanged beyond 6 mg L⁻¹. Obviously, the terpolymer exhibits a threshold effect, when chelated Ca²⁺ reached upper limits, the inhibition efficiency tended to be constant.

3.7. XRD characterization of CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$ scales

X-ray powder diffraction examinations of the morphology of the calcium carbonate polymorphs formed with and without terpolymer AA-APES-H₃PO₃ are shown in Figs. 8 and 9. Calcite, aragonite, and vaterite are three mineral phases of CaCO_3 , among which calcite is the most thermodynamically stable and vaterite is the least thermodynamically stable. As shown in Fig. 8a, in the absence of terpolymer, strong peaks appearing at 23.075°, 29.537°, 31.469°, 36.038°, 39.460°, 43.224°, 47.511°, and 48.658°, are corresponding to calcite forms faces of (012), (104), (006), (110), (113), (202), (018) and (016), respectively. In Fig. 9b, there are strong peaks

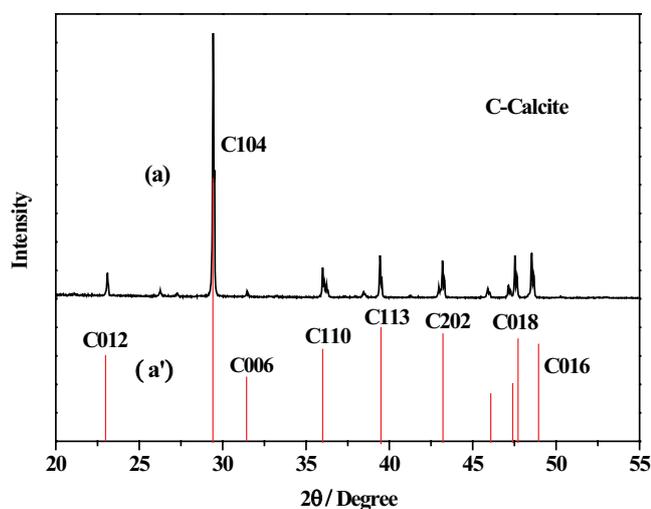


Fig. 8. XRD spectrum for calcium carbonate: (a) without AA-APES-H₃PO₃ and (a') the reference pattern for calcite.

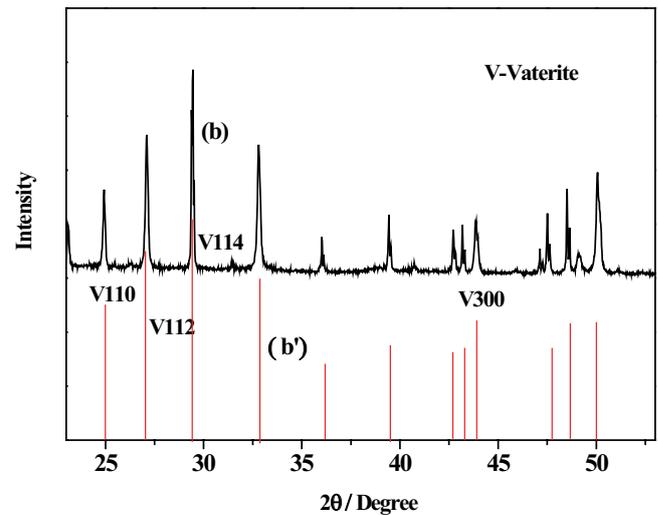


Fig. 9. XRD spectrum for calcium carbonate: (b) with AA-APES-H₃PO₃ and (b') the reference pattern for vaterite.

at 24.968°, 27.141°, 29.416°, and 43.908° [28,29], corresponding to the faces of (110), (112), (114), and (300) of vaterite. As the kinetic, least dense and most soluble anhydrous polymorph, vaterite form is favored and the scale is floppy and can be removed easily. These results indicate that the terpolymer could inhibit or disturb the calcite growth and induce vaterite growth, which is harder to adhere to metal surface and easy to disperse in water solution [30].

Fig. 10 exhibits the XRD spectra of $\text{Ca}_3(\text{PO}_4)_2$ crystals without and with the addition of AA-APES-H₃PO₃. It is found that characteristic peaks appeared similarly as seen from results in curve (a) and (b). Thus, it is obvious that the diffraction peaks have changed and the peaks' intensities in curve (b) are weaker than those in curve (a). This means that the crystallinity degree of the calcium phosphate crystal has changed and reduced with the addition of terpolymer, which will lead to loose structure of calcium phosphate scale and prevent the formation of a dense layer of scale. As a result, the formation of $\text{Ca}_3(\text{PO}_4)_2$ deposition was prevented.

3.8. SEM and TEM characterization

The SEM images are very important to prove the existence of calcite and vaterite visually as shown by XRD data. SEM of CaCO_3 is measured as shown in Fig. 11. It indicates that the presence of the terpolymer AA-APES-H₃PO₃ has a significant effect on the growth and morphology of calcium carbonate crystal. Without the terpolymer, calcium carbonate deposits show calcite structure with regular integrated symmetrical monoclinic hexahedron shape and glossy surface. After adding AA-APES-H₃PO₃, the regular structure of calcium carbonate crystal tends to be obviously destroyed and lots of vaterite phases being more dispersive appear, which are easy to break into pieces and set into the bunch crystal. Therefore, the terpolymer AA-APES-H₃PO₃ is capable of modifying the formation of calcium carbonate.

In order to analyze the influence of the terpolymer on the growth of calcium phosphate crystal, TEM was utilized and images of $\text{Ca}_3(\text{PO}_4)_2$ scale particles are shown

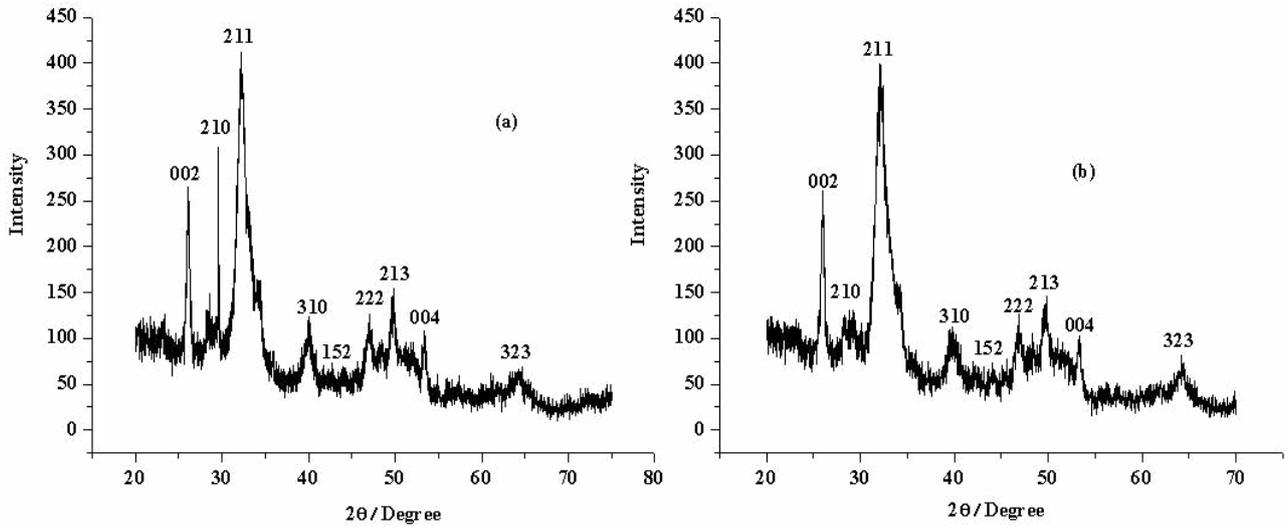


Fig. 10. XRD spectrum for calcium phosphate: (a) without AA-APES-H₃PO₃ and (b) with AA-APES-H₃PO₃.

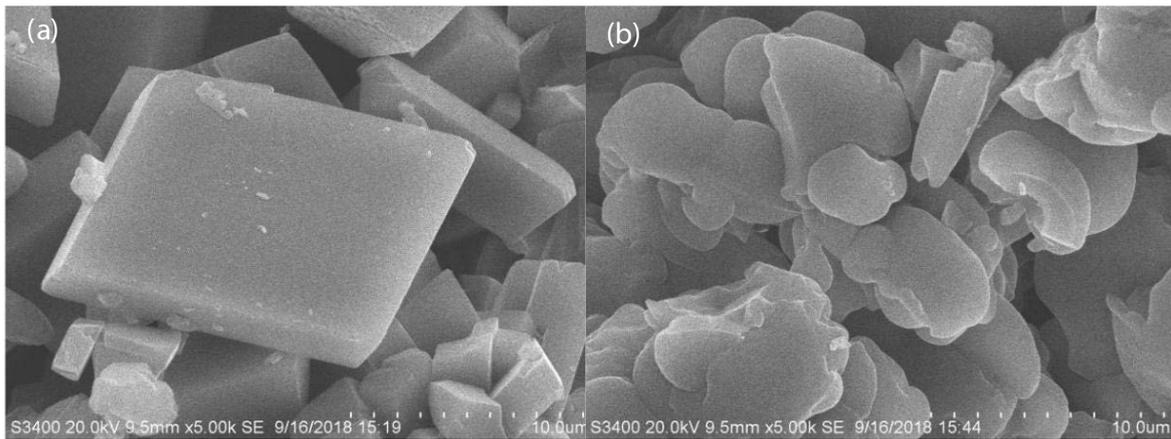


Fig. 11. SEM images for calcium carbonate: (a) without AA-APES-H₃PO₃ and (b) with AA-APES-H₃PO₃.

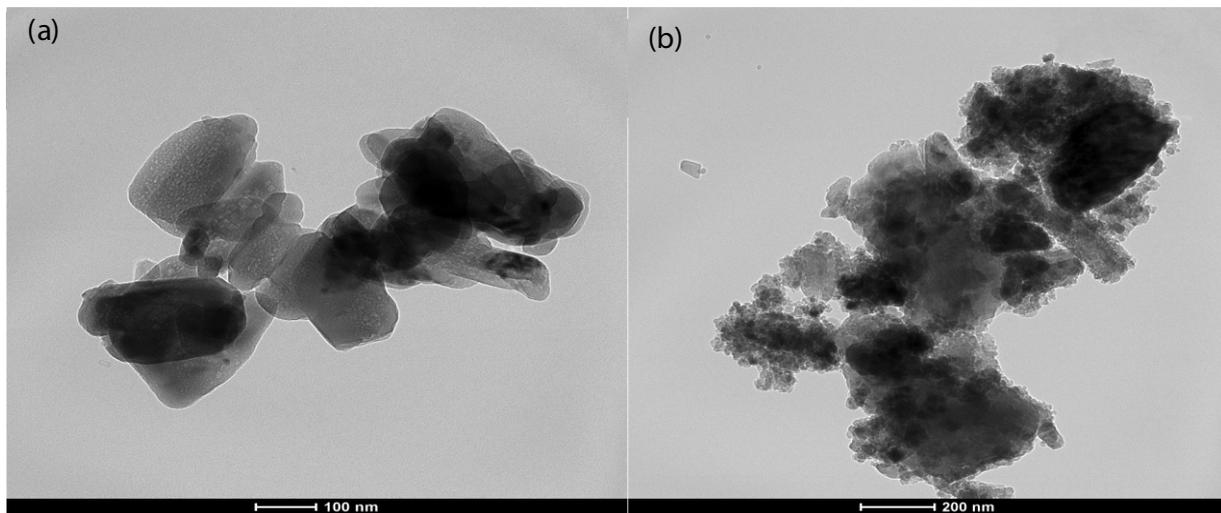


Fig. 12. TEM images for calcium phosphate: (a) without AA-APES-H₃PO₃ and (b) with 4 mg L⁻¹ AA-APES-H₃PO₃.

in Fig. 12. Without AA-APES- H_3PO_3 , lots of bulk-shaped calcium phosphate particles of a size of about 200 nm are obtained as shown in Fig. 12a. And in the presence of AA-APES- H_3PO_3 , the structure becomes irregular and the size is about 5–100 nm (Fig. 12b), illustrating that the terpolymer decreased the size of calcium phosphate solid particles and dispersed them throughout a fluid.

3.9. Inhibition mechanism

The inhibitor, AA-APES- H_3PO_3 , shows a significant effect on preventing the formation of calcium carbonate due to the strong specific interaction between functional groups and the crystals. First of all, carboxyl and phosphonate groups could chelate positively charged calcium ions and dissolve well in water. According to dynamics theory of crystal growth, if complexation occurred between the tiny crystals and scale inhibitors, the crystal could not grow normally in accordance with an array of crystal lattice strictly, and then the structure of crystals could be significantly distorted and weakened, resulting in fracture of the crystal. Thus, the generated scales were loose and could be easily washed away by water. Meanwhile, with the help of ethyleneoxy groups, the complex compounds could dissolve in water better. Consequently, the terpolymer owned excellent ability of scale-inhibition toward CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$.

4. Conclusions

A new scale inhibitor, AA-APES- H_3PO_3 terpolymer, containing carboxylic, hydroxylic, sulfonic, amide groups and low phosphorous, was successfully synthesized through free-radical polymerization. With simple synthesis procedure, multifunctional groups, low phosphorus and decreasing eutrophication, AA-APES- H_3PO_3 is a potentially new environmentally safe scale inhibitor. The terpolymer possessed excellent inhibition performance toward CaCO_3 and $\text{Ca}_3(\text{PO}_4)_2$. Moreover, parameters of the circulating water, such as temperature, pH value and concentration of Ca^{2+} , were investigated. Finally, the changes of the calcium scales were studied by using XRD, SEM, and TEM. All of the above results illustrated that AA-APES- H_3PO_3 could be used as a kind of water treatment agent for calcium scales, which was promising. Thus, its stability and anti-corrosion performance are still low and needed to be improved.

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