A study on fluorescence properties of carboxymethyl-quaternary ammonium oligochitosan and its performances as a tracing agent

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ABSTRACT

Carboxymethyl-quaternary ammonium oligochitosan (CM-QAOC) exhibited high inhibition to scaling and microbial formation and also remarkable fluorescence. In this paper its fluorescent properties and application as a fluorescent tracing chemical for industrial water treatment were studied in detail. The fluorescence intensities of CM-QAOC were in good linear agreement with its content in the concentration range of 5 to 500 mg/L and in the range of pH 7 to 9, which shows CM-QAOC can trace itself directly. The results showed the fluorescence would not be influenced by common phosphorus-containing organic and inorganic water treatment chemicals and N-dodecyl-N,N-dimethylbenzenemethanaminium chloride. This means CM-QAOC is compatible with those chemicals. The metal ions Ca$^{2+}$, Mg$^{2+}$, Fe$^{3+}$ and Cu$^{2+}$ from raw water or corrosion products could cause obvious enhancement in fluorescence intensities and sometimes blue-shifts in the fluorescence maxima, which demonstrated CM-QAOC could also be used as tracer to monitor damages like corrosion and scaling in water systems, by varying changes of fluorescence intensities and maximum emission wavelength. The fluorescence of CM-QAOC may be influenced by NaClO, and be quenched by sunshine slightly. Its ratio of biochemical oxygen demand to chemical oxygen demand was 0.53, which indicates CM-QAOC is a biodegradable chemical. Therefore, CM-QAOC can be applied as a tracer and environmental-friendly chemical for industrial cooling water treatment.

Key words | carboxymethyl-quaternary ammonium oligochitosan, compatibility, fluorescence, tracer, water treatment chemical

INTRODUCTION

Chitosan is the most abundant polysaccharides on the earth and also a kind of renewable resource (Mourya & Inamdar 2008). It has been widely applied in agricultural, food, pharmaceutical, cosmetic, biomedical, and paper industries due to its environmental friendliness and nontoxicity. Chitosan has a great amount of amino and hydroxyl groups, which can complex with various ions or organic molecules. The complexation capacity makes chitosan versatile in water treatment (Gupta & Suhas 2009).

Corrosion, scaling and microorganic growth are three major damages in various industrial water systems as they can impact heat transfer, obstruct pipes and even burst the pipes. To resolve these problems, various methods are adopted. The most common and effective one is the application of water treatment chemicals. There are various kinds of chemicals that can inhibit corrosion, scaling and microbial growth. For the corrosion inhibition domain, the phosphorus inhibitors once hold a dominant position (Touir et al. 2010). However, they will lead to water eutrophication and over-growth of algae. At the same time, the awareness of ‘green chemistry’ has been well-developed with all-around and meticulous consideration in every aspect of chemical industry. The development of free-phosphorus and biodegradable inhibitors has been drawing increasing attention (Choi et al. 2002). Further, the multifunctional water chemicals have become popular. Moreover, it is of crucial importance to keep a
proper dosage of effective agent so as to promote smooth and safe running in water systems. Therefore, it is very important to judge the true situation of damage and to determine the concentration of water treatment agents rapidly and accurately. The traditional mode is to measure pH, conductivity, hardness, and phosphorus concentration in the water system, and to add agents manually according to the measured parameters. But it is difficult to control the dosage accurately and resolve the fluctuation of water treatment chemicals in time. Due to its high sensitivity, low detection limit and multiple spectral parameters, fluorescence tracing technology has become the most effective and popular measurement (Henderson et al. 2009; Serres-Piole et al. 2012). This on-line method can monitor technical indexes of a water system continuously and omnidirectionally, reflect fluctuation of water treatment chemicals accurately and easily be used with large monitoring equipment (Singh et al. 2014). The critical factor in fluorescence tracing technology is the development of fluorescent tracers. The traditional fluorescent tracers used in the technology are usually responsible for specific chemicals and have a sole function of tracing. There are lots of complaints about most existing tracers regarding their unsatisfactory reliability and timeliness due to their indirect-response nature. Their application will increase the kinds and consumption of chemicals and complicate handling and administration (Koelmans et al. 2001). So it is valuable to develop multi-functional fluorescent agents for water treatment practices. Presently, there are three methods to prepare fluorescent tracer: physical blending by the fluorescent reagent and a substantially non-fluorescent water treatment agent (Hoots & Hunt 1987), copolymerization of fluorescent monomer (Pereira et al. 2008; Wang et al. 2014), and fluorescent labeling (Nagai et al. 2010). The tracer prepared by physical blending method cannot respond to the concentration fluctuation of the water treatment agent sensitively, as the tracer can combine with other components in water. Copolymerization can be achieved by two different ways generally, one of which is copolymerization of a functional monomer with the fluorescent monomer, and the other is copolymerization between the fluorescent-tagged functional monomer and normal functional monomer (Campo et al. 2006). The fluorescent labeling is to bond the fluorescent groups onto the polymers, in which, functional groups like carbonyl, amino, etc., are requisite on the backbone polymer. All the methods of copolymerization and chemical modification make the fluorescent tracer structure stable, which can ensure, therefore, a precise reflection of the real concentration. But simultaneously, the inhibition performances for scaling, corrosion or microbial growth can be influenced by these indicators prepared by copolymerization and chemical modification (Schweinsberg et al. 2005). Considering this, it is valuable to design a fluorescent water treatment chemical that has both concentration tracing properties and water treatment functionalities. As a concentration tracer, it should have stable fluorescent properties and good responses to concentrations without any influence in water treatment.

As fluorescence is usually sensitive to pH, metal ions and other factors in water, the functions of water treatment chemicals based on fluorescent properties can be influenced by the water environment in application. Thus, it is important to discuss the influence of water chemistry on fluorescent properties. The objectives of this study are to evaluate the fluorescent properties of one multifunctional inhibitor, carboxymethyl-quaternary ammonium oligochitosan (CM-QAOC), which can be applied in recirculated cooling water systems under different conditions, and to explore the possibility of this kind of chitosan derivative to indicate the concentration of itself or of other components in a cooling water system without introducing any other fluorescent groups or fluorescent reagents.

**EXPERIMENTAL**

**Material**

Chitosan (AR, degree of deacetylation > 95%, molecular weight = 350 kDa determined through Ubbelohde viscometer) was purchased from Jinan Haidebei Marine Bioengineering Co. Ltd, Shandong, China. Chloroacetic acid (AR) was purchased from Tianjin Guangfu Fine Chemicals Research Institute, Tianjin, China. 2,3-Epoxypropyl trimethyl ammonium chloride (GTAC, AR) was purchased from Longhao Chemical Co. Ltd, Shandong, China. 2-Phosphonobutane-1,2,4-tricarboxylic Acid (PBTC,AR) and 1-hydroxyethylidene-1,1-diphospho-nicacid (HEDP, AR) were purchased from Changzhou Yuanquan Hongguang Chemical Co., Ltd, Jiangsu, China. Polycrylic acid (PAA, AR), dodecyl dimethyl benzyl ammonium chloride (surfactant 1227, technical) and acrylic acid-acrylate-1-acrylamido-2-methylepropanesulfonic acid terpolymer (AR) were purchased from Tianjin Zhengda Science & Technology Co., Ltd, China. Zinc chloride (AR) and sodium hypochlorite (AR) were purchased from Keruisi Fine Chemicals Co., Ltd. All reagents were used directly without further treatment.

**Preparation and characterization**

In our previous work (Zhang et al. 2015) CM-QAOC was successfully prepared via carboxymethylation and quaternization of oligochitosan (OC) with chloroacetic acid and GTAC. 
The OC was obtained from depolymerization of chitosan by NaNO₂ and CH₃COOH in advance. Proton nuclear magnetic resonance (¹H-NMR) spectra of OC and CM-QAOC were acquired on an AV400 NMR spectrometer (Bruker, Switzerland) in D₂O/CH₃COOD or D₂O solution at 25 °C individually. IR spectra were collected from samples in KBr pellets at a resolution of 0.05 cm⁻¹ over 4,000–400 cm⁻¹ using a Tensor (Colthup et al. 1990) FT-IR (Fourier transform infrared) spectrometer (Bruker, Germany) with a DTGS (deuterized triglycerine sulfate) detector. OC, ¹H-NMR (D₂O/CH₃COOD, δ/ ppm): 4.49 (s, 1H), 2.60 (t, 1H), 3.58 (m, 1H), 4.13 (s, 1H), 2.36 (s, 2H), 3.17 (s, 9H) (Colthup 1965). IR (KBr, cm⁻¹): 3,400 (OH, NH₂, str.), 2,924 (CH, str.), 1,655 (NH₂, def.), 1,599 (NH₂, def., m), 1,478 (NH₂, def.), 1,365 (CH₃, def.), 1,312 (CH₃, def.), 1,282 (CH₃, def.), 1,152 (COC, str.), 1,080 (CO, str.), 895 (β-CH, def.). CM-QAOC, ¹H-NMR (CM-QAOC, D₂O, δ/ppm): 4.49 (s, 1H), 2.60 (t, 1H), 3.58–3.95 (m, 5H), 4.26 (s, 2H), 2.89 (m, 2H), 4.13 (s, 1H), 3.36 (s, 2H), 3.17 (s, 9H) (Colthup et al. 1990). IR (KBr, cm⁻¹): 1,599 (NH₂, def., m), 1,478 (CH₃, def.), 1,282 (CH₃, def.), 1,152 (COC, str.), 1,080 (CO, str.), 895 (β-CH, def.).

**Measurement**

UV–visible spectra of OC and CM-QAOC were collected with a LAMBDA double-beam UV/VIS spectrophotometer (Perkin-Elmer, USA) using deionized water as solvent and reference. Fluorescence properties of CM-QAOC under different conditions were measured on an F-4500 fluorescence spectrophotometer (Hitachi, Japan) with an excitation source of 150 W xenon arc lamp at a scanning rate of 240 nm/min, a voltage of 700 V, and a width of 10 nm for both excitation and emission slits.

Chemical oxygen demand (COD) was determined by volumetric titration (Vyrides & Stuckey 2009). The sample solution was sealed and digested in an incubator for 2 h at 150 °C before determination. Biochemical oxygen demand (BOD₅) was measured by dilution and seeding method according to ISO/TC-147 (Jouanneau et al. 2014) in which the water sample is diluted and incubated in a 20 °C oven for 5 days. The dissolved oxygen (DO) was measured before and after incubation, and BOD₅ can be calculated from difference between the DO before and after incubation.

**RESULTS AND DISCUSSION**

**The spectroscopic properties of CM-QAOC**

UV–visible spectra of CM-QAOC and fluorescence spectra of CM-QAOC and OC in their aqueous solutions were studied in our previous work (Zhang et al. 2015) and a linear relationship between fluorescence intensities and CM-QAOC concentrations in a pH range of 7 to 9 was observed. UV–visible spectra demonstrated that there is no adsorption corresponding to a conjugated structure in the range of 200 to 400 nm, which seems to be consistent with the molecular structure of CM-QAOC. Regarding fluorescence spectra, CM-QAOC presented two excitation bands at 250 nm and 380 nm, and one emission band at 450 nm, which is similar to the excitation and emission spectra of the fourth generation (G4) NH₂-terminated PAMAM (polyamidoamine) dendrimer (Wang & Imae 2004). In comparison with CM-QAOC, OC exhibited fewer fluorescence emission intensities. These results demonstrated that CM-QAOC adopted some special fluorescence-activated factors via carboxymethylation and quaternization. The reason why it can produce fluorescence is not clear so far. Probably the structure acquired after modification triggers the fluorescence. After modification, the –C=O and –NH₂, –NH~ or –OH groups were introduced into the molecules, which can provide π and n orbitals with nonbonding electrons respectively. On the other side, abundant intramolecular and intermolecular hydrogen bonds formed in the aqueous solution make the chitosan molecules compact. These features are similar to PAMAM, in which the n→π* transition and the densely globular structure are thought to be two decisive factors to induce fluorescence (Larson & Tucker 2001; Liang et al. 2015).

Fluorescence intensity of CM-QAOC linearly responded to the concentration of CM-QAOC in the range of 5 and 100 mg/L, which means CM-QAOC can indicate its concentration by itself without addition of any other chemicals. The CM-QAOC residual can be revealed by the change of fluorescence intensity of itself only in the pH range of 5 to 9 because it was found that the fluorescence intensities depended on the pH greatly at pH above 9 and below 5. When the pH decreased from 9 to 5, there was no significant change in emission intensities. It is well known that the industrial cooling water systems are conventionally operated within a pH range of 7 to 9. Therefore, the fluorescent property of CM-QAOC will not be affected by normal pH fluctuation of cooling water when it is applied in typical industrial cooling systems. On the other hand, the fluorescent variation trend of CM-QAOC can also indicate the change of pH in a water system. If the fluorescence intensities keep stable and the emission maximum is nearly unchanged, it demonstrates the pH value keeps in a range of 7 to 9, indicating a normal pH value of the water system. Once fluorescence intensities change obviously and the emission maximum shifts, it demonstrates that the pH value changes to below 5 or above 9, indicating that severe corrosion or scaling may probably occur respectively.
CM-QAOC compatibility with corrosion and scaling inhibitors

In order to eliminate damage like scaling, corrosion, and bio-fouling in industrial cooling water, various water chemicals such as scaling inhibitors and dispersants, corrosion inhibitors and biocides are usually used in combination with each other (Ramesh et al. 2003). The common corrosion and scaling inhibitors used in the recirculated cooling water are organic and inorganic phosphorus compounds. The prime inhibitors are organophosphonic compounds, such as HEDP, PBTCa, and amino tri-(methylene phosphonic acid) (ATMP). PAA, acrylic acid-acrylate-1-acrylamido-2-methylpropanesulfonic acid terpolymer (PAA-A-AMPS), acrylic acid-1-acrylamido-2-methylpropanesulfonic acid copolymer (PAA-AMPS) are polymer inhibitors, while zinc chloride, zinc sulfate, sodium molybdate, sodium hexametaphosphate are common inorganic inhibitors.

To examine the compatibility and stability of CM-QAOC coexisting with these common water chemicals in water, the fluorescence intensities of 50 mg/L CM-QAOC aqueous solution were recorded when it was compounded with different concentrations of PBTCa, HEDP, PAA, PAA-A-AMPS, and zinc chloride (ZnCl₂), respectively. The results showed that there was no precipitate when CM-QAOC was mixed with these water treatment chemicals. Figure 1 indicates there was no shift of emission maximum when CM-QAOC was compounded, and the fluorescence intensities hardly changed, which demonstrated there was little influence on the fluorescent properties for CM-QAOC and further on its tracer indication. CM-QAOC is stable chemically and physically, and will not be influenced by these corrosion or scaling inhibitors if they are applied in the cooling water system together. Hence, CM-QAOC is compatible with these common water chemicals, and CM-QAOC can be used together with other corrosion and scaling inhibitors without interference to its fluorescent and tracing performances.

CM-QAOC stability to biocides

Biocides such as bactericides, algae and fungi inhibitors are applied to inhibit microbial generation and bio-fouling in the recirculated cooling water (Bott 1998). Usually, the different biocides are used alternately or as a continuous addition, or a shock feeding can be employed individually or alternately. The biocides can be oxidative or non-oxidative. The oxidizing biocides include oxidative chlorine-containing compounds, oxidative bromine-containing compounds, and peroxidates. The non-oxidizing biocides include quaternary ammonium salts, chlorinated phenolic compounds, and organic sulfur compounds.

To evaluate influence of biocides on fluorescence properties of CM-QAOC, sodium hypochlorite (NaClO), and dodecyl dimethyl benzyl ammonium chloride were added into the solution of CM-QAOC individually. Figure 2 shows the fluorescence intensities of 50 mg/L CM-QAOC aqueous solution with various concentrations (0.6, 1.0, 1.8, 2.2, 3.0 and 4.0 mg/L) of NaClO. It indicates that the increasing dosage of NaClO causes rapid decrease of fluorescence intensities with an addition of agent below 3.0 mg/L, and slow decreases with an addition of agent above 3.0 mg/L. The decrease of fluorescence intensities may be attributed to the strong oxidativeness of NaClO,
which is likely to make CM-QAOC degrade to smaller molecules (Vanier et al. 2012). The degradation, verified by IR analysis later, can destroy the 3D-hydrogen bonded network and the rigid configuration to some extent, the most important factors inducing fluorescence and weakening the fluorescence of CM-QAOC (Yoo et al. 2005). So, this should receive great attention when the CM-QAOC is used together with oxidizing biocides.

In order to know more about what happened to CM-QAOC being disposed of with NaClO, FT-IR spectra were acquired over pristine CM-QAOC and CM-QAOC treated with NaClO. Figure 3 shows the FT-IR spectra of CM-QAOC, from which it can be seen that after treatment with NaClO, the absorption of \(-\text{CH}_3\) deformation vibrations at 1,478 cm\(^{-1}\) became weaker while the absorption of \(-\text{OH}\) bending appeared at 1,263 cm\(^{-1}\), which may be interpreted as the shedding-off of quaternary ammonium groups. The fingerprint region is sensitive to the NaClO with an apparent change, implying that some of CM-QAOC molecule’s moieties had been changed under the oxidation of NaClO (Garcia-Vasquez et al. 2014). The IR results are consistent with the observation of fluorescent behaviors above.

Dodecyl dimethyl benzyl ammonium chloride is a common non-oxidizing bactericide and its influence on CM-QAOC fluorescent behaviors was also evaluated. It was added in different dosage into a series of 50 mg/L CM-QAOC solutions respectively. Their fluorescent intensities are shown in Figure 4, and the results demonstrated clearly that there was no shift in emission wavelength, and the fluorescence intensities hardly changed with an increasing of the agent concentration from 100 mg/L to 600 mg/L. Thus, the addition of the aforementioned quaternary salt has no influence on fluorescence properties of CM-QAOC, and CM-QAOC can be used in the presence of the non-oxidative dodecyl dimethyl benzyl ammonium chloride biocide with its proper functioning and responses.

**Influence of negative ions on fluorescent properties of CM-QAOC**

Negative ions have influence on the subtle structure of the molecules, which often causes fluctuation and variation of fluorescence of fluorescent substances (Li et al. 2012). Various anions exist in water systems, such as HCO\(_3\)\(^-\), Cl\(^-\), F\(^-\), SO\(_4\)\(^{2-}\), SiO\(_3\)\(^{2-}\), NO\(_3\)\(^-\), and NO\(_2\)\(^-\), among which Cl\(^-\) and SO\(_4\)\(^{2-}\) are the most common and even harmful in cooling water systems.

In this paper, different contents of Cl\(^-\) or SO\(_4\)\(^{2-}\) were added into a series of CM-QAOC solutions. At concentrations of 0, 500, 1,000, 1,500 and 2,000 mg/L, the corresponding fluorescence intensities (F) were determined using the blank CM-QAOC solution as a reference (F\(_0\)) and shown as Figure 5. It can be seen that, to each set of data, the F/F\(_0\) values at different concentrations keep nearly constant, always near the value of 1.0, which means the Cl\(^-\) and SO\(_4\)\(^{2-}\) cause little change of fluorescence of CM-QAOC. Thus, these two common anions in water systems have no interference towards the fluorescence of CM-QAOC when it acts as a concentration tracer in water systems (Henderson et al. 2009).

**Influence of hardness and corrosion product ions on fluorescent properties of CM-QAOC**

Some metal ions coexist in cooling water universally, such as the hardness ions of Ca\(^{2+}\) and Mg\(^{2+}\) and the corrosion
product ions of Cu$^{2+}$ and Fe$^{3+}$. Considering the coordination with fluorescent groups with these ions, the hydrogen bonding and the molecular construction of CM-QAOC may alter. The variation in emission intensities and the wavelength of fluorescent CM-QAOC will take place correspondingly. So the fluorescent behaviors of 50 mg/L CM-QAOC aqueous solutions with different metal ion at a concentration of 1 mmol/L were recorded, shown as Figure 6. The results indicated that different ions cause varying degrees of increase in fluorescence intensities. Simultaneously, the peak wavelength blue-shifted from 450 nm to 440, 420, 434 and 445 nm with presence of Ca$^{2+}$, Cu$^{2+}$, Mg$^{2+}$ and Fe$^{3+}$, respectively. If CM-QAOC is added to its set point, the sudden changes in fluorescence can reflect concentration changes of these metal ions.

In order to evaluate the influence of different concentrations of hardness components and corrosion product ions on the fluorescence, the fluorescence spectra of CM-QAOC with different coexisting ions were measured, and the results are shown in Figures 7 and 8.

The fluorescence spectra (Figure 7(b)) of CM-QAOC solution in the presence of different concentrations of Ca$^{2+}$ showed that when the concentration of Ca$^{2+}$ was 50 mg/L, the intensities of fluorescence doubled from 1,000 to about 2,000 comparing to the CM-QAOC solution with absence of Ca$^{2+}$, and the maximum emission wavelength blue-shifted from 450 nm to 440 nm. Then with the increasing concentration of Ca$^{2+}$ above 50 mg/L, the intensities increased further but by smaller amounts. The emission band position barely changed any more with the corresponding increase in concentration. A similar phenomenon was observed for Mg$^{2+}$ (Figure 7(a)). When Mg$^{2+}$ was present, the fluorescence intensities had an apparent increase, while the maximum emission wavelength blue-shifted from 450 nm to 434 nm. The fluorescence intensities are parallel to the increasing concentrations of Mg$^{2+}$ but the increasing rate turned to be small and stable above 40 mg/L. The difference for Ca$^{2+}$ is that there is still a blueshift of the emission maximum wavelength with the increasing concentration. So it can be perceived that the concentration of hardness ions, Ca$^{2+}$ or Mg$^{2+}$, become larger in the water system if the fluorescent intensities become stronger and the maximum emission wavelength blue-shifts.

The spectra of 50 mg/L CM-QAOC solution with the presence of Cu$^{2+}$ and Fe$^{3+}$, which normally result from corrosion, are shown in Figure 8(a) and 8(b); the concentrations of these two ions were set at 0.1, 0.5, 0.8, 1.5, 2.0, 3.0 mg/L and 0.2, 0.6, 1.0, 2.0, 3.0 mg/L, respectively. From the figure, it can be seen that the fluorescence intensities changed to be stronger with the increasing concentration of Cu$^{2+}$ or Fe$^{3+}$; when the concentration of these two ions is 3.0 mg/L, the intensities are 1.6 and 1.4 times larger than that of original intensities respectively. On the other hand, the band position of emission spectra in presence of Cu$^{2+}$ blue-shifted continuously with the increasing of its concentration. For the case of Fe$^{3+}$, it is different from the above situation of Cu$^{2+}$: the band positions of emission spectra in presence of Fe$^{3+}$ ion blue-shifted to 445 nm and there was no further blue-shift as the concentration increased continuously. Usually
paramagnetic metal ions (Cu$^{2+}$, Fe$^{3+}$) can quench fluorescence via complexation (Frimmel & Hopp 1986), but in this study it’s interesting that both Cu$^{2+}$ and Fe$^{3+}$ caused an obvious increase in intensities to different levels. This may be because the fluorescence of CM-QAOC was produced by a special rigid molecule structure; the Cu$^{2+}$ and Fe$^{3+}$ can probably make the molecules more rigid and compact due to electric charge effect (Staneva et al. 2015). The more rigid and compact the molecule structure is, the stronger the fluorescence intensities are. As for Ca$^{2+}$ and Mg$^{2+}$, CM-QAOC can also reflect the concentration changes of Cu$^{2+}$ and Fe$^{3+}$, which means CM-QAOC is able to indicate whether facilities have been corroded via different changes in fluorescence intensities and maximum emission wavelength.

In general, the fluorescent properties of CM-QAOC are influenced by Ca$^{2+}$, Mg$^{2+}$, Cu$^{2+}$ and Fe$^{3+}$. But on the other side, it demonstrates that CM-QAOC can signal the occurrence of scaling or corrosion by responding to the concentration changes of hardness ions and corrosion product ions under certain conditions.

### Influence of sunshine time

In an open system, the cooling tower and some constructions will be solarized, which can influence the quantum yield of the fluorophor in the water.

The 50 mg/L CM-QAOC solution was exposed to the sun, and the fluorescence spectra of CM-QAOC were measured at set intervals. The results are shown in Figure 9, which demonstrated clearly that with the illumination time prolonging, the fluorescence intensities decreased gradually. But the change showed a slower trend and remained stable after 9 h, with 24 percent decrease of intensities compared to the one that wasn’t solarized. This indicated that the solarization can quench the fluorescence to some degrees.

### Biodegradability of CM-QAOC

It is generally accepted that chemicals are easily biodegradable when their BOD$_5$/COD is larger than 0.6. They are biodegradable with a BOD$_5$/COD in the range of 0.3 to 0.6, but they will be difficult to biodegrade when the ratio
is between 0.1 and 0.3 and they are not biodegradable when the ratio is under 0.1. The COD and BOD$_5$ of chitosan, oligochitosan and CM-QAOC were determined, then the values of BOD$_5$/COD were calculated based on COD and BOD$_5$. All the results are listed in Table 1.

As molecules of chitosan and oligochitosan are made of C, H, O and N, these two chemicals are biodegradable. Further, the BOD$_5$/COD values of chitosan and oligochitosan are 0.72 and 0.80, respectively, both of which are greater than 0.6. This demonstrates the chitosan and its degraded product have a good biodegradability. In addition, CM-QAOC, the carboxymethylation and quaternionization product, can still be biodegradable as BOD$_5$/COD value is 0.53, being greater than 0.3. This means that the fluorescent water treatment chemical is environmentally friendly, and this is one of the most important advantages of CM-QAOC over other fluorescent water treatment chemicals that possess conventional fluorescent groups (Gutowski et al. 2015).

Table 1 | COD and BOD$_5$ value of chitosan and its derivatives

<table>
<thead>
<tr>
<th></th>
<th>COD (O$_2$, mg/L)</th>
<th>BOD$_5$ (O$_2$, mg/L)</th>
<th>BOD$_5$/COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan</td>
<td>817.31</td>
<td>589.12</td>
<td>0.72</td>
</tr>
<tr>
<td>Oligochitosan</td>
<td>787.26</td>
<td>631.08</td>
<td>0.80</td>
</tr>
<tr>
<td>CM-QAOC</td>
<td>336.54</td>
<td>177.91</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Figure 8 | Influence of scaling ions on the fluorescence of a CM-QAOC solution of 50 mg/L: (a) Cu$^{2+}$; (b) Fe$^{3+}$.

Figure 9 | Influence of the sunshine time on the fluorescence intensity.
CONCLUSION

CM-QAOC showed interesting fluorescence when we used it as a kind of water treatment chemical in industrial cooling water and here we have explored the possibilities of its fluorescent tracing application. The linear relation between the agent concentration and fluorescence intensities shows that the agent’s concentration can be monitored by the fluorescence emission spectra at the common pH values of 5 to 9 for industrial cooling water. We also investigated the fluorescent properties of this chitosan derivative under different common conditions for cooling water. The fluorescent properties were compatible to those of common water chemicals serving as corrosion inhibitors, scaling inhibitors, dispersants and non-oxidizing biocides, causing no apparent change in fluorescence, but CM-QAOC is sensitive to the oxidizing biocide NaClO and solarization to some extent. The positive ions have a clear and great influence on the fluorescence. In our previous study, it had been proved that once the pH is not within the common range of 5 to 9, fluorescence of CM-QAOC would change tremendously in intensity and the emission maximum. It is well known that water will be corrosive when the pH is below 5, and likely to scale when the pH is above 9. So CM-QAOC can also indicate the change of pH in a water system, implying occurrence of corrosion or scaling. In conclusion, CM-QAOC has high efficiency in scaling and bio-fouling inhibition, and the fluorescence properties endow this agent with the possibility of being used as a concentration tracer without any further modifications. It can trace itself, damaged components and even abnormal conditions with its intrinsic fluorescence originating from its molecular construction. The multi-functional water treatment chemical could be economical and also could simplify handling and operation, making control management easier.

This study is constructive and instructive as it inspired us to design a new type of fluorescent tracer, by which the concentration of water treatment agents and damage ions can be followed up with its fluorescent properties instead of introducing a fluorescent group or other fluorescent chemicals. On the other side, the fluorescent properties are insensitive to pH value and positive ions like Ca$^{2+}$, Mg$^{2+}$, Cu$^{2+}$ and Fe$^{3+}$, which means that CM-QAOC can reflect the change in water chemistry such as pH or metal ion concentration and residual agents, acting as an indicator of scaling or corrosion. The mechanism of the fluorescence is not clear, but it may be the structure factor that plays the key role in producing fluorescence. So, more work should be done to study its mechanism.

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REFERENCES


Colthup, N. B., Daly, L. H. & Wiberley, S. E. 1990 *Introduction to Infrared and Raman Spectroscopy*. Harcourt Brace

Jovanovich, San Diego, CA, USA.


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