State of art bio-materials as scale inhibitors in recirculating cooling water system: a review article

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ABSTRACT

During the operation of the circulating cooling water system, the inorganic scale deposition may cause technical problems, such as reduction of heat transfer efficiency in cooling systems and obstruction of pipes. In the industry, chemicals are often used as scale inhibitors in scale deposition control, antiscalants popular in industry are generally phosphorus and nitrogen containing chemicals, which may lead to eutrophication. However, increasing environmental concern and discharge limitations have guided antiscalants to move toward biodegradable, nontoxicity and cost-effectiveness. This paper reviews current researches on application of using bio-materials as scale inhibitors, including proteins and amino acids, polysaccharides, plant extracts, microbial reagents, and microbiological product. The non-bioaccumulation, low cost, readily biodegradability and sustainably available characters promote the development of green scale inhibitor chemistry.

Key words: bio-materials, calcium carbonate scaling, cooling water system, scale inhibitors

HIGHLIGHTS

• Scale inhibition mechanisms, evaluation methods and traditional scale inhibitors were prepared.
• Scale inhibition efficiency of various bio-materials including proteins, polysaccharides, plant extracts are comprehensively reviewed, critically evaluated and along with their scale inhibition mechanism thoroughly discussed.
• Utilizing biological method on scaling control was proposed as future research direction.

ABBREVIATIONS

ACC amorphous calcium carbonate
AM acrylic amide
ATMP aminotrimethylene phosphonic acid
\(\beta\)-CD \(\beta\)-Cyclodextrin
\(\beta\)-CD-PEG polyethylene glycol modified \(\beta\)-cyclodextrin
BACC borated aminated cellulose citrate
CA chronoamperometry
CIT citrate
CMCS carboxymethyl chitosan
CMI carboxymethyl inulin
CMP compound microorganism preparation
CMS carboxymethyl starch
CTS Chitosan
DETPMP diethylenetriaminedipentamethylene phosphonic acid
EDS energy dispersion spectrosopies
EEM 3-D excitation/emission matrix
EIS electrochemical impedance spectroscopy
EPS extracellular polymeric secretions
FCP fast controlled precipitation method
FESEM Field emission scanning electron microscope

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1. INTRODUCTION

As a fact of global water shortage, wastewater has now been recognized as a significant source of water for non-potable uses (Wade Miller 2006; Metcalf Eddy 2007), especially as makeup water for industrial cooling circuits. However, due to poor quality, secondary-treated municipal wastewater usually contains appreciable amounts of hardness, phosphate, ammonia, dissolved solids, and organic matter compared to the amounts in fresh water (Weinberger 1966). In recirculating cooling systems, the water constituents become concentrated many times (typically 4–8 times) due to constantly water evaporation, the inorganic ions are usually 4 to 8 times higher than the supplemental water. The scaling ions, especially Ca²⁺ and carbonate alkalinity, gradually concentrate to exceed the solubility and form scale deposition on heat exchange equipment surfaces, according to the following equation:

\[
Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3(s) + CO_2(g) + H_2O
\]

In general, scale deposition is recognized as a crystallizing procedure involving four stages (Al-Rawajfeh et al. 2005; Hasson & Semiat 2006):

- Oversaturation
- Nucleation
- Crystal growth around nucleus
- Continuous growth of microcrystals along with scale layer thickening.

Adherent scale deposition on heat exchange equipment surfaces can cause severe technical problems, such as reducing heat transfer efficiency and obstructing pipelines in cooling systems, 2 mm layer of scale in thermal pipeline can reduce...
47% heat transfer efficiency, which leads to great economic pressure in industrial production, therefore, effective countermeasures must be taken to solve scaling problems (Gauthier et al. 2012; Xu et al. 2012; Liu et al. 2013).

Addition scale inhibitors is the most common method for controlling scale deposition, using antiscalants can reduce scaling on heat exchange surface, increase cooling water concentration ratio and lift efficiency during the desalination processes (Greenlee et al. 2010; Li et al. 2011). The scale inhibition mechanisms are multiple for different varieties of antisclants as described in Figure 1. In general, scale inhibition mechanisms involve as follows:

1. Threshold inhibition. Threshold scale inhibitors can effectively inhibit scale formation at tiny dosage, even 1,000 times less than a balanced stoichiometric ratio of scaling cations (Cooper 1979).
2. Scale inhibitors molecules can complex with free scaling ions (e.g., Ca$^{2+}$ and Mg$^{2+}$), prevent them from being precipitated via strongly chelation and dispersion effects, keep them suspended in aqueous solution (Zhang et al. 2013).
3. Scale inhibitors’ molecular functional groups can adsorb onto active sites of the scale crystals’ particular growth location, thereby, scale precipitation is prevented by modifying the crystal morphology and distorting the crystal lattice (Zeng et al. 2014; Amjad & Demadis 2015).

Multitudinous materials have been proposed and successfully experimented as antiscalants scale inhibitors, these chemical agents are chosen according to the operating conditions of cooling water reservoirs and transportation pipelines. The phosphorus scale inhibitors include phosphates and phosphonates, which are the most popular commercial scale inhibitors benefit from their low cost and high effectiveness, however, their utilization has been restricted due to the phosphorus-containing property contributes to the total environmental phosphate content, which promotes eutrophication of the receiving surface water. In addition to phosphorus scale inhibitors, synthetic non-phosphorus scale inhibitors include polycarboxylic acids, polysulfonic acids, and their derivates are also widely used in industry, these synthetic polymeric scale inhibitors exhibit high scale inhibition efficiency with excellent chelation and dispersion effect, however, their scale inhibition performance is significantly affected by molecular weight, moreover, their feasibility at high temperature conditions indicated they were non-biodegradable (Kumar et al. 2018).

Nowadays, environmental protection pressure and government legislation lead the research on scale inhibitors to move toward ‘green’ scale inhibitors, which are characterized as follows: (1) excellent antiscaling capacity; (2) nontoxicity;
Ca\(_{2}^{+}\) precipitation. The Fast Controlled Precipitation (FCP) method (also known as CO\(_{2}\) degasification method) was first developed in 1994 (Martin-Dominguez 1994) and has been used in many studies (Tlili et al. 2001; Fathi et al. 2006; Karoui et al. 2010), the principle of this technique is based on the motivation of the calco-carbonic equilibrium in the direction of CaCO\(_{3}\) precipitation with dissolved-CO\(_{2}\) continually degassing, which can be achieved by either agitation or nitrogen sparge, the reaction is basing on the following equation (Menzri et al. 2017):

\[
\text{Ca}^{2+} + 2\text{HCO}_3^- \leftrightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \uparrow
\]  

(2)

The advantage of FCP method is simultaneously quantifying the scaling propensity and CaCO\(_{3}\) crystal nucleation, however, considering influence of partial pressure of CO\(_{2}\), the ambient temperature, and other experimental parameters, the FCP tests should be ran in parallel (Gauthier et al. 2012).
### Table 1 | Schematic Structures of proteins as scale inhibitors cited in this work

| Scale Inhibitors | Schematic Structure/Synthetic route | Type of scale | Maximum inhibition efficiency/ Functionality | Test methods | Refs. |
|-----------------|------------------------------------|---------------|---------------------------------------------|--------------|-------|
| Pteroyl-L-glutamic acid (PGLU) | ![Schematic Structure](image1) | CaCO₃ | 100% | static jar test | Kumar et al. (2010) |
| Thiamine(50%) and Pyridoxine(50%) | ![Schematic Structure](image2) | CaCO₃ | 66.78% | Chronoamperometry | Menzri et al. (2017) |
| Cysteine-rich Mdm2 peptide | ![Schematic Structure](image3) | CaCO₃ | 58% | constant composition method | Dalas et al. (2006) |
| Casein peptone N1 19516/tryptone N1 19553 | ![Schematic Structure](image4) | BaSO₄ and CaCO₃ | Extend the scaling time of the test tube | dynamic tube blocking tests | Mady & Kelland (2017) |
| Casein Micelle | ![Schematic Structure](image5) | | | | |
| poly (citric acid) | ![Schematic Structure](image6) | CaSO₄ | 98.8% | static jar test | Zhao et al. (2016) |
| citrate | ![Schematic Structure](image7) | CaCO₃ | increased induction period from 1 min at 0% CIT/Ca to 30 min at 100% CIT/Ca | Turbidity measurement | Montanari et al. (2017) |
| sodium citrate (SC) + 10-Methylacridinium iodide (MAI) | ![Schematic Structure](image8) | CaCO₃ | 98.3% | static jar test | Zhang et al. (2020) |
| curcumin-citric acid-aspartic acid polymer (PCCA) | ![Schematic Structure](image9) | CaSO₄/CaCO₃ | 99.7% /98.8% | static jar test | Yuan et al. (2020) |
2.3. (NH₄)₂CO₃ vapor diffusion method

Scale crystallization occurs in the millisecond range in the process of vapor diffusion method, which shows significant attractiveness in the research of CaCO₃ crystallization (Addadi et al. 1987; Gehrke et al. 2005; Tourney & Ngwenya 2009). Generally, its key distinction with other methods is that CaCO₃ crystals are precipitated from experimental solution which gradually supersaturates under the continuously decomposing ammonium carbonate in a closed container, according to the following:

Table 2 | Schematic Structures of Chitosan based polysaccharides as scale inhibitors

| Scale inhibitors                             | Schematic Structure/Synthetic route | Type of scale | Maximum inhibition efficiency | Test methods             | Refs.                  |
|----------------------------------------------|------------------------------------|--------------|-------------------------------|--------------------------|------------------------|
| CTS–MA–SS–AM                                | ![CTS–MA–SS–AM](image)             | CaCO₃        | 95.62%                        | static jar test          | Guo et al. (2012)     |
| Chitosan biguanidine hydrochloride (CG)      | ![Chitosan biguanidine hydrochloride (CG)](image) | CaCO₃/ CaSO₄ | 91% 95%                      | Membrane scaling experiments | Maher et al. (2020) |
| carboxymethyl chitosan (CMCS)                | ![carboxymethyl chitosan (CMCS)](image) | CaCO₃        | 50 ppm of CMC obviously extended the precipitation time from 18 min to 50 min | dynamic tube block tests | Macedo et al. (2019) |
| O-carboxymethylchitosan                     | ![O-carboxymethylchitosan](image) | CaCO₃        | Reducing average particle size from 9–25 μm to 1.5–17 μm | vapor diffusion method    | Yang et al. (2010)   |
| O-(hydroxyisopropyl) chitosan (HFCHS)       | ![O-(hydroxyisopropyl) chitosan (HFCHS)](image) | CaCO₃        | reducing crystallization degree and the average particle size | calcium carbonate crystallization | Yang et al. (2009) |

Table 3 | Schematic Structures of Cellulose based polysaccharides as scale inhibitors

| Scale inhibitors                             | Schematic Structure/Synthetic route | Type of scale | Maximum inhibition efficiency | Test methods             | Refs.                  |
|----------------------------------------------|------------------------------------|--------------|-------------------------------|--------------------------|------------------------|
| sodium carboxymethyl cellulose (SCMC)        | ![sodium carboxymethyl cellulose (SCMC)](image) | CaCO₃        | 93%                          | pH displacement method   | Xu et al. (2019)      |
| Borated aminated cellulose citrate (BACC)    | ![Borated aminated cellulose citrate (BACC)](image) | CaCO₃        | 91.57%                       | static jar test          | Gan et al. (2018)     |
The vapor diffusion method is appropriate for slow CaCO₃ crystallization benefits from the relatively stable gas-liquid phase contributes to eliminate the interference of other factors, this promotes well-faceted calcite crystals’ formation for further microscopic observations (Gehrke et al. 2005; Liu et al. 2016a).

2.4. Turbidity method

Deposition of scaling particles aggregates cause haze and further increases solution turbidity, hence, changes on turbidity index can be utilized to evaluate antiscalants’ performance. During the experimental processes, the antiscalting performance of scale inhibitor can be derived from monitoring turbidity rate as a function of time while the dispersion effect can be derived from inspecting size and quantity of the obtained precipitation particles. Turbidity method is simple and feasible to obtain antiscalants’ performances, especially convenient on prescreening of antiscalants, it not only provides information on scale inhibitor performance, but also rich in information on scale formation kinetics and inhibition mechanisms (Tantayakom et al. 2005a, 2005b; Wallace et al. 2009; Zhou et al. 2010; Al-Hamzah et al. 2014). However, since several experimental factors can interfere scale crystallizing procedure, this in turn affects the reproducibility of turbidity measurement.

Table 4 | Schematic Structures of Glucose based polysaccharides as scale inhibitors

| Scale inhibitors | Schematic Structure/Synthetic route | Type of scale | Maximum inhibition efficiency/Functionality | Test methods | Refs. |
|------------------|------------------------------------|---------------|---------------------------------------------|--------------|-------|
| SG               | ![Schematic Structure of SG](image) | CaCO₃         | Lowering the CaCO₃ formation kinetics for four times | light-scattering method | Ou & Chiang Hsieh (2016) |
| MA-SSS-OS        | ![Schematic Structure of MA-SSS-OS](image) | CaCO₃         | 98.87%                                      | static jar test | Guo et al. (2013) |
| CMS              | ![Schematic Structure of CMS](image) | CaCO₃         | 89.80%                                      | static jar test | Wang et al. (2017) |
| St-g-PAA         | ![Schematic Structure of St-g-PAA](image) | CaCO₃         | 95.79%                                      | static jar test | Yu et al. (2018) |
| B-CD–PEG         | ![Schematic Structure of B-CD–PEG](image) | CaCO₃         | 89.1%                                       | static jar test | Liu et al. (2016) |
| β-CD–MA–SSS      | ![Schematic Structure of β-CD–MA–SSS](image) | CaCO₃         | 99.9%/95.5%                                 | static jar test | Gu et al. (2013) |
| SL               | ![Schematic Structure of SL](image) | CaCO₃         | 45.2%                                       | static jar test | Ouyang et al. (2006) |

equation (Sarkar et al. 2013):

\[(\text{NH}_4)_2\text{CO}_3 \rightarrow 2\text{NH}_3 \uparrow + \text{CO}_2 \uparrow + \text{H}_2\text{O}\]  \hspace{1cm} (3)

\[\text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{CaCO}_3 \downarrow + 2\text{HCl}\]  \hspace{1cm} (4)
2.5. Critical pH method

The critical pH method was first proposed by (Feitler 1972) in order to detect CaCO₃ deposition, with continual addition of sodium hydroxide, the solution pH value exceeding the critical supersaturation leading the carbonate precipitation occurs (Sousa et al. 2016), H⁺ generated by precipitation reaction result in an immediate pH decrease, however, the stronger antiscaling performance the inhibitor possesses, the higher critical pH it can tolerate (Zhang et al. 2011; Sousa et al. 2016).

2.6. Ultimate carbonate hardness method

Ultimate carbonate hardness method has a certain guidance on field application of antiscalants’ running in recirculating cooling water system. In formal running period, concentration ratio represents the concentrating situation with respect to cooling water system, which can be calculated either by ratio of chloridion or hardness value. Ideally without scale deposition, both chloride and hardness concentration ratio maintain numerical equality (equal in magnitude), however in real operation, the nucleation and crystallization of scaling ions result in decrements on alkaline concentration ratio, this gives rise to a numerical difference between concentration ratio of chloride and alkalinity, such difference become larger as water become concentrated with continually evaporation. The total solution carbonate hardness is considered as ultimate carbonate hardness.

### Table 5 | Schematic Structures of Plant extracts as scale inhibitors

| Scale inhibitors | Main constituents | Functionality | Test methods | Refs. |
|------------------|------------------|---------------|--------------|-------|
| Herniaria glabra | herniaria saponins I-VII, flavonoids, umbelliferone, herniarin, phenolic acids, tannins, and essential oil. | completely inhibition CaCO₃ formation at 50 mg/L | Fast Controlled Precipitation method | Horner et al. (2017) |
| Spergularia rubra | Phytoecdysteroids, di-C-glycosyl-flavone, 36 C-gly cosyl-flavone | completely inhibition CaCO₃ formation at 30 mg/L | | Cheap-Charpentier et al. (2016) |
| Parietaria officinalis | mucus, potassium nitrate, tannin, sulfur, glucan, and flavonoid pigments. | completely inhibition CaCO₃ formation at 100 mg/L | | |
| Hylocereus undatus | amino acids, sugars, polysaccharides, organic acids, fatty acids, and flavonoid | completely inhibition CaCO₃ formation at 24 mg/L | | |
| Mazuj gall | 4-Methyl-3-penten-2-one 2-Methoxyfuran 4-Hydroxy-4-methyl-2-pentanone 1-(2-Butoxyethoxy) ethanol 1,2,3-Benzenerioli Hexadecane 5,4,3-Trihydroxybenzoic acid methyl ester n- Hexadecanoic acid Heptadecane | 1,000 ppm of Mazuj gall extract provided a high inhibition efficiency of 97.2% in against 592 ppm total hardness | static beaker tests | Mohammadi & Rahsepar (2018) |
| Bistorta Officinalis | Pyridine, Toluene, 2-Nonanone, p-Xylene, Benzene, Decane, Undecane, Tritetracontane, Ethanol, Tridecane, Propanedioic acid, 1,2-Benzenedicarboxylic acid, Benzoic acid, Eicosane, 1,2-Benzenedicarboxylic acid, Heptacosane, Tetracosane, Octacosane, Nonacosane, Heptacosane | 1,000 ppm of Bistorta Officinalis extract provided a high inhibition efficiency of 99.5% in against 592 ppm total hardness | | Mohammadi & Rahsepar (2019) |
| Gambier extract | 40% of tannic acid, 25% of catechin, and 12% of quercetin. | 200 ppm Gambier extract brought 70–80% CaCO₃ inhibition efficiency | bottle-roller batch method | Suharso et al. (2011) |
| Modified Gambier extract with benzoic and citric acid | Ratio of Gambier extract modification =2:1:2 (Gambier:benzoic acid:citric acid). | showed an inhibition efficiency of 12–92% under the concentration range of 50–300 ppm | bottle-roller batch method | Suharsoa (2017) |
| Curcumin | accounts for about 77%; demethoxycurcumin for about 17% and bisdemethoxycurcumin about 3% | showed the highest CaSO₄ scale inhibition rate of 95.0% at 10 ppm | static jar test | Nayunigari et al. (2016) |
hardness value when the numerical difference exceed 0.2, thus higher ultimate carbonate hardness value attribute to superior scale inhibitor with remarkable scaling tolerance.

2.7. Static jar test

Static jar test is the most widely used test method for evaluating scale inhibition efficiency due to its low cost and quickness. Static assessment based on scale precipitation formation experiment through mixing two chemically incompatible brines (NaHCO₃ and CaCl₂ for CaCO₃ usually) along with the scale inhibitors to form precipitation, after which, an incubation period, usually 10 h water bath, is implemented on mixed brines with and without scale inhibitors, once finished, aliquots are filtered to analyze free Ca²⁺ ions and the scale inhibition efficiency is obtained by dividing numerical differences according to NACE Standard Testing Methods (NACE International 2002; NACE International 2015) and Chinese National Standard (Chinese National Standard 2008; Chinese National Standard 2019).

2.8. Electrochemical methods

Electrochemical techniques, including chronoamperometry (CA), chronoelectrogravimetry, and impedancimetry, have proven very useful in the study of scale processes in a range of media (Belarbi et al. 2016; Menzri et al. 2017; Piri & Arefinia 2018), with the cathodic potential applied, the reduction of dissolved dioxygen form hydroxyl ions leading the electrode interfacial pH to increase, this accelerate CaCO₃ deposition according to the following equations:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]  \hspace{1cm} (5)

\[ \text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \]  \hspace{1cm} (6)

\[ \text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3(s) \downarrow \]  \hspace{1cm} (7)

### Table 6 | Schematic Structures of microbiological product as scale inhibitors cited in this work

| Scale inhibitors | Schematic Structure/ Main Constituents/ Synthetic route | Type of scale | Maximum inhibition efficiency/Functionality | Test methods | Refs. |
|------------------|----------------------------------------------------------|---------------|---------------------------------------------|--------------|-------|
| EPS of a cyanobacterium (Schizothrix.sp) | polysaccharides, proteins, humic-like substances, nucleic acid, lipids, and glycoproteins | CaCO₃ | inhibiting CaCO₃ precipitation pH recording in CaCO₃ precipitation | static jar test | Kawaguchi & D Ec Ho (2002) |
| s-EPS of Bacillus cereus | | CaCO₃ | 87.60% showed an inhibition impact in against 2,664 mg/L Ca²⁺ and 2,544 mg/L CO₃²⁻ ions at pH 9 under a concentrations range of 100–1,000 mg/L | static jar test | Yang & Xu (2011) |
| Xanthan gum | | CaCO₃ | exhibited a limit concentration ratio of 3.87 ultimate carbonate hardness method | | Chen et al. (2019) |
| Compound Microorganism Preparation | dry powder of nitrobacteria, bacillus subtilis, photosynthetic bacteria and thiobacillus denitrifcans. | mixed | showed high calcium adsorption capacity of 1.94 mg Ca²⁺/g protein at pH 10, 150 °C and 1 atm pressure. Adsorption experiments | | Han et al. (2017) |
| Protein of Tepidimonas fonticaldi | proteins | CaCO₃ | 100% | static jar test | Shi et al. (2017) |
| PIA-co-ESA | | CaCO₃ | 81.2% | static jar test | Cui & Zhang (2019) |
| IA/SAS/SHP | | CaCO₃ | 95.1% | static jar test | Zhenfa Liu (2015) |
The non-conductive calcareous deposition on the electrode surface reduces the current density which is simultaneously recorded by chronoamperometric measurements, it reaches to the scaling time when the electrode surface is completely covered by the insulating layer of CaCO₃, which represents the scaling condition of a sampling solution. Generally, among these electrochemical techniques, chronoamperometric is more basic and commonly used to evaluate scale inhibition efficiency while electrochemical impedance measurements allow observing the nucleation, growth, and total surface coverage of the deposition (Ketrane et al. 2009; Zuo et al. 2020).

2.9. Dynamic tube blocking test
Dynamic tube blocking test is one of the main testing methodologies to evaluate the minimum inhibitor concentration (MIC) required to prevent the formation of scale under dynamic flow condition. In principle, it involves measurements of the increasing pressure caused by scale deposition on the test tube wall. Scale inhibition efficiency is represented by the ratio of the time needs to obstruct the tube flow in the presence and the absence of the inhibitors (Macedo et al. 2019; Sanni et al. 2019).

2.10. Pilot plant test
The pilot plant tests are conducted in a recirculating cooling water system or in a simulating device to test the field application performance of a scale inhibitor (Neveux et al. 2016; Chen et al. 2019). Comparing to other methods, pilot plant test can not only offer a flexible operation as the system can be directly controlled by computer, but also directly obtain the feasibility of the tested agent. However, such experiment condition of pilot plant tests is difficult to achieve in general laboratories.

3. TRADITIONAL SCALE INHIBITORS
During the last few decades, various types of inhibition chemicals and antiscalants have been widely used to prevent mineral scale deposition. Current scale inhibitors applied in industrial cooling water treatment can be classified into the following categories.

3.1. Phosphorus-containing scale inhibitors
Inorganic phosphonates and organophosphorus are mainly phosphorous-containing scale inhibitors that have been used for many years. Inorganic phosphonates, mainly refer as sodium tripolyphosphate (Na₅P₃O₁₀) and sodium hexametaphosphate (Na₆P₆O₁₆), are effective scale inhibitors due to the presence of phosphate group (-PO₃)(Lin & Singer 2005). Their application as antiscalants has been limited because of low solubility and lower thermal stabilities. However, organophosphorus, such as aminotrimethylenephosphonic acid (ATMP), polyamino polyether methylenephosphonate (PAPEMP), and diethylenetriaminonpentamethylene phosphonic acid (DETMPMP), overcome this shortcoming due to C–P bonds in its molecular are more stable than O–P–O bonds at higher temperatures (Ghani & Al-Deffeeri 2010; Mpelwa & Tang 2019).

Phosphorus-containing scale inhibitors display a high strong scale inhibition action by sequestering scalants through a threshold effect at sub-stoichiometric amounts. However, on account of phosphorus-based inhibitors serve as nutrients after discharge, which will lead to eutrophication difficulties, therefore, high levels of phosphorus-containing scale inhibitors in industrial applications are becoming increasingly restricted (Rahman 2013).

3.2. Polycarboxylates scale inhibitors
Polycarboxylates scale inhibitors possess functional carboxyl groups (–COOH) in its molecular structure, making them have strong chelating and dispersing abilities on Ca²⁺. During CaCO₃ crystallization process, polycarboxylates can significantly inhibit CaCO₃ crystal growth by adsorption on crystal surface, modify the regular CaCO₃ crystal morphology (Wada et al. 2001). Widely known polycarboxylates scale inhibitors are poly-maleic acid, polyacrylic acid and poly (methacrylic acid) due to their high performance-price ratio. Moreover, polycarboxylates scale inhibitors are also reported to copolymerized with other functional groups for better performance (–NH₂, -OH, -COOH, -SO₃H and so on.) (Shakkthivel & Vasudevan 2006; Yang et al. 2017; Dong et al. 2018), in the cases of monomers embedded to polymer molecules, multiple functional groups acted synergistically to enhance both dispersion and adsorption capacity when polymer preventing scale nucleation and growth.
3.3. Organic Green scale inhibitors

With the severe restriction of waste water discharge to the environment, green chemistry demands scale inhibitors to move towards the direction of environmentally friendly, which is readily biodegrability, no-bioaccumulation, and non-toxic. Broadly speaking, polyaspartic acid (PASP), polyepoxysuccinic acid (PESA) and carboxymethylulinulin (CMI) are three typical representatives of green inhibitors, their antiscaling properties have been well documented as well as toxicity, solubility, biodegradability, and synthetic routes, their non-nitrogenous, non-phosphorus and environmental acceptability together with excellent antiscaling properties allow them to be the most promising alternatives to conventional scale inhibitors (Hasson et al. 2011; Chaussemier et al. 2015; Kumar et al. 2018; Mpelwa & Tang 2019).

Among the above-mentioned scale inhibitors, several recent studies modified PASP with B-cycloextrin (Fu et al. 2020), urea (Zhang et al. 2016a, 2016b), glycine (Migahed et al. 2016), tyrosine (Tyr) and tryptophan (Trp) (Zhang et al. 2017) by grafting copolymerization, such modifications improved its scale inhibition efficiency in different degrees, giving PASP-based copolymer inhibitors a superior performance in against CaCO3, CaSO4 and Ca3(PO4)2. Moreover, molecular dynamics simulations indicated that scale inhibition ability by sulfamic/amino modified PASP came from preventing the growth of CaSO4 crystal planes ((040), (041) and (113)) (Zhang et al. 2017), this provided an in-depth study on its scale inhibition mechanism at atomistic level.

PESA as a green scale inhibitor was first synthesized in the beginning of 1990s in USA, its nonhazardous and highly biodegradable properties enable it to displace traditional scale inhibitors. In a previous work, PESA was regarded as the alternative scale inhibitor of PASP due to the better performance in against CaCO3 deposition (Liu et al. 2012). In a recent study (Huang et al. 2019), PESA with hyper-branched structure showed a stronger antiscaling performance than linear PESA, the relate scale inhibition mechanisms include prolonging the CaCO3 crystal nucleation and reducing the number of crystal nucleus.

In addition, carboxymethylulinulin (CMI) is a polysaccharide-based polycarboxylate isolated from the roots of Inula heliennium, benefits from carboxylic acid groups in its molecular structure, CMI possesses remarkable antiscaling property in preventing calcium carbonate crystallization. Study from (Krboga & Öner 2012) indicated negatively charged functional groups in CMI molecular assumed the main responsibility in retarding CaCO3 precipitation. Moreover, CMI molecules can interact closely with the calcite crystal surfaces of (012), (104), (110) and (110) through Van Der Waals intermolecular interactions, electrostatic interactions, and hydrogen-bonding interaction, consequently leads a high efficiency in inhibiting the growth of the calcite (Zhang et al. 2016a, 2016b).

3.4. Blending scale inhibitors

Specifically, a blending scale inhibitor usually functions more efficiently than any single inhibitor. For an enhanced synergistic inhibition, blended scale inhibitors should be adopted according to a certain proportion and guarantee the concentration of each component not below the minimum inhibitor concentration. It’s worth noting that the synergistic action of blending scale inhibitors usually occurs under the circumstances when each component possesses different scale inhibition mechanisms. Synergistic effect between some scale inhibitors have been found in some literatures, for example ATMP and DTPMPA (Zeino et al. 2018), PBCTA, HEDP and ATMP (Li et al. 2014), sodium gluconate (SG) and PBTC (Ou & Chiang Hsieh 2016).

4. APPLICATION OF BIO-MATERIALS AS SCALE INHIBITORS

Bio-materials, derive from natural environment, possess potential functionalities for antiscaling effect due to the presence of polylphosphates, carboxylic acid, alcohol, and aromatic amines groups in their molecular. The non-bioaccumulation, low cost, readily biodegradability and sustainably available characters help them gain widespread concern. Most importantly, bio-materials with non-poisonous, low cost, and easily biodegradable, possess great potential in applying as industrial scale inhibitors. In this part, bio-materials are classified into 4 categories, proteins and amino acids, polysaccharides, plant extracts and microbial products, their scale inhibition performance along with mechanisms are discussed separately.

4.1. Proteins and amino acids molecules as scale inhibitors

Except polyaspartic acid, various proteins and amino acids have proven excellent anti-scaling capacity. In a previous study (Kumar et al. 2010), a type of water-soluble vitamin M, Pteroyl-L-glutamic acid (PGLU), was conducted as scale inhibitor, 120 mg/L of PGLU showed 100% CaCO3 scale inhibition efficiency according to static jar tests at 70 °C. Dynamic tube
blocking tests also showed the minimum inhibitor concentration (MIC) required for scale inhibition at 110 °C is 160 mg/L, it is therefore concluded that PGLU could be a favorable green scale inhibitor. Besides PGLU, a mixture of another two vitamins, RS1066 (Thiamine and Pyridoxine), was applied as scale inhibitor by (Menzri et al. 2017), they conducted CO2 degasification method and chronoamperometry experiments to test its anti-scaling performance. As a result of CO2 degassing by stirring, 160 mg/L RS1600 inhibited calcite scale via delaying the nucleation time from 30 to 72 min in tested Hamma hard water. The chronoamperometry showed the scaling time increased 2 times under the presence of 40 mg/L of RS1600, corresponded a 66.78% inhibition efficiency. The FTIR, XRD and Raman spectroscopy demonstrated the vitamins blending scale inhibitor, RS1600, modified the crystalline structure and made the calcite crystalline to form a metastable phase to inhibit the calcite crystal formation. In a previous study, a 48-amino-acid-long peptide, cysteine-rich Mdm2 peptide, was tested as a scale inhibitor (Dalas et al. 2006) by constant composition method to investigated the calcite inhibition by cysteine-rich Mdm2 peptide. For a total calcium concentration range of 80–120 mg/L, Mdm2 peptide reached a maximum inhibition of 58% on calcite crystal growth. Side terminal carboxyl groups of Mdm2 peptide fragment were regarded as binding sites which interact with calcite surface through hydrogen bonding, making the crystal surface grow sites blocked.

Recently, (Mady & Kelland 2017) investigated the barium sulfate and calcium carbonate inhibition performance of a series natural proteins, in their dynamic tube blocking tests, variation of tube pressure indicates tube flux changes was regarded to represent antiscalping performance. The inhibitor dosage when rapid tube blocking occurs was also recorded as fail inhibitor concentration (FIC). As a result, under a pH range of 5 – 7 at 100 °C and 80 bar, peptone plus 19544, casein peptone N1 19516, and tryptone N1 19553 exhibited excellent performance on preventing barium sulfate scaling in heat pipe, corresponding a FIC of 50, 50 and 20 ppm, respectively. For calcium carbonate scaling inhibition, casein peptone N1 19516 and tryptone N1 19553 were superior than commercial scale inhibitors (ATMP and DTPMP), their FIC was 5 ppm for each 8 min run.

Besides, citric acid has long been proven to be a scale inhibitor (Reddy & Hoch 2001; Wada et al. 2001), however, recent antiscalping researches have lay emphasis on its derivatives, such as poly (citric acid) (Zhao et al. 2016), citrate (Tobler et al. 2015) and polymerized citric acid (Yuan et al. 2020). In the study of (Zhao et al. 2016), the calcium sulfate inhibition performance of poly (citric acid) was investigated by static jar tests according to Chinese standard GB/T16632–2008. With a total hardness of 2,040 mg/L, 2.5 mg/L poly (citric acid) showed an CaSO4 inhibition rate over 90%, which eventually up to 98.8% when the dosage reached 25 mg/L, such antiscaling performance is preeminent. Moreover, for higher concentration of 6,000 mg/L Ca2+ and 7,000 mg/L SO4 2-, 25 mg/L poly (citric acid) possessed an 80% scale inhibition rate, indicated poly (citric acid) was a suitable scale inhibitor for high hardness. The scale inhibition mechanism carried from SEM, FTIR and XRD indicated that suspended carboxylic groups on the PCA molecules could maintain Ca2+ ions free in solution by complexation, making PCA molecules easy to absorbed on active sites of growing CaSO4 crystals. That consequently, distorted the CaSO4 crystal lattice and inhibited the CaSO4 scale deposition.

The deprotonated form of citric acid, citrate (CIT), is a well-known complexing agent for dissolving calcium and inhibiting CaCO3 growth, its excellent biodegradability making it a promising green scale inhibitor. During the process of CaCO3 crystallization, the presence of CIT could effectively retard calcium carbonate nucleation, the nucleating induction period increased with an increase in CIT/Ca ratio, from 1 min at CIT/Ca = 0% (pure system) to 30 min at 100% CIT/Ca (Montanari et al. 2017), such remarkable scaling prevention performance was closely related to hydroxyl and carboxyl groups which absorbed on crystal surfaces, led calcite crystals with modified morphologies and sizes (Tobler et al. 2015). In a recent study, sodium citrate (SC) was found to cooperate with 10-Methylacridinium iodide (MAI) as a blending scale inhibitor (Zhang et al. 2020), the authors conducted static jar tests to evaluate the antiscaling performance of MAI–SC mixture in guidance of GB/T 16632-2008, an enhanced CaCO3 scale inhibition effect was found as MAI–SC mixture (MAI 50 mg/L and SC 150 mg/L) reached a peak antiscaling efficiency of 98.3% at 60 °C, the morphology of CaCO3 crystals was changed and the crystal form was altered. Such scale inhibition mechanism tends to be like interaction between -COOH/-OH and Ca2+ allowed the antiscalants adsorbed on calcium carbonate scale surface, a further quantum chemical calculation demonstrated such absorption mainly take place on (104) and (102) faces for calcite, (002) and (020) faces for vaterite respectively, thanks to this, MAI–SC mixture could therefore occupy the active growth sites of calcium carbonate deposition in solution and hinder the further growth of the crystals.

Another recent research reported (Yuan et al. 2020) a new polymer of citric acid, curcumin-citric acid-aspartic acid (PCCA), acted as a suitable antiscalant for both CaSO4 and CaCO3 scale. According to static jar tests, PCCA owned a maximum inhibition efficiency of 99.7% with merely 4 mg/L dosage in against CaSO4, even when Ca2+ ions reached up to 16,000 mg/L, the inhibition efficiency remained 90.7% at 10 mg/L dosage. Moreover, PCCA also possessed outstanding
capacity in against CaCO₃, a 20 mg/L dosage of PPCA exhibited 98.8% calcite inhibition efficiency under a tested water containing 500 mg/L high calcium bicarbonate at 80 °C.

4.2. Polysaccharides as scale inhibitors

Polysaccharides are widely distributed in nature, some of which constitute the cell walls, such as chitosan and cellulose, some are stored as nutrients for plants and animals. With widespread usage in the food, chemical, pharmaceutical, and other industries, polysaccharides also have great potential to applied as scale inhibitors. In this section, applications of polysaccharides as scale inhibitors are classified and reviewed.

4.2.1. Chitosan

Chitosan (CTS), a widely distributed biopolymer in nature, has been chemically modified and shown the potential of green scale inhibitor due to its nontoxic, CTS and its derivatives with broad areas of application had been reported in many studies as scale inhibitor. Previously (Guo et al. 2012), chitosan was copolymerized with maleic anhydride (MA), styrene sulfonic sodium (SSS), and acrylic amide (AM) to prepare CTS-MA-SSS-AM, which was highly effective as a CaCO₃ scale inhibitor, according to static jar tests (GB/T 16632-2008) at 70°, with an advanced CaCO₃ inhibition efficiency of 95.62%, 0.2 g/L CTS-MA-SSS-AM was capable in against Ca²⁺ 0.006 mol/L and HCO₃⁻ 0.0045 mol/L precipitated into calcite scale.

Recent research reported chitosan biguanidine hydrochloride (CG), obtained by modified chitosan with guanidine group, showed a good performance in retarding scale formation during real membrane desalinating application (with cross-flow unit for 6 h) (Maher et al. 2020), with only flux declines of 2.6 and 5% for CaSO₄ and CaCO₃ in feed water under concentrations of 10 and 15 mg/L respectively. Moreover, SEM analysis showed that CG strongly changed the precipitated scale crystals morphology, the initial needle-like CaSO₄ crystal structure was modified and transformed into an irregular structure while cubic CaCO₃ crystals were regulated to be cracked and distorted. The authors explained the antiscaling mechanism of CG that introducing chitosan backbone with guanidinium group increased its cationic charges, made CG can strongly combine with scalants along with anionic charges on its surfaces and consequently inhibited scale growth.

Another derivate of chitosan, carboxymethyl chitosan (CMCS) was also found to mediate the crystal growth of calcium carbonate previously (Liang et al. 2004), SEM and XRD demonstrated that high CMCS dosage of 1,000 mg/L significantly changed the crystal morphology of precipitated CaCO₃ crystals and facilitated them transfer to calcite form. In a dynamic tube block tests according to (NACE International 2005) NACE TM05110, carboxymethyl chitosan (CMCS) was functioned as a scale inhibitor of CaCO₃ under synthetic brine solution (Macedo et al. 2019). It was found that CMCS significantly reduced the scaling tendency of tested water, the precipitation time was obviously extended from 18 to 50 min under 50 mg/L of CMC, the minimum inhibitor concentration (MIC) of CMCS was 170 ppm for preventing scale formation at T = 70 °C and 1,000 psi. SEM along with infrared spectroscopy analysis showed CMCS effectively interacted with calcium ions through its carboxylate ions and lone pair of electrons on -OH and -NH₂ groups, which resulted in deforming the CaCO₃ crystal morphology and made the scaling ions hard to organize and preventing the scale formation.

These results showed consistency with previously results by (Yang et al. 2010), who investigated the impact of CMCS on CaCO₃ crystallization by vapor diffusion method, at 40°, they found the presence of CMCS obviously reduced the size of CaCO₃ particles from a particles range of 9–25 to 1.5–17 μm. From surface characterization results on obtained CaCO₃ particles, the authors suggested that during CaCO₃ crystallization, CMCS complexed with Ca²⁺ ions by -COO⁻– groups in its molecule, generated CMCS/Ca²⁺ complexes to reduce Ca²⁺ ions participated in CaCO₃ precipitation, led lattice distortion, and inhibited the growth of CaCO₃ nanoparticles.

Except carboxymethyl chitosan (CMCS), O-(hydroxyisopropyl) chitosan (HPCHS), which was obtained by modified chitosan with poly (ethyleneoxide)–poly (propyleneoxide)–poly (ethyleneoxide) (EO)ₓ(PO)ᵧ(EO)ｚ, also exhibited a regulation effect on CaCO₃ particle sizes distribution and morphology (Yang et al. 2009), the CaCO₃ precipitates were first obtained under the presence of HPCHS and then characterized by SEM, XRD and TGA methods, results showed the increased HPCHS dosage decreased the particle size and roughened the crystal surfaces. Based on the results of molecular dynamic simulation, the authors proposed a mechanism that under the presence of lone pair electrons of nitrogen atoms, HPCHS molecules could adsorb on the (104) surface and the edge of the CaCO₃ particles, thus achieved a regulatory effect on CaCO₃ formation.
4.2.2. Cellulose

Cellulose is also a widely distributed polysaccharide in nature with nontoxic, easy degradation and biocompatibility, cellulose and its derivatives are widely used in food, medicine, detergent, paper, energy, and environmental protection. Cellulose possesses remarkable potential to be effective scale inhibitor benefits from the abundant hydroxyl and carboxyl groups in its molecular, in a recent research (Xu et al. 2019), sodium carboxymethyl cellulose (SCMC) was applied as a scale inhibitor in industrial circulating water system. Several methods were conducted to evaluated scale inhibition performance of SCMC, including pH displacement method (by measuring pH change of the test solution before and after scaling), electrochemical impedance spectroscopy (EIS), and real application tests, the results showed consistency that SCMC possessed a promising prospect on fouling inhibition. Under a concentration range of 50–200 mg/L, SCMC exhibited 95 and 75% inhibition efficiency by pH displacement method and EIS study, respectively, while in real simulated dynamic circulating cooling water system, SCMC reached a scale inhibition efficiency of 93.2% under 200 mg/L (determined by fouling resistance changes). Based on these results, a further study of molecular dynamics simulation was carried out to explore the scale inhibition mechanism (Zhao et al. 2019), results indicated there was a strong interaction between oxygen atoms in SCMC and calcium ions in calcite (104) crystal planes, such strong interaction would distort and deform the plane of calcite and further hinder the normal growth of calcite crystal.

(Gan et al. 2018) Another multifunctional cellulose derivative, borated aminated cellulose citrate (BACC), showed excellent scale inhibition performance in a simulated cooling water, in which the Ca\(^{2+}\) was concentrated twice contrasted with original brine described in Chinese National Standard method GB/T-16632, as a result, an 91.57% CaCO\(_3\) inhibition efficiency was obtained under the presence of 150 mg/L BACC at 70 °C. The characterization results on deposited crystals suggested the active functional groups (-C=O, –OH, N-C=O, and B –O) in BACC molecular structure played an important role in forming stable Ca\(^{2+}\) – BACC complexes and further prevented scale deposition.

4.2.3. Glucose based polysaccharides

Glucose is one of the most widely distributed and important monosaccharide in nature, its derivatives, starch (St) and sodium gluconate (SG) have been identified as effective threshold CaCO\(_3\) scale inhibitors in several recent studies. Recently, sodium gluconate (SG) showed an obvious synergistic effect with 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) on preventing CaCO\(_3\) deposition (Ou & Chiang Hsieh 2016). Light-scattering experiment for investigating the scale inhibition kinetics and mechanisms was carried out in "synthetic" water which containing 600 mg/L Ca\(^{2+}\) under mixed SG/PBTC for 10 and 1 ppm respectively. As a result, in the presence of SG/PBTC, the formation kinetics of CaCO\(_3\) is 4 times lower than that of PBTC alone, while the SEM, XRD and particle size distribution (PSD) analysis identified that the scale inhibition occurred through forming dissoluble Ca-complex, stabilizing the metastable phase of aragonite and vaterite and distorting the CaCO\(_3\) crystal morphology.

Another polysaccharides with widespread availability and environmental friendly was starch (St), starch is a type of natural polymer which mainly composed of polyhydric glucose, due to abundant oxygen-containing functional groups in its molecular framework, St is talented in scale inhibition, however, St is usually modified with other molecules rather than directly used as a scale inhibitor, a suitable modification can significantly improve its antiscalant performance, according to static jar tests described in National Standard of China GB/T16632-2008, after a water bath at 70° for 10 h, MA-SSS-OS (prepared by oxidized starch (OS) copolymerized with maleic anhydride (MA) styrene sulfonic sodium (SSS)) showed a noteworthy increase in NaCl antiscaling performance from 65.26% to 98.87% in a dosage range of 0.2 g/L to 0.8 g/L (Guo et al. 2013), CMS (6) performed a high inhibition efficiency of 89.80% in against CaCO3 under a concentration of 40 mg/L while Stg-PAA exhibited an antiscaling performance of 95.79% inhibition efficiency under a concentration of 40 mg/L (Wang et al. 2017; Yu et al. 2018), these results proved starch-based polymers have great potential in scale inhibition.

\(\beta\)-Cyclodextrin (\(\beta\)-CD), which is a kind of starch that consists of seven glucose units linked by a-1,4 glucosidic bonds, was regarded as effective scale inhibitor, in a previous study (Liu et al. 2016), \(\beta\)-CD was modified with polyethylene glycol to obtain a novel scale inhibitor namely polyethylene glycol modified \(\beta\)-cyclodextrin (\(\beta\)-CD–PEG), the CaCO\(_3\) inhibition performance of \(\beta\)-CD–PEG was evaluated by static jar tests, the results showed 180 mg/L \(\beta\)-CD–PEG reached a peak scaling inhibition efficiency of 89.1% in against 200 mg/L Ca\(^{2+}\) at 40 °C. SEM and XRD analyses suggested that cyclodextrin cavity, –OH and –O– in the copolymer had strong chelating capacity to disperse the Cu\(^{2+}\) ions, the scale inhibitor molecules could also absorb on crystal surfaces and occupy key points of crystal structure. However, \(\beta\)-CD–MA–SSS(synthesized by \(\beta\)-CD, maleic anhydride(MA) and styrene p-sulfonic sodium(0.5S) monomers) acted more effectively towards calcium...
carbonate and calcium phosphate formation (Gu et al. 2015). According to static jar tests, for a total Ca\(^{2+}\) of 200 mg/L at pH range of 5.0–6.0 and 70 °C, 10.3 mg/L β-CD–MA–SSS terpolymer exhibited nearly 99.9% of scale inhibition efficiency for CaCO\(_3\) and 95.5% for Ca\(_3\)(PO\(_4\))\(_2\). The transmission electron microscopy (TEM) microscopy displayed a morphologic change on CaCO\(_3\) deposits under the impact of β-CD–MA–SSS, from regular cubic shape with a compact arrangement to flower patterns with floppily accumulation, this was ascribed to carboxyl, anhydride, cyclodextrins cavity and sulfonic acid groups in β-CD–MA–SSS which could easily chelate with Ca\(^{2+}\) and altered oriented crystal growth.

In an earlier research, sodium lignosulfonate (SL), another glucose-based polysaccharide, was copolymerized with other monomer for scale inhibition in cooling water system (Ouyang et al. 2006), according to static jar tests (Ca\(^{2+}\) concentration of 240 mg/L at 60 °C for 6 h), SL had nearly no scale inhibition capacity of which the inhibition efficiency range was 1.0 to 2.5% under a SL dosage of 4 to 50 mg/L, a limited scale inhibition efficiency was obtained after SL modified with acrylic acid, which was 30.7 and 45.2% at the dosages of 20 and 50 mg/L, respectively, suggested an enhancement on CaCO\(_3\) inhibition capability happened after SL modified with acrylic acid, the authors attributed this effect to the existence of both carboxyl and sulfonic groups allowed modified SL to strongly absorb onto CaCO\(_3\) crystalline substrate and leading a lattice distortion.

4.3. Plant extracts as scale inhibitors

In this direction, there have been many studies on applying plant extracts as scale inhibitors, although some were reviewed before (Chaussemier et al. 2015; Kumar et al. 2018), recent years, novel antiscalants derived from different plant extracts have emerged, we have followed up with the latest research on applying plant extracts as antiscalants, their antiscalant performances along with the mechanisms are described in detail.

In a few studies, FCP (fast controlled precipitation) method along with CA were conducted to assess the scale inhibition performance of several plant extracts, including Hernia glabra (Horner et al. 2017), Spergularia rubra, Parietaria officinalis (Cheap-Charpentier et al. 2016) and Hylocereus undatus (Lourteau et al. 2019). The FCP method was conducted at 50 °C in synthetic water (Ca\(^{2+}\) = 100 mg/L) with 850 rpm stirring rate. The results showed that among the four plant extracts, Hylocereus undatus was the most efficient scale inhibitor with the lowest dosage of 24 mg/L to completely inhibit CaCO\(_3\) formation (reached an efficiency of 100% as determined by FCP resistivity response), followed by 50 mg/L for Spergularia rubra and 50 mg/L for Hernia glabra, the least effective was P. officinalis, for which a dosage up to 100 mg/L was required for complete scale inhibition. However, in CA experiments, a higher dosage of plant extracts was generally required for preventing extra CaCO\(_3\) deposition on the electrode surface. Among the four plant extracts, the n-butanolic extract of H. glabra with a minimum dose of 75 mg/L was able to totally inhibit the precipitation of CaCO\(_3\), however, to achieve the same effect using Hylocereus undatus extract, a slightly higher concentration of 180 mg/L was required while large doses of 300 and 700 mg/L were needed by S. rubra and P. officinalis respectively. SEM and XRD characterization indicated the crystal morphology became irregular and the vaterite polymorph was preferentially favored to form. The authors suggested surface complexation between the carboxylate groups of these plant extract molecules and calcium atoms on the CaCO\(_3\) surface led an adsorption effect on the calcite crystal surface, reduced the crystal growth, and modified its geometry.

In two recent reports, the scale inhibition performance of Mazuj gall and Bistorta Officinalis extract were both evaluated by static beaker tests (Mohammadi & Rahsepar 2018; Mohammadi & Rahsepar 2019). The CaCO\(_3\) crystallization process was kept in a 50 °C water bath for 18 h at pH = 8.5 after the extracts was incubated, residual Ca\(^{2+}\) concentration within the filtrate was determined by EDTA titration. Consequently, 1,000 ppm of Mazuj gall extract provided a high inhibition efficiency of 97.2% in against 592 ppm total hardness while Bistorta Officinalis extract provided a slightly enhanced scale inhibition efficiency of 99.5% under the same experimental condition, it was thus concluded that both Mazuj gall and Bistorta Officinalis extracts could be used as effective antiscalcing additives in cooling water solution.

Previously, Gambier extract from Uncaria gambier Roxb leaves was reported as a green inhibitor for CaCO\(_3\) formation (Suharso et al. 2011), by bottle-roller batch method, they found 200 ppm Gambier extract brought 70–80% CaCO\(_3\) inhibition efficiency at 80 °C. Subsequently, the authors modified Gambier extract with benzoic and citric acid at a ratio of (Gambier extract: benzoic acid: citric acid/2:1:2) to strengthen its antiscaling capability (Suharsoa 2017). Consequently, modified Gambier extract showed an inhibition efficiency of 12–92% under the concentration range of 50–300 ppm, such antiscalcing effect was slightly diminished compared with original Gambier extract, which showed an inhibition efficiency of 60–100% under the concentration range of 50–250 ppm. SEM and particle size distribution analyses indicated both Gambier extract and its modified product could not only induce irregular changes on CaCO\(_3\) morphology but also reduce particle sizes, it was
such phenomenon was attributed to microbial activities, the authors speculated, the combination of \( \text{H}^\cdot \) and \( \text{CO}_2 \) in water contribute to the further formation of \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \).

\[ \text{H}^\cdot + \text{CO}_2 \rightarrow \text{HCO}_3^- \]  
\[ \text{HCO}_3^- + \text{Ca}^{2+} = \text{Ca}\text{(HCO}_3\text{)}_2 \]  

\[ \text{HCO}_3^- + \text{Ca}^{2+} = \text{Ca}\text{(HCO}_3\text{)}_2 \]  

4.4. Microbial product as inhibitors on antiscaling application

In this part, we summarized application of using microbial product on antiscaling, either using microbial agents or microbiological products. Microorganisms and their secreta with abundant sources and broad applying prospects, have promoted the development of ‘green’ scale inhibitors.

In a previous study, (Kawaguchi & D Ec Ho 2002) reported a new idea for \( \text{CaCO}_3 \) precipitation inhibition by using extracellular polymeric secretions (EPS) of a cyanobacteria, \( \text{Schizothrix sp.} \) They found the role of \( \text{Schizothrix sp.} \) EPS on inhibiting \( \text{CaCO}_3 \) precipitation in marine stromatolites was possibly due to acidic ionic functional groups in EPS could bind with \( \text{Ca}^{2+} \) and consequently inhibit calcification. Based on the previous study, a recent study provided a new sight in scale inhibition on industrial water treatment using soluble EPS (s-EPS) of \( \text{Bacillus cereus} \) (Li et al. 2019), the soluble EPS (s-EPS) of \( \text{Bacillus cereus} \) (\( \text{B. cereus} \)) was extracted and investigated its \( \text{CaCO}_3 \) inhibition effect by static jar tests, results showed the \( \text{CaCO}_3 \) scale inhibition efficiency reached up to 87.60\% at a concentration of 80 mg/L s-EPS. The obtained morphology of precipitated \( \text{CaCO}_3 \) crystals was modified from rhomb-shaped to disorderly granular crystals, in addition, the authors found tryptophan and protein-like substances in s-EPS might take primary responsibility in complexing with \( \text{Ca}^{2+} \) determined by 3-D excitation/emission matrix (EEM), the O and N atoms in the functional groups of protein-like substances had higher negative charges and provided many \( \text{Ca}^{2+} \) ions binding sites, which enabled EPS to inhibit calcium scale crystal formation.

Xanthan (XC), a microbial produced polysaccharide by the \( \text{Xanthomonas campestris} \), showed an scale inhibition impact in against 2,664 mg/L \( \text{Ca}^{2+} \) and 2,544 mg/L \( \text{CO}_3^{2-} \) ions. The SEM showed that under the presence of XC, the obtained \( \text{CaCO}_3 \) particles stacked into ones compared with those rhombohedral crystals without XC. The presence of XC significantly lowered the peak intensities of calcite crystals, this was attributed to XC molecules offered an absorption function on \( \text{CaCO}_3 \) particles surfaces. A deeper antiscaling mechanism of XC was revealed in a subsequent study (Elkholy et al. 2018), the authors conducted Monte Carlo (MC) simulation method to investigate the adsorption tendency of xanthan on growing calcite (\( \text{CaCO}_3 \)) and anhydrite (\( \text{CaSO}_4 \)) crystals. Adsorption tendency between gums and mineral surface (\( \text{CaCO}_3 \) 1(10), \( \text{CaSO}_4 \) 001)) was expressed in terms of the values of adsorption energy calculated from Monte Carlo simulation method. They found xanthan gum polymer (XGP) possessed a strong adsorption at low polymerization degree, under those circumstances, XGP exhibited a higher tendency to \( \text{CaCO}_3 \) 1(10) and \( \text{CaSO}_4 \) 001) surface at low PD values, the authors suggested that through Coulomb interactions between the negatively charged functional groups of the scale inhibitors and free \( \text{Ca}^{2+} \), XGP could occupy the growing points of calcite or anhydrite crystals and hinder the further scalants’ aggregation.

In a recent study, a biological method successfully handled the corrosion and scaling problem in a cooling water system makeup by urban reclaimed water (Chen et al. 2019). Such biological treatment was implemented by application of compound microorganism preparation (CMP) that consists of \( \text{nitrobacteria, bacillus subtilis, photosynthetic} \) bacteria and \( \text{thiobacillus denitrificans} \), which might provide new thinking approaches in circulating cooling water treatment. The results from ultimate carbonate hardness method showed such CMP successfully reduced carbonate scaling, as CMP exhibited a limit concentration ratio of 3.87, which was higher than common chemical treatment in China (generally for 2-3) (Ma et al. 2010; Tao et al. 2011). Moreover, a decrease in pH from 8.33 to 6.66 during the 30-day trial period was observed, such phenomenon was attributed to microbial activities, the authors speculated, the combination of \( \text{H}^+ \) produced by bacteria and \( \text{CO}_3^{2-} \) in water contribute to the further formation of \( \text{HCO}_3^- \) according to the following equation:

\[ \text{CO}_3^{2-} + \text{H}^+ = \text{HCO}_3^- \]  
\[ \text{HCO}_3^- + \text{Ca}^{2+} = \text{Ca}\text{(HCO}_3\text{)}_2 \]  

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thus, allowing the stable existence of high concentration of Ca$^{2+}$ in cooling water system. Besides, microbial reagent was also used by (Han et al. 2017), who found one of Thermophilic bacterial strain Tepidimonas fonticaldi showed high calcium adsorption capacity of 1.94 mg calcium/g protein at pH 10, 150 $^\circ$C and 1 atm pressure. Compared with intracellular fraction, calcium absorption was predominant in extracellular at a temperature of 55$^\circ$C, indicated Tepidimonas fonticaldi could become an effective bio-sorbent to remove calcium and reduce scaling.

Itaconic acid (IA) is a secondary metabolite produced by Aspergillus terreus, its chemical structure makes it easy to polymerize or act as co-monomer with different other components, its copolymer has been suggested as attractive anti-scaling agents in many studies, for instance, 2-acrylamido-2-methylpropane sulfonic acid copolymer (IA/AMPS) (Cui & Zhang 2019), itaconic acid – sodium allylsulfonate – sodium hypophosphite copolymer (IA/SAS/SHP) (Zhenfa Liu 2015), and poly (itaconic acid-co-epoxysuccinic acid) (PIA-co-ESA) (Shi et al. 2017). Among these studies, the anti-scaling performance of the three itaconic acid copolymers were all conducted by static jar tests according to GB/T16632, the highest scale inhibition efficiency was attributed to PIA-co-ESA, reached to 100% at a dosage level of 18 mg/L, such impact was even more effective than PBTC (Shi et al. 2017). Besides, SEM found that added PIA-co-ESA (10 mg/L) not only reduced the size of precipitated CaCO$_3$ crystals, but also changed the crystal shape to irregular floccule and loose. The scale inhibition mechanism of PIA-co-ESA was proposed according to MD simulation results, the PIA-co-ESA molecules retarded the growth of calcite through absorbing onto (104) and (110) crystal surfaces by hydrogen bond and electrovalent bond, but the binding energy showed a slightly larger binding force for (110) surface than (104) surface. Such consequences are in line with (Cui & Zhang 2019), in which the authors suggested that the binding strength of IA/AMPS with the calcite surface (110) was firmer than (104) surface as well. The novel itaconic acid copolymer (IA/AMPS) was a very promising scale inhibitor for both CaCO$_3$ and CaSO$_4$, from the results of static jar tests, 14 mg/L IA/AMPS exhibited a CaCO$_3$ inhibition efficiency of 81.2% while 18 mg/L IA/AMPS owned a CaSO$_4$ inhibition efficiency of 80.6%. SEM and XRD indicated that IA/AMPS achieved the scale inhibition effect through occupying the active sites on the crystal surface, leading scale crystal orientation distortion and preventing the crystal growth. In another study (Zhenfa Liu 2015), IA/SAS/SHP was regarded as a new bio-degradable scale inhibitor synthesized by introducing sulfonic acid and phosphonic acid groups to the IA monomer, it displayed an excellent antiscaling performance according to static jar tests, showed an inhibition efficiency of 95.1% at a concentration of 24 mg/L in confronting 600 mg/L Ca$^{2+}$ and 1,200 mg/L HCO$_3^{-}$. From SEM and XRD analysis, after added IA/SAS/SHP, the morphology of calcite crystals changed from regular rhombohedral lattice to flower-shaped and cascade-like, the peak strengths of crystal surfaces (104) and (116) were greatly reduced, the authors suggested that IA/SAS/SHP could adsorb on the crystal surfaces to destroy crystal habits, resulting in reducing the scale crystals growth rate.

5. FUTURE PROSPECTS

Aiming at scaling problems in industrial water systems, using bio-materials as green scale inhibitors exhibit great potential, researches which found bio-materials with scaling resistance filled the gap of interdisciplinary studies between bio-materials chemistry and carbonate deposition. In this review, the listed biomaterials proteins and amino acids, polysaccharides, plant extracts and microbial products, showed excellent antiscaling performance according to different evaluation methods, these functional materials displayed multiple antiscaling mechanisms of which the uppermost was the interaction between organic functional groups in scale inhibitor molecules and Ca$^{2+}$, such functional groups including carboxyl, hydroxyl, anhydride, amino and sulfonic groups. The wide acceptable scale inhibition mechanisms of bio-materials are refer as that on one hand, scale inhibitor molecules apply complexation effect to increase Ca$^{2+}$ solubility, on the other hand, scale inhibitor molecules can absorb on scale crystal surfaces, occupying the active grow sites and retarding crystal growth.

Despite bio-materials accord with the development direction of green scale inhibitor chemistry, considering multiple factors, further studies are still necessary before real application, the primary work is assessing economic affordability on account of some proteins and amino acids may go through complex steps to extract, this is even more complicated for some plant extracts. Researchers also need to consider wastes and reaction products generate by extraction, which may cause other environmental threats. Besides, as most scale inhibition researches conducted static jar tests with convenience and quickness but lack validation on long-term scale inhibition performance, extra scale inhibition tests under field operation conditions are required which is essential for industrial cooling water application, after all, the field operation condition differentiates with laboratory level, it involves some special water conditions with high hardness or secondary water. So, in general, the feasibility of bio-materials as scale inhibitors on large-scale application still needs to be validated.
Another future perspective emerges due to the scale inhibition tests of biomaterials is usually in single formulation, for reason that multiple inhibitors act different scale inhibition mechanisms to impose a higher scale inhibition resistance than inhibitor using alone, thus, it can be speculated that synergistic effect may occurs when bio-materials cooperate with other scale inhibitors. In addition, modification and graft copolymerization for purpose of improving scale inhibition performance are also significant for the development of bio-materials as scale inhibitors, the carboxylic group, sulfonic group, and other groups may offer extra dispersion effect or electrostatic interaction to scaling ions as well.

Last but not least, relative researches on scale inhibition mechanisms mainly launched their investigation from the aspects of inorganic calcium scale formation, took simple molecules or scale inhibitors contain single functional groups as research object to study the influence of inhibitors on scale formation. However, their scale inhibition mechanisms are still vague as rarely explanation on relationship between the structure and the performance of scale inhibitors was performed from molecular and microscopic aspects, this needs further theoretical investigations like molecular dynamics simulation or computational modeling which will provide a considerable contribution to this field.

6. CONCLUSION

Scaling is a major challenge for industrial circulating cooling water system, in recent years, increasing environmental concerns and discharge limitations have restricted the utilization of conventional antiscalants greatly, hence, various types of bio-materials were screen out to apply as environmentally friendly scale inhibitors, grafting modification and compound formulation were also conducted in order to obtain higher inhibition efficiency.

Here, we summarized bio-materials as scale inhibitors in recirculating cooling water treatment, including proteins, polysaccharides, plant extracts and microbiological products. Thanks to the negatively charged functional groups on its molecular backbone chain, such as (-COOH, -OH etc.), those bio-materials displayed excellent scale inhibition performances, not only had a good chelation and dispersion effect on free Ca\textsuperscript{2+}, but also showed a regulation on scalants crystal morphology. Moreover, scale inhibition can also be achieved by interaction between antiscalants and crystal surfaces, like CaCO\textsubscript{3} (104) and CaSO\textsubscript{4} (001), which provided a popular perspective for further study of scale inhibition mechanism.

Finally, the biodegradation properties with low toxicity and low bioaccumulation make bio-materials have a promising application potential of being used as scale inhibitors, however, since assessing antiscalant efficiency was usually performed by individual solutions, pilot scale tests with mixed salt solution are needed for further evaluation.

DECLARATION OF INTERESTS

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

DATA AVAILABILITY STATEMENT

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

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