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State of art of natural inhibitors of calcium carbonate scaling. A review article

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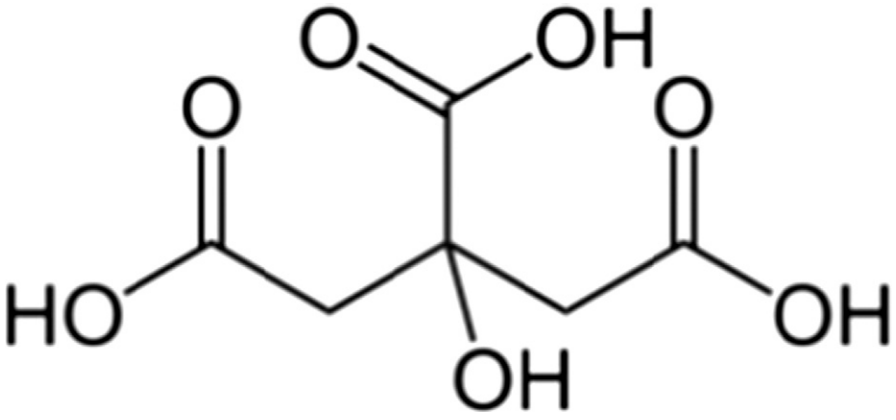
HIGHLIGHTS

- A lot of efforts have been done to obtain green inhibitors.
- They could be obtained from plant extraction or by using natural organic molecules.
- Such green inhibitors might be used in varied technical areas, i.e. energy, water, food and beverages industries.

GRAPHICAL ABSTRACT



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ABSTRACT

The formation of calcium carbonate in water has some important implications in geoscience researches, ocean chemistry studies, CO_2 emission issues and biology. In industry, the scaling phenomenon may cause technical problems such as reduction of heat transfer efficiency in cooling systems and obstruction of pipes.
The use of chemicals which act as antiscalant is a common approach in the control of scale deposition. However, inorganic nitrogen and phosphorous compounds are involved in eutrophication process. Therefore, it is of prime importance to find alternative solutions, *i.e.* green inhibitors of scale formation. This last decade, several new scale inhibitors, that are more ecological compared with conventional inhibitors, have been reported in the literature. Plant extracts have been also recently used as new green antiscalants. Indeed, as they can be easily extracted and are environmentally friendly, they represent an interesting alternative source of "natural" organic molecules.
In this review, a focus of some green antiscalants derived from petrochemicals has been reported. Then the efforts done those last years to obtain green inhibitors, either by using "natural" organic molecules or extracted from plants were summarized. Such green inhibitors might be used in various technical areas, *i.e.* energy, water, food and beverages industries.

Abbreviations: EDX, energy dispersive X-ray analysis; EIS, electrochemical impedance spectroscopy; FCP, fast controlled precipitation; HPLC, high pressure liquid chromatography; PASP, poly(aspartic acid); PESA, polyepoxysuccinic acid; PGLU, pteroyl-L-glutamic acid; RCP, rapid controlled precipitation; SCE, saturated calomel electrode; SEM, scanning electron microscopy; XC, xanthan; XRD, X-ray diffraction.

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Contents

1. Introduction

The formation of calcium carbonate ($CaCO_3$) in water has some important implications in geoscience researches, ocean chemistry studies, CO_2 emission issues and biology [1,2]. In nature, this process is involved in biomineralization and leads to high-performance materials as protective shells for living organisms [3]. It is also a major concern in some industrial processes, *i.e.* energy production [4–6]. Indeed, the scaling phenomenon can cause technical problems such as reduction of heat transfer efficiency in cooling systems and obstruction of pipes. The non-productive expenses related to scaling were estimated at 1.5 billion Euros per year in France [7]. The same expenses were about 0.8 billion $US in Great Britain, 3 billion $US in Japan and 9 billion $ in the USA [8]. It is therefore crucial to understand the calcium carbonate formation and to control scaling process, as it may help to the development of new high-performance materials or find effective ways to prevent it.

A common method for controlling scale deposition is the use of chemicals which act as antiscalants. When properly applied, they can avoid scale formation with concentrations typically below 10 mg/L. In this respect, phosphorous and nitrogen compounds have been fruitfully used against scale formation [9,10]. However, these inorganic chemicals are involved as nutrients in eutrophication process. Such antiscaling treatments may lead to the massive development of biological species and to the death of aquatic organisms, due to deoxygenation of water [11]. Nowadays, discharges of chemicals which modify biological cycles are strictly controlled by legislation. It is therefore of prime importance for industry to find alternative solutions, *i.e.* green inhibitors against scale formation. A chemical is defined as being "green" according to three criteria: non toxicity, non-bioaccumulation and biodegradation [12,13].

In the fifties, McCartney et al. showed that the rates of nucleation and crystal growth of calcium sulfate dihydrate (one possible form of scale) was strongly reduced by addition of small amounts of natural organic molecules (*i.e.* not obtained by organic synthesis) such as gelatin (concentration of 13 mg/L). These molecules might be adsorbed on the crystal surface [14]. This last decade, several new scale inhibitors that are more ecological compared with conventional inhibitors have been reported in the literature [13]. Plant extracts have been also tested as scale inhibitors in order to develop new green inhibitors. Indeed, plant extracts represent an interesting alternative source of organic molecules because they are environmentally friendly and they can be easily extracted.

In this review, a focus of some green antiscalants derived from petrochemicals has been reported. Then the efforts done those last years to obtain green inhibitors, either by using "natural" organic molecules or plant extracts were summarized. An update on some promising green organic molecules derived from petrochemicals was also performed. Such inhibitors might be used in various domains such as energy, water and food industry.

2. Physical methods for inhibitors studies

In this section, the "non-usual" techniques quoted in this review are briefly presented. During the last twenty years, various methods have been developed in order to estimate the scaling propensity of waters and to investigate scaling processes [15]. These methods involve the precipitation of calcium carbonate ($CaCO_3$), the main component of scale. Three categories of methods can be roughly distinguished, *i.e.* the electrochemical methods, carbon dioxide degassing based methods and the non-electrochemical methods. All these methods, which are complementary with each other, have contributed to improve the knowledge on $CaCO_3$ precipitation, scaling propensity evaluation and scaling mechanisms.

Electrochemical methods such as chronoamperometry and impedance measurements have been fruitfully used to investigate scaling processes [16–21]. Chronoamperometry is a popular electrochemical technique, involving a three-electrode cell, in which the working electrode is polarized at -0.9 V (vs. SCE) to reduce dissolved dioxygen as following:

$$O_{2(\text{dissolved})} + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

The production of hydroxyl ions in the vicinity of the working electrode induces the precipitation of calcium carbonate on electrode surface, according to:

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_{3(s)} + H_2O \quad (2)$$

The resulting current density is monitored as a function of time during the calcareous deposition. An isolating layer of $CaCO_3$ is progressively formed onto the electrode surface, leading to a decrease of current. When the surface of the working electrode is totally covered by scale, the current density reaches a steady-state called the residual current, which value depends on the porosity of the scale layer. In addition to chronoamperometry, the impedance measurements allow observing the nucleation, growth and total surface coverage phenomena occurring on the working electrode surface.

The Fast Controlled Precipitation method is a non-electrochemical method which consists in CO_2 degassing from water by a moderate agitation [22,23]. The process of nucleation-growth of $CaCO_3$ is therefore close to that of a real scaling phenomenon. FCP method allows quantifying the scaling propensity for natural water, and studying the nucleation-growth process of $CaCO_3$ in various conditions [24].

The constant composition method, the static jar tests, dynamic test and dynamic tube blocking test are non-electrochemical techniques usually used to study the effect of an inhibitor on $CaCO_3$ crystallization and/or scaling. The constant composition method allows determining accurately the mechanisms and the nature of the precipitated crystalline polymorphs [25,26]. In this method, the pH of the studied solution is adjusted to a given value, and the experiment starts immediately after the introduction of the inhibitor in solution. The pH of the solution, which is maintained at constant temperature, is monitored as a function of time; it remains constant until the solution precipitates. The precipitation phenomenon triggers the addition of titrant from two mechanically coupled burettes with appropriate salts. Therefore, the initial conditions of the solution can be maintained constant throughout the