Environmentalist (2008) 28:421–428
DOI 10.1007/s10669-008-9163-7

Evaluation of some organic-based biopolymers as green inhibitors for calcium sulfate scales

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Published online: 11 March 2008

Abstract This study focused on using scale inhibitors for calcium sulfate that are not only highly effective, but also comply with present restrictive environmental control legislations. In this respect, some biodegradable compounds-based biopolymers, such as carboxymethyl starch (CMS), carboxymethyl cellulose (CMC), and chitosan (Ch), were evaluated at temperatures 90–95 and 130°C. The results obtained were compared with the performance of polyaspartic acid (PAA), which is well known in this application, as well as other chelating synthetic polymers (polyacrylamide and amphoteric polyacrylamide). The role of the degree of substitution (DS) of carboxymethylated biopolymer and the charge density of polyacrylamide (AmPAM-30 and AmPAM-50) on inhibition performance of scale were also examined. The synergistic effect of PAA with investigated inhibitors was studied for economic and environmental purposes. The results revealed that both the degree of substitution of carboxymethylated biopolymers and charge density of polyacrylamide have a profound effect on improving the performance of the investigated scale inhibitors. The efficiency values were correlated to the thermal degradation behavior (TGA) of biopolymers. PAA had the highest synergistic effect of all investigated inhibitors, where the inhibition efficiency was found to range from 98% to 100%, at a temperature of 130°C, with low doses of both PAA (2 ppm) together with biopolymers. This efficiency is observed using 20–40 ppm of PAA. The synergistic effect of PAA (2 ppm) also showed enhancement of the performance of low doses of polyacrylamides (5 ppm) in maintaining soluble Ca^{2+} in solutions, increasing the efficiency from ~57% to ~100%, as well as its ecotoxicological property.

Keywords Scale inhibitor · Green inhibitor · Environment · Biopolymer

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1 Introduction

Mineral scales of inorganic precipitates, such as calcium carbonate and magnesium hydroxide (called alkaline scale), as well as calcium sulfate, are regarded as one of the major difficulties in many process industries. They are usually formed in water distribution systems, boilers, oil well casings, cooling towers, salt refineries, and other types of industrial equipment.

These scales can build up on solid surfaces with the formation of an effective insulating material. The resulting decrease in thermal capacity requires an increase in temperature difference and/or heat transfer surface necessary to maintain a constant production rate, which leads to increasing the operating costs. Resistance to heat flow is not the only undesirable property of scale. When excessive deposits build up inside tubes or orifices severe restriction to fluid flow results.

Scale formation occurs when the solubility of a particular salt is exceeded. Most scaling compounds have inverse solubility curves, resulting in greater scaling intensities at high temperatures (Comstock 1991). Alkaline scales are easily controlled by acidifying and maintaining pH below 7.5. Low pH can cause additional problems due to system corrosion. Since $CaSO_4$ scale cannot be readily removed by

acid cleaning, its deposition must be prevented (Frohner and Panahandeh 1975).

Deposit control and inhibition are accomplished by mechanical and chemical means. Mechanical control is exercised through a boiler blow down to limit impurity concentration in the water. But blowdown alone is not sufficient to inhibit deposit formation. It must be accompanied by chemical treatment, e.g., addition of chelants.

Sodium salt of ethylenediamine-tetraacetic acid (EDTA), nitrilo-triacetic acid (NTA), and synthetic dispersant polymers are the most common boiler-water chelating agents. Because economical chelant treatment requires low-hardness feedwater (less than 2 ppm total), as well as the presence of oxygen, and chelant can heighten the corrosion process, its use is often limited to softened or demineralized makeup (Strauss 1997).

Synthetic copolymers development, including polymalic acid, modified polyacrylic acid, and polyacrylamides (all carboxylated), were used with polyacrylates and some modified natural organics at rather low doses—often 10–20 ppm (active) in boiler water. Polyacrylates are reported not to be the best chemicals for controlling calcium scale and iron oxide deposition (product of corrosion); they can react with calcium hardness, leaving calcium polyacrylate deposits on the high-heat flux surface of boilers.

Other synthetic polymers, such as dispersant polymers, developments included polyphosphates, polyaminopolyether methylene phosphonate (PAPEMP), and polyaspartic acid (Gill et al. 1995; Gill 1999; Bayer 2001). PAPEMP is very tolerant of calcium/magnesium in the water and is capable of controlling both calcium carbonate and calcium sulfate scales at extremely high super saturations (Gill 1999). Fluorescent-tagged polymer is also used as a dispersant polymer in cooling water systems (Moriarty et al. 2001). This type of polymer makes it feasible to measure polymer activity online without reagent.

Environmental criteria have recently been required for every product and process. Most dispersant synthetic polymers are essential for the successful operation of a majority of industrial fields; however, associated with this is the risk of their subsequent entry into the environment. Because of their non-degradability by environmental effect, as well as the harmful effect of monomer remaining in the product, these polymers influence living organisms where they are removed with water by blowdown.

Since the 1950s, the use of organic materials, such as sulfonate lignins (SL), as a by-product of the pulp and paper industry, and tannin as a biodegradable polymer, has been a fairly common practice (Strauss 1997). This is due to its large usage dosage (100–500 ppm) for effective performance of scale inhibition. Recent studies on SL have again attracted more attention due to the threat of the petroleum resource crisis. It is anticipated that SL can become the multi-functional water treatment agent through chemical modification; however, SL shows a limited scale inhibition performance because it is able to complex some calcium ions weakly (Meister and Yin 1993; Fekdman et al. 1986). The literature also reported that the contents of hydroxyl and sulfonic radical groups and molecular weight distribution of SL are the main factors affecting the performance of corrosion and scale inhibition (Williams and Rycoroft 1994; Ouyang 2002). Scientific efforts, therefore, have increased to develop a new scale inhibitor to meet these environmental regulations.

The natural polymers of the starch, cellulose, and chitosan can be made for a suitable partial, or complete, substitution of synthetic polymers in certain applications by chemical modifications, such as hydrogels, flocculants, and slow release encapsulating agents as well as starch phosphate as scale inhibitors (Weaver et al 1974; Khalil and Farag 1998; Hitoshi and Aiba 2004; Marton 2001). These biopolymer compounds have the following advantages:

- they are non-toxic,
- they are degradable by environmental effect, and
- they come from renewable raw materials and exoskeletons of crabs.

This work is directed toward evaluating the performance of carboxymethyl starch and cellulose as well as unmodified chitosan as a biopolymer, to prevent $CaSO_4$ scale formation at temperatures of 90–130°C. The evaluation is done by comparing their efficiencies with that obtained from using polyaspartic acid, which is well known in this application; polyaspartic acid sodium salts proved at least 60% degradable (Silveman 1995).

The degree of carboxymethylation and the added dose of biopolymer is optimized using rotatable design and represented in the multi-regression equation and 3D-surface plots. The possibility of reducing the dosage amounts of commercial inhibitor (PAA) and enhancing the performance of biopolymer-based inhibitors, or polyacrylamides with different charge densities and their synergistic effect is also studied.

2 Experimental

2.1 Inhibitors

- Different degrees of substitution of carboxymethyl starch, CMS (DS 0.13, 0.3, and 0.6), were lab prepared in a completely heterogeneous procedure, in a methanol/water slurry activated with aqueous sodium hydroxide (45% w/v), using monochloroacetic acid as the etherifying agent, as the method described elsewhere (Heinz et al. 2001). The average degree of

substitution was determined by the conventional method (Conner and Eyler 1950).

- Different degrees of substitution of carboxymethyl cellulose, CMC (DS 0.4, 0.67, and 1.3), were supplied by Herculs Inc.
- Chitosan from crab shells, Ch (degree of deacetylation 86–88%), supplied by Sigma Chemical Co. Inc was used without any further purification and powdered (200 mesh) before being dissolved in 1% glacial acidic acid.
- Polyacrylamide (PAM) was supplied by BDH Laboratory.
- Amphoteric polyacrylamide with 30% (AmPAM-30) and 50% (AmPAM-50) charge density was provided by Material Department, SCUT-China.
- Sodium salt of polyaspartic acid was supplied by Bayer's Chemicals Inc.

2.2 Evaluation of scale inhibitors

Laboratory screening tests were carried out to determine the ability of scale inhibitors to prevent the precipitation of $CaSO_4$ for solutions according to the NACE standard method TM 03–74 and also to Vogel. A supersaturated solution of $CaSO_4$ was prepared from anhydrous $CaCl_2$ (8.288×10^{-2} M) (solution A) and $NaSO_4$ (7.507×10^{-2} M) (solution B). All inhibitors tested were also prepared as 1% solution. All solutions were prepared in distilled water, except in the case of chitosan which was dissolved in 1% glacial acetic acid.

Screening tests in static condition were prepared at the desired temperature by mixing 50 ml of each solution A and B with the examined dose of inhibitor (5–40 ppm) in clean, dry, capped bottles. Bottles were lifted at 90–95°C for 24 h, while lifted only for 3 h in an autoclave at 130°C. After that, the tested bottles were removed. An aliquot of the supernatant was withdrawn for analysis to determine soluble calcium ions using EDTA titration. The difference between the soluble calcium and total calcium present at the beginning of the experiments is equivalent to the deposited calcium.

The efficiency % of the scale reduction can be calculated as follows:

$$\text{Efficiency}\,\%\,\text{of scale reduction} = (\text{soluble Ca}/\text{total Ca}) \times 100.$$

2.3 Mathematical equation

To optimize and correlate the degree of substitution of biopolymer (X_1) and the added amount (X_2) with efficiency of inhibiting $CaSO_4$ scale (Y), two-factor rotatable design with $\alpha = 1.0$ and the following second order quadratic equation were selected. This is because this equation is the simplest non-linear equation that can be used for optimization with responsible surface methodology.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2 \quad (1)$$

The regression constant b_0 and the coefficients b_1 to b_{12} of the above model were obtained using multiple-regression analysis (Dixon and Massey 1983; Deming and Morgan 1987).

2.4 Thermal analysis

Thermogravimetric analysis (TG and DTG) of the investigated sheets was done using PERKIN ELIMER (Thermogravimetric Analyzer TGA7). Analysis was performed with a heating rate of 10°C/min and a nitrogen flow rate of 50 cm^3/min, under non-isothermal conditions. The activation energy of thermal degradation was calculated as mentioned in Coat and Redfern (1964) and Basta (1999).

2.4.1 TG-curve analysis

Kinetic studies, based on the weight loss data, were obtained by TG curve analysis. The activation energy has been evaluated by applying the Coat and Redfern method of analysis (Coat and Redfern 1964). For pseudo homogeneous kinetics, the irreversible rate of conversion of the weight fraction of reactant was expressed by the following equation:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (2)$$

where α is the fraction of material decomposed at time t, k is the specific rate constant, and n is the order of reaction. The temperature dependence of k is expressed by the Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (3)$$

where A is the frequency factor ($s-1$) and T is the absolute temperature.

For linear heating rate, a, (deg min^{-1}):

$$a = \frac{dT}{dt} \quad (4)$$

For calculating the activation energy, E_a, of thermal decomposition when $n = 1$, Eq. 5 was used.

$$\log\left[-\log\frac{1-\alpha}{T^2}\right] = \log\frac{AR}{aE_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT} \quad (5)$$

When $n \neq 1$, Eq. 6 was used;

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T2(1-n)}\right] = \log\frac{AR}{aE_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT} \quad (6)$$

Plotting the left-hand-side value of the equation {i.e., $\log[1-(1-\alpha)^{1-n}/T2(1-n)]$} against $1/T$ using various

values of "n" should give a straight line with the most appropriate value of "n"(Basta 1999). The least square method was applied for the equation, using values of "n" ranging from 0.0 to 3.0 in increments of 0.5. The correlation coefficient (r) and the standard error (SE) were calculated for each value of "n". The "n" value, which corresponds to the maximum r and minimum SE, is the order of the degradation process. The activation energies and frequency factors were calculated from the slope and intercept, respectively, of the Coat-Redfern equation with the most appropriate value of "n."

3 Results and discussion

3.1 Performance of biopolymers as scale inhibitor

To clarify the possibility of using the investigated biopolymers as inhibitors of $CaSO_4$ scale, at 90–95°C, we first optimized the degree of carboxymethylation (X_1) and dosage amounts (X_2) which achieved high efficiency in preventing scale formation (Y). In this respect, two-factor rotatable design with $\alpha = 1$, as well as 3D-response surface plots, were used.

Figure 1 shows the change in percentage of the efficiency reduction of scale caused by changing the degree of carboxymethylation, DS, and the added dose of starch- and cellulose-based biopolymers.

At constant DS, the reduction of $CaSO_4$ scale formation gradually increased as the added dosage was increased and reached maximum value at 40 ppm added biopolymer. It was also obvious that increasing the degree of carboxymethylation resulted in increasing the inhibition performance of biopolymer. Where, at an added dose of 40 ppm, increasing the DS of CMS from 0.13 to 0.6, the reducing efficiency of scale increased from 19.03% to 93.3%, while increasing the DS of CMC from 0.4 to 1.3 increases the efficiency from 85.7% to 98.2%.

On the basis of the multiple regression equation in Table 1, the regression constant b_0 and the coefficients b_1 to b_{12} obtained prove the following points:

- By varying both the DS (X_1) and the added dose (X_2), the reduction of scale formation on using CMC is more significant by the independent variable X_2 (high b_2) than X_1; while the reverse was noticed in the case of CMS inhibitor.
- The optimum inhibitions in scale formation are achieved by using CMS and CMC with DS 0.6 and 1.3, respectively, and at a dosage amount of 40 ppm. Using CMC generally achieves relatively high inhibition behavior compared to CMS.
- Adding 40 ppm of CMC enables a greater improvement in inhibiting scale formation, (efficiency = 98.2%), compared to CMS (efficiency = 93.3).

Data relevant to the mathematical model as recorded in Table 2 (at optimum response) indicated a good agreement between the observed and the predicted values due to high values of determination coefficient, R^2.

The positive effect of the foregoing investigated biopolymers may be ascribed to the behavior of the carboxymethylate groups containing biopolymer to inhibit the scale formation by two mechanisms. In the first mechanism, the biopolymers are adsorbed on the scale

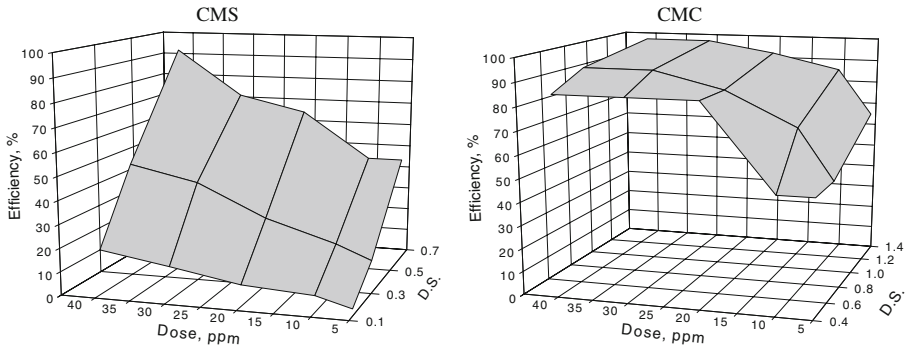

Fig. 1 3D-surface plots showing response reduction in $CaSO_4$ scale as a function of degree of carboxymethylation (DS) and amount of added biopolymers

Table 1 Determination coefficient and multiple regression equations of the inhibition efficiency of biopolymer in functions of degree of carboxymethylation (DS) and added dose (ppm)

Biopolymer	R^2	Equation
CMS	0.99919	$Y = -11.82 + 104.43X_1 + 3.00X_2 - 26.96X_1^2 + 4.76X_2^2 + 1.83X_1X_2$
CMC	0.98498	$Y = 20.73 + 1.04X_1 + 3.73X_2 + 9.51X_1^2 - 5.66X_2^2 - 0.166\ X_1X_2$

Where, R^2: determination coefficient

Table 2 Independent variables of the optimum response inhibition efficiency

Biopolymer	X_1	X_2	$Y_{experimental}$	$Y_{predicted}$	Deviation (%) (ΔY, %)
CMS	0.6	40	93.30	93.96	+0.66
CMC	1.3	40	98.20	98.08	−0.12

nuclei surface during nucleation stage and prevent further propagation (growth), leading to distortion of the crystal structure with a decreased ability of scale forming. In the second mechanism, however, the anionic carboxymethylate may form some sort of chelates or sequestration with scale responsible calcium cations, when the chelating bonds are very stable and remain in the solution, therefore Ca^{2+} ions are incapable of nucleation and growth. Additional inhibition of $CaSO_4$ scale is also probable from the presence of anionic carboxylic groups and sodium ions in biopolymers. Both ions interfere the charges of $CaSO_4$, where the similar charges repel one other, i.e., this polymer retard the precipitation of salts when it's concentrated on distillation (threshold effect). With increasing the degree of substitution the latter mechanism is more probable.

Further study to compare the performance of carboxymethylated biopolymers at optimum DS (CMS at DS 0.6 and CMC at DS 1.3) with other available chitosan-based biopolymer and synthetic chelating polymer (polyacrylamide, PAM) was carried out, at temperatures of 90–95°C and within a 24-h timespan. Both biopolymers and synthetic polymers are compared with the commercial polyaspartic acid (PAA). The results obtained are shown in Fig. 2. The main observation of the results in Fig. 2a is that, at different inhibitor doses the CMC achieved best inhibition efficiency than CMS and chitosan. Adding 40 ppm of CMC had nearly the same inhibition efficiency like PAA. As can be seen, all investigated biopolymers are more effective as $CaSO_4$ scale inhibitor than synthetic polyacrylamide (Fig. 2b).

Experiments similar to those described above were carried out to explore the effect of the cationic and anionic contents of polyacrylamide on the performance of the scale inhibitor in reducing calcium sulfate formation. Figure 2b represents the effect of amphoteric polyacrylamide with a charge density of 30% (AmPAM-30) and 50% (AmpAM-50) on reduction of $CaSO_4$ scale in comparison with neutral polyacrylamide (PAM). As seen in Fig. 3, amphoteric polyacrylamide, especially AmPAM-30, has higher reduction efficiency of scale formation, compared to PAM. But this efficiency (57%) is still low compared to biopolymers inhibitors (87–98%). This is probably related to the higher chelating tendency of the anionic charge on AmPAM-30. In other words, this observation may be related to the presence of additional anionic groups, beside cationic groups (i.e., each molecule behaves both cationically and anionically. Related to the behavior of anionic groups to chelate the Ca^{2+} ions, is also the ability of the cationic groups reacting with sulfate anions and preventing the formed protonuclei to pass back into solution. In this case, the reduction in scale formation is due to crystal distortion more than threshold effect, as in the case of biopolymers.

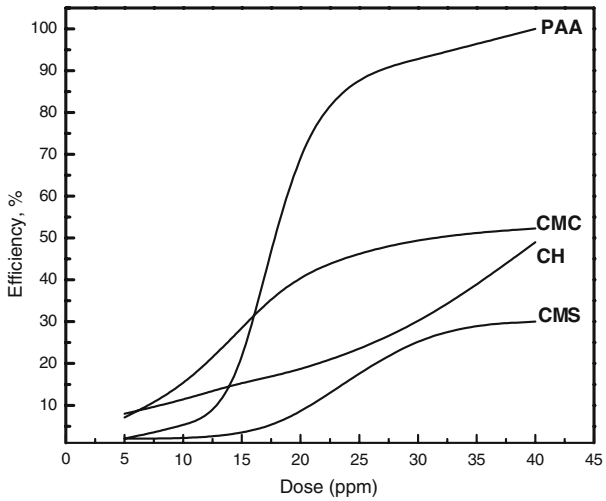

Fig. 3 Effect of dose amount of some biopolymers on reduction of $CaSO_4$ scale at temp. up to 130°C

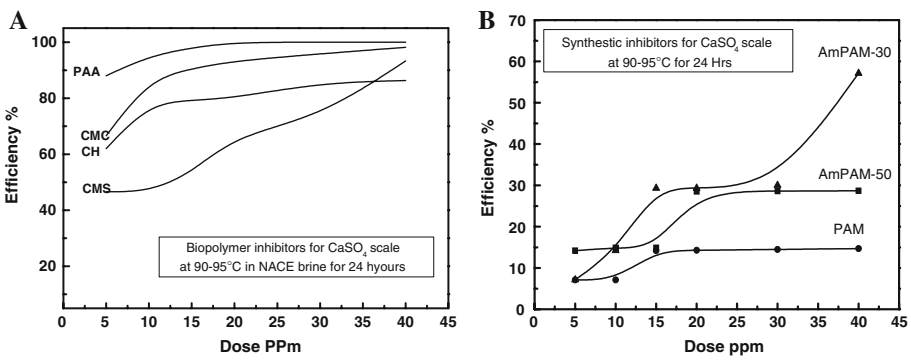

Fig. 2 Effect of the type and added dose of biopolymers on efficiency of reduction of scale formation, in comparison to

In some cases it is necessary to increase the temperature of some industrial operations to increase the productivity of the unit; this may affect the structure of the inhibitor used and decrease its performance. Therefore it is necessary to study the performance of the investigated biopolymer inhibitors with increasing the temperature from 90 to 130°C (Figs. 2 and 3), as well as the thermal stability of these biopolymers (Figs. 4 and 5). As shown in Figs. 2 and 3, a sharp decrease in the efficiency of all biopolymer inhibitors accompanied by the increased testing temperature.

This may be ascribed to the thermal degradation of the inhibitor compound and release of the calcium cations which are ordered to form protonuclei, nuclei, and then scale crystals. The TGA and DTG curves under non-isothermal conditions are emphasized in this view (Fig. 4). The weight loss at 130°C in the case of CMS, CMC, and chitosan are 10.14%, 7.81%, and 10.86%, respectively. As

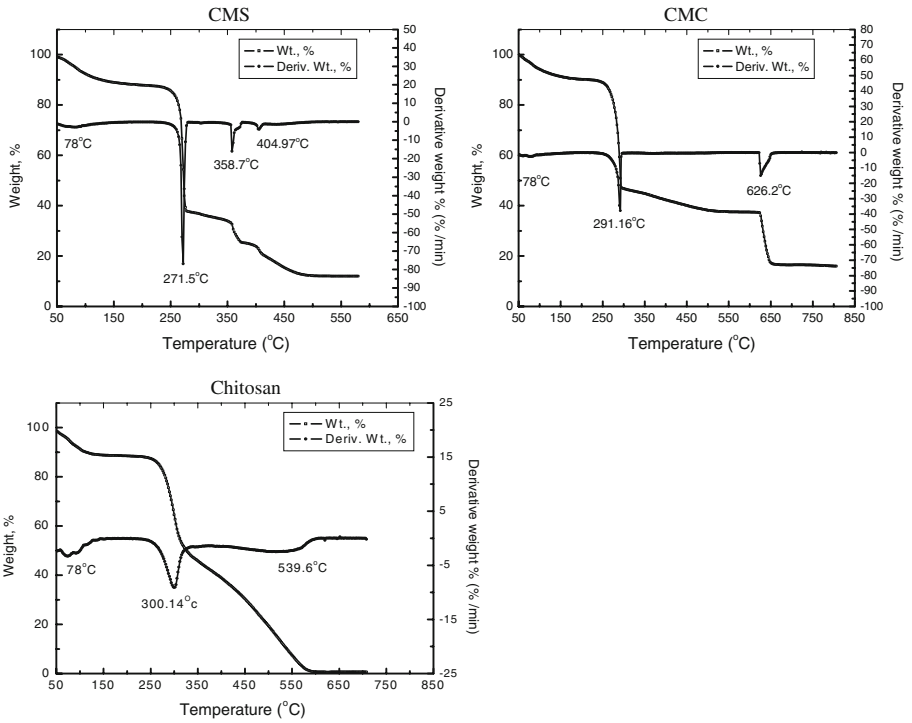

Fig. 4 TG and DTG curves of biopolymers

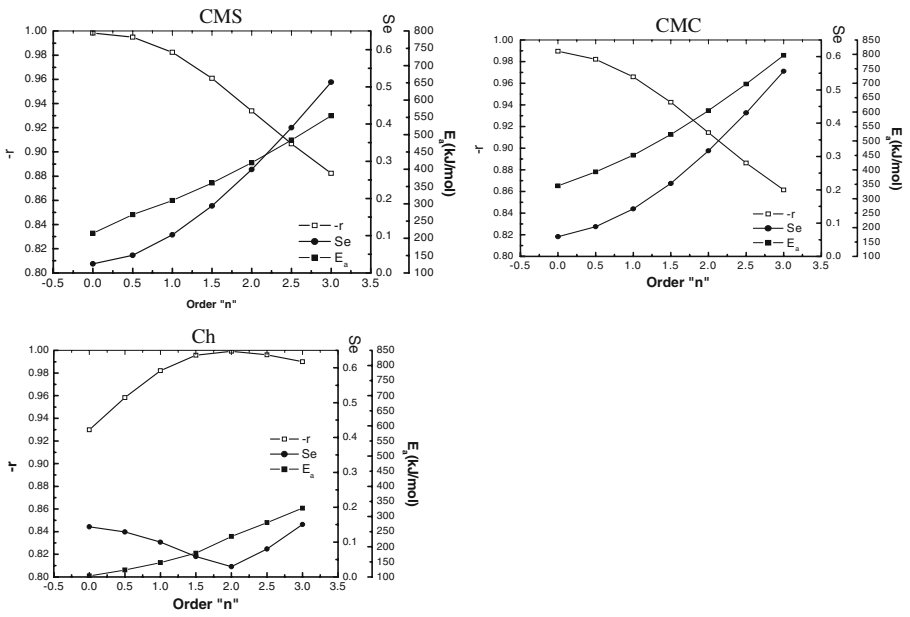

Fig. 5 Statistical determination of order '*n*' and activation energy 'E_a" of main degradation stages of investigated biopolymers

Table 3 Thermal degradation measurements of biopolymers

Biopolymer	Step	Temperature range (°C)	Maximum weight loss temperature (°C)	$-r$	Se	"n"	E_a (kJ/mole)	Wt.[a] (%) 130°C
CMS	1st	50–240	85	–	–	–	–	89.862
	2nd	236 – 283	271.5	0.9982	0.0241	0	214.805	
	3rd	348–375	358.7	0.9951	0.0608	–	–	
	4th	393–465	405	–	–	–	–	
CMC	1st	50–247	65	–	–	–	–	92.186
	2nd	247–297	291.2	0.9895	0.0594	0	344.481	
	3rd	619–660	626	–		–	–	
Chitosan	1st	50–236	70	–	–	–	–	89.14
	2nd	240–351	300	0.9992	0.0295	2	234.072	
	3rd	374–598	540	–	–	–	–	

[a] Weight remains at 130°C

well, the calculated activation energies in Table 3 show that the thermal stability of the investigated biopolymer inhibitors increased in the following sequence CMC > Ch > CMS. Furthermore, the efficiency of biopolymer as scale inhibitor is correlated with the activation energy by the following equation;

$$\text{Efficiency}, \% = -1316.5 + 11.12E_a - 0.023E_a^2 \quad \left(R^2 = 1.0,\ \text{Se} = 0\right)$$

3.2 Effect of synergism

From the foregoing data it is obvious that the best performance of scale inhibition was attained by using PAA at a temperature range of 95–130°C. However, inhibition efficiency of the investigated CMC, CMS, and CH showed high and promising efficiency and can prevent scale formation with efficiency up to 86–98% at a temperature of 95°C. Therefore, it would be beneficial if the synergistic effect of the PAA is tested at 130°C, with all the investigated inhibitors.

Figure 6 shows the effect of incorporating 2 ppm of PAA with different doses of all the investigated inhibitors. It is obvious that PAA had a high synergistic effect of all the prepared inhibitors which gave an inhibition efficiency of 100% in most prepared inhibitors, the only inhibitor CMS showing a low efficiency with PAA.

Due to the excellent performance attained with the synergistic effect of 2 ppm of PAA this inhibitor was tested at 1 ppm to explore its effect at a lower concentration. Figure 7 shows the effect of 1 ppm of inhibitor PAA on the prepared compounds. It showed that the presence of 1 ppm of PAA could affect the performance of the investigated inhibitors and increase their efficiency together with reducing the ecotoxicity of synthetic polymer, and at the same time the investigated inhibitors minimizing the dose of PAA to achieve high performance ($\sim$100%) from 20 to 1 ppm.

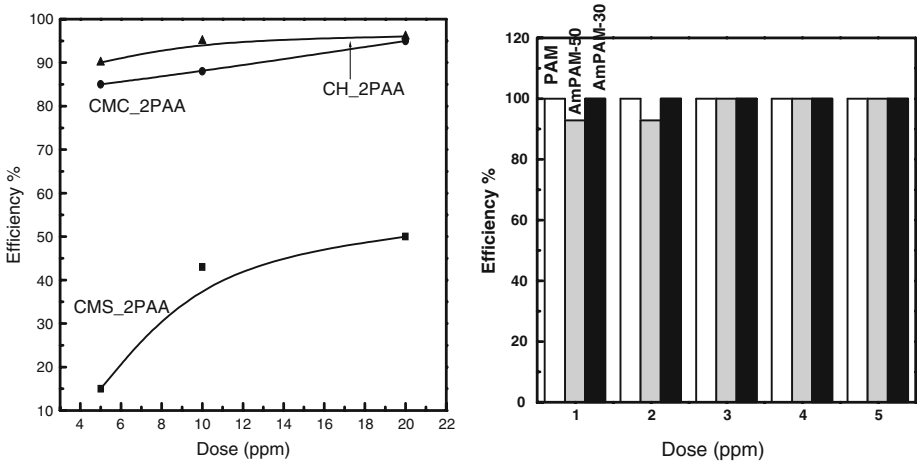

Fig. 6 Synergistic effect of 2 ppm PAA for biopolymers- and PAM-based inhibitors in NACE brine for $CaSO_4$ scale at 130°C for 3 h

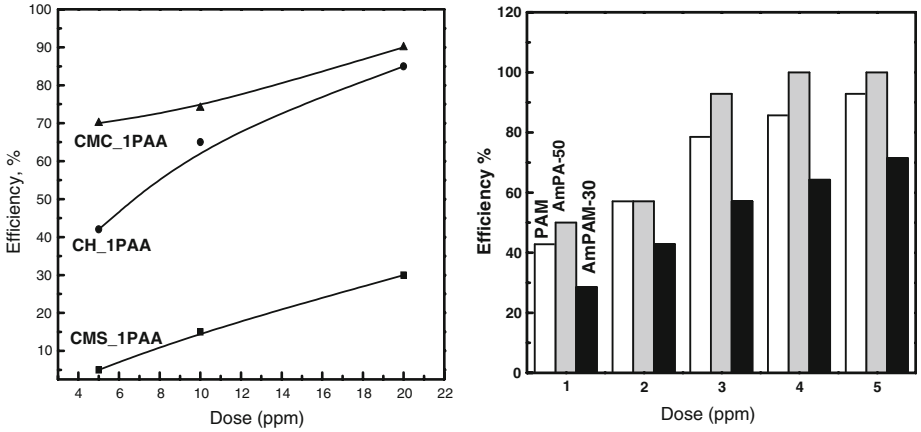

Fig. 7 Synergistic effect of 1 ppm PAA for biopolymers- and PAM-based inhibitors in NACE brine for $CaSO_4$ scale at 130°C for 3 h

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