

Polyacrylic acid and polyacrylic acid sodium salt as inhibitors of calcium oxalate crystal formation

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In both industrial machinery and medical field, calcium oxalate (CaOx) crystal formation is a significant issue. This formation must be minimized to avoid problems and ensure optimal equipment performance in industries. To contribute to the development of preventative measures, this research aimed to examine the inhibitory effects of polyacrylic acid (PAA) and polyacrylic acid sodium salt (PAANa) on CaOx crystal formation. A batch crystallization technique was used to investigate the inhibitory effects of PAA and PAANa on CaOx crystal formation at four different concentrations (0.5, 0.75, 1, and 2 ppm) in aqueous solutions at 37°C. The Langmuir adsorption isotherm was utilized to investigate the adsorption mechanism of the inhibitors. The study found that PAA prevented crystal growth by 50–90%, while PAANa was more effective, reducing it by 95–98%. Additionally, the differential heat of adsorption of Q_{diff} for the kink Langmuir adsorption isotherm for PAA and PAANa was 41.56 and 49.28 KJ/mol, respectively. The findings demonstrate the potential use of PAA and PAANa as inhibitors and advance our understanding of the fundamental principles underlying CaOx crystal formation. Therefore, this research contributes to the development of preventative measures to avoid these problems, ensure optimal equipment performance in industries and prevent kidney stone formation in the medical field.

Keywords: Calcium oxalate, Scale formation, Inhibitors, Polyacrylic acid sodium salt.

INTRODUCTION

In many industries, fouling of industrial plant equipment by inorganic and organic foulants is a serious concern [1]. Among these foulants, calcium oxalate fouling is especially problematic, affecting a wide range of industrial operations. Oxalate ion concentrations rise in numerous industrial process streams as larger organic species degrade, particularly in strongly alkaline conditions. CaOx phases can precipitate in the presence of Ca^{2+} due to their low solubility [2]. Scale formation caused by the accumulation of these oxalate compounds is a major issue in many industries, including pulping and papermaking, as well as in cane sugar mill evaporators [3, 4].

Scale formation causes significant processing challenges in cane sugar mills, with calcium oxalate and amorphous silica being the most difficult scale components generated on the calandria tubes. The formation of these deposits necessitates an increase in energy consumption in order to meet the operating requirements. If the energy input becomes uneconomical, the sugar mill must close in order to remove the scale using chemical and/or mechanical procedures. Failing to remove the scale on a regular basis can result in sucrose deterioration due to prolonged residence time and tube damage [5]. These shutdowns can be costly due to missed production and cleaning costs [6].

Scale formation occurs in the pulp and papermaking industry when oxalate ions interact with various alkaline earth metal ions, such as calcium ions and barium ions, under alkaline circumstances, resulting in poorly soluble oxalates. These oxalates rapidly deposit on the surface of pulp pipelines, washing, and screening equipment, and are difficult to remove once formed. The accumulated deposits can cause pipe obstruction and screen blocking, interfering with the normal operation of machinery [4]. As a result, controlling scale development caused by oxalate compounds is a serious challenge for these businesses.

Scale inhibitors are commonly employed to avoid scaling in a variety of industrial processes. The usage of scale inhibitors is critical in many industries, including sugar manufacturing, to preserve the effectiveness and longevity of equipment. Scale inhibitors act by interfering with the crystallization process of scale components at low concentrations, typically a few parts per million. They have the ability to prevent or greatly inhibit precipitation. The type of scaling substance influences the polymer employed as a scale inhibitor, with anionic polymers typically utilized in the sugar sector for calcium salt inhibition [6].

Using distinct inhibitors at different phases of evaporation allows certain scale components to be targeted without interfering with one another.

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Scale inhibitors can work in three different ways.

The first involves nucleation interference, in which the inhibitors loosely bind to scale-forming ions and damage crystal embryos. The polymers' second effect includes their impeding crystal growth by adhering to the active growth sites of a crystal, causing the crystal morphology to be distorted. Inhibitors interact with the crystal surfaces to repel other charged particles, blocking binding, and functioning as dispersants [6]. Overall, scale inhibitors are a significant tool for preserving equipment efficiency and preventing scaling in a variety of industrial processes.

The presence of a carboxyl group on every two carbon atoms of the main chain gives poly(acrylic acid) (PAA) a high negative charge density. Acrylic polymers have a wide molar mass distribution because they are manufactured industrially through radical polymerization of acrylic acid or sodium acrylic acid. PAA, along with poly (sodium acrylate), is a water-soluble anionic polyelectrolyte that is widely utilized in the creation of hydrogels, superabsorbent and ion exchange resins, as well as dispersion and binding agents. Because of their low toxicity, PAA and PAANa are frequently utilized in industrial applications, such as adhesives, coatings, textiles, and water treatment. Their beneficial features, including hydrophilicity, nontoxicity, and binding capacity, make them an appealing material for changing the structure of bentonite components in foundry binders [7]. PAA was found to be an efficient inhibitor of calcium oxalate monohydrate (COM) crystal formation in a study by Akyol and Öner [8]. The research found that PAA was adsorbed onto the surface of the COM crystals, preventing further crystal formation. The authors hypothesized that PAA's high negative charge density contributed to its effectiveness as a COM crystal growth inhibitor.

This study holds great importance for industries aiming to minimize scale formation and maintain optimal equipment performance. Specifically, we conducted a comparison between the inhibitory effects of PAA and PAANa on calcium oxalate (CaOx) crystals. The findings of this research have the potential to revolutionize scale prevention strategies by introducing more efficient and cost-effective inhibitors. Additionally, this study provides valuable insights into the mechanisms of calcium oxalate inhibition and opens up possibilities for the development of novel inhibitors. In summary, this research underscores the significance of comprehending the inhibitory capabilities of PAA and PAANa polymers, along with their prospective industrial applications.

EXPERIMENTAL

A one-liter Pyrex glass jar with a water-jacket was used to carry out the experiment. Supersaturated solutions were made by progressively combining calcium chloride and sodium oxalate solutions in equal proportions, with freshly prepared solutions frequently added to the oxalate component. In order to conduct the growth investigations, a predetermined amount of stock solutions containing 0.7 mM CaCl_2 and $\text{Na}_2\text{C}_2\text{O}_4$ were added, with the latter being added only after the equilibrium temperature was reached. Software was used to continuously track the temperature, pH (6.7), and calcium concentration during the crystallization process.

The experiments were conducted at 37°C with additive concentrations ranging from 0.5 to 2 mg/L and a starting $[\text{Ca}^{2+}]/[\text{C}_2\text{O}_4^{2-}]$ ratio maintained at 1. To determine the impact of the polymer on the rate of calcium oxalate precipitation, solution conductivity was measured, and the decline in conductivity with time was noted. A detailed explanation of the entire experimental methods has already been published [9].

In order to evaluate the impact of polymers, we compared the rate at which crystals were formed in the absence of polymers (R_0 , mol/L^{-min}) to the rate of crystal formation in their presence (R_i , measured in mol/L^{-min}) under identical experimental conditions. The ratio of R_0 to R_i was utilized as a quantitative measure of the additive's influence. The rate of rapid growth was determined by analyzing the slope of the calcium ion concentration over time graphs for each individual experiment. Specifically, we calculated the slope using the tangent line at the point where the curve displayed its initial clear change in direction. The reported rates were obtained by averaging the outcomes from a minimum of three separate experiments.

RESULTS AND DISCUSSION

The purpose of the experiments was to determine how PAA and PAANa polymers affected the rate of calcium oxalate crystallization at 37 °C. The study's findings are presented in Table 1. We examined the growth inhibition of calcium oxalate crystals with and without polymer to ascertain the impact of additives on crystal growth. The R_0/R_i ratios were used to quantify the polymer's capacity to prevent crystal formation; a greater ratio denotes a more potent inhibitor. By contrasting the growth rates of the solutions with and without the additives (R_0 and R_i , respectively), the efficiency of the additives was ascertained (R_i). The following formula was then used to determine the inhibitory activity:

$$\text{Inhibition (\%)} = \frac{R_0 - R_i}{R_0} \times 100$$

The results of this study showed that both PAA and PAANa were effective inhibitors of calcium oxalate crystal formation. PAA inhibited the formation of calcium oxalate crystals by 50%, 56%, 70%, and 90% at concentrations of 0.5, 0.75, 1, and 2 ppm, respectively. PAANa, on the other hand, was a more potent inhibitor and inhibited the formation of calcium oxalate crystals by 95%, 97%, 98%, and 98% at concentrations of 0.5, 0.75, 1, and 2 ppm, respectively. The results suggest that PAANa is a more effective inhibitor of calcium oxalate crystal formation than PAA.

The findings of this study highlight the effectiveness of both PAA and PAANa as inhibitors of calcium oxalate crystal formation. The inhibitory mechanism of these polymers is attributed to their ability to disrupt the nucleation and growth processes of calcium oxalate crystals. Notably, the results reveal that PAANa exhibits a greater inhibitory potency compared to PAA. This heightened efficacy may be attributed to the

presence of sodium ions in PAANa, which potentially enhance its interaction with calcium ions and consequently inhibit the formation of calcium oxalate crystals. Moreover, the elevated negative charge density of PAANa contributes to its inhibitory activity by electrostatically repelling calcium ions. However, it is important to note that the inhibitory effect of both polymers primarily arises from their adsorption onto the surfaces of the crystals. PAANa, in particular, exhibits a stronger affinity for the surfaces of calcium oxalate crystals. This assumption will be further supported and explored in the forthcoming section addressing the adsorption mechanism within this research.

Overall, the present study demonstrates the potential of PAA and PAANa as effective inhibitors of calcium oxalate crystal formation, with potential applications in various industries. The ability of these polymers to inhibit the formation of calcium oxalate crystals could lead to improved product quality and reduced maintenance costs in industrial settings.

Table 1. Effect of PAA and PAANa on the growth of calcium oxalate crystals.

Polymer	Concentration (mg/L)	R_0/R_i	Inhibition (%)
Control	-	1	-
PAA	0.5	2	50
	0.75	2.85	56
	1	3.33	70
	2	10	90
PAANa	0.5	20	95
	0.75	28.57	97
	1	50	98
	2	50	98

Table 2. Calculated K and Q_{diff} values for CaOx crystal formation in the presence of PAA and PAANa.

Polymers	Adsorption model	K (mole/mole) ⁻¹	Q_{diff} (KJ/mole)	R^2 (corr. coeff.)
PAA	Kink	1×10^7	41.56	0.9896
	Terrace	4×10^7	37.98	0.9732
PAANa	Kink	5×10^9	49.28	0.8941
	Terrace	1×10^8	47.49	0.8943

Adsorption mechanism

The crystal surface is impacted by polyelectrolytes that hinder or prohibit further crystallization even at low concentrations. The limited amount of polymer present in the solution suggests that the prevention of growth is likely due to the obstruction of active growth sites on the seed

crystals, rather than the binding of calcium ions in the solution. Research on crystal morphology and growth rates has explored the effect of additives, with theoretical models based on the concept of additive adsorption onto different crystal surface sites. Cabrera and Vermilyea (CV) [10], for instance, examined the adsorption of impurities at kinks and

surface terraces. According to this model, the growth of crystals is inhibited by a barrier of adsorbed inhibitor ions on the smooth crystal surface. As Vermilyea notes, an inhibitor stops a step moving across the crystal surface. Even a few percent of inhibitor ions covering the available crystal surface can block the growth of various mineral salts, suggesting that preferential adsorption of the inhibitor at active growth sites on the surface is responsible for the inhibition mechanism.

Vermilyea noted that an inhibitor would halt a step moving across the crystal surface. The blocking of crystal growth by a few percent of inhibitor ions covering the available crystal surface for various mineral salts suggests that the inhibition mechanism may be due to the preferential adsorption of the inhibitor at active growth sites on the surface. Kubota and Mullin have recently developed a new kinetic model for crystal growth in the presence of impurities, which describes the adsorption of impurities along steps [11]. The model introduces an impurity effectiveness factor α and assumes that step velocity linearly decreases with increasing surface coverage by impurities adsorbed on the growing crystal.

The relationship between the fraction coverage, θ_i , of the surface in the presence of an impurity and the relative growth rate R_i/R_0 in a spiral growth mechanism can be expressed as follows:

$$\left(\frac{R_0 - R_i}{R_i}\right)^n = \alpha^n \theta_i \quad (1)$$

In the case of impurity adsorption occurring at kinks in step edges, as in the Kubota-Mullin model, the exponent n equals 1, while an exponent of 2 represents adsorption on surface terraces, as in the CV model. The coverage of adsorption active sites, θ_i , can be described by the Langmuir adsorption isotherms.

$$\theta_i = \frac{KC_i}{1 + KC_i} \quad (2)$$

In Eq. (2), K is the Langmuir constant given by:

$$K = \exp\left(\frac{Q_{diff}}{RT}\right) \quad (3)$$

The differential heat of adsorption, Q_{diff} , corresponds to impurity coverage θ_i of the available adsorption sites. By combining Eq. (1) with the Langmuir isotherm (Eq. (2)), we can obtain an equation that is linear in $1/C_i$ for n equal to 1.

$$\begin{aligned} & \left(\frac{R_i}{R_0 - R_i}\right) \\ &= \frac{1}{\alpha} \left(1 + \frac{1}{KC_i}\right) \end{aligned} \quad (4)$$

For $n = 2$,

$$\begin{aligned} & \left(\frac{R_i}{R_0 - R_i}\right)^2 \\ &= \frac{1}{\alpha^2} \left(1 + \frac{1}{KC_i}\right) \end{aligned} \quad (5)$$

To verify the validity of the models, we fitted our kinetic data to Eqs. (4) and (5) and plotted the results in Fig. 2. The crystal growth rate, R , dependence on C_i allowed us to calculate K from the experimental data. Figs. 1 and 2 display the plots of $R_i/(R_0 - R_i)$ and $[R_i/(R_0 - R_i)]^2$, respectively, against $1/C_i$ for the models involving impurity adsorption at kinks (n equal to 1) and on surface terraces (n equal to 2).

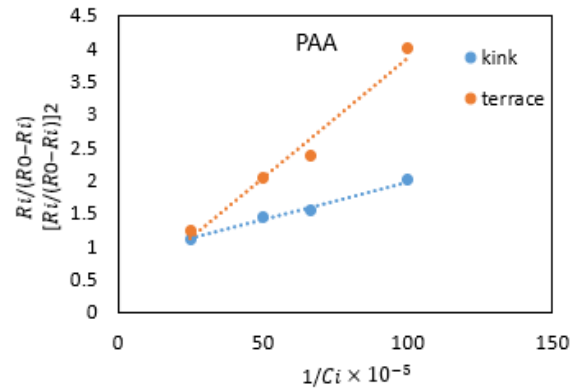


Figure 1. Plots of $R_i/(R_0 - R_i)$ and $[R_i/(R_0 - R_i)]^2$ against $1/C_i$ for PAA.

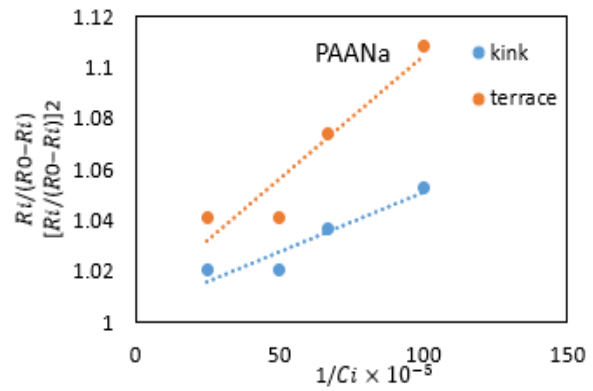


Figure 2. Plots of $R_i/(R_0 - R_i)$ and $[R_i/(R_0 - R_i)]^2$ against $1/C_i$ for PAANa.

We analyzed the experimental data of the COM crystal growth in the presence of polymers using Eqs. (4) and (5). From the slopes of the plots, we determined the values of constant K and estimated the heats of adsorption, Q_{diff} , using Eq. (3). Fig. 5 shows that there is no significant difference between the plots for the exponents 1 and 2. However, it is worth noting that the values of Q_{diff} for kinks or terrace are comparable (as shown in Table 2) and cannot be used to distinguish between adsorption at kinks and on the surface terrace. This suggests that the Langmuir adsorption isotherm does not significantly differ when impurity adsorption occurs

at kinks (Kubota-Mullin model) or on the surface terrace (CV model) as it was stated in a previous study [8].

CONCLUSION

In conclusion, this study focused on investigating the inhibitory effects of polyacrylic acid and polyacrylic acid sodium salt on calcium oxalate crystal formation. The findings demonstrate that both PAA and PAANa are effective inhibitors of CaOx crystal formation, with PAANa exhibiting higher potency compared to PAA. Through the utilization of a batch crystallization technique and analysis of adsorption mechanisms using the Langmuir adsorption isotherm, it was observed that PAA inhibited crystal growth by 50-90%, while PAANa showcased a higher level of effectiveness by reducing crystal growth by 95-98%. Moreover, the differential heat of adsorption values (Q_{diff}) further supported the superior inhibitory properties of PAANa (49.28 KJ/mol) compared to PAA (41.56 KJ/mol).

These findings have significant implications for various industries facing CaOx-related problems, as well as in the medical field to prevent kidney stone formation. The potential use of PAA and PAANa as inhibitors of CaOx crystal formation is evident, highlighting the importance of understanding the fundamental principles underlying this process. By developing preventative measures based on the inhibitory capabilities of these polymers, industrial

equipment performance can be optimized while minimizing issues caused by CaOx crystal formation. Additionally, the insights gained from this study contribute to the broader scientific understanding of CaOx crystal formation, paving the way for future research in this field.

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