Available online at www.sciencedirect.com

Journal of Applied Research and Technology

CCADET
CENTRO DE CIENCIAS APLICADAS Y DESARROLLO TECNOLÓGICO

Journal of Applied Research and Technology xxx (2016) xxx–xxx

www.jart.ccadet.unam.mx

Original

Application of poly(aspartic acid-citric acid) copolymer compound inhibitor as an effective and environmental agent against calcium phosphate in cooling water systems

Yu-ling Zhang *, Cai-xia Zhao, Xiao-dong Liu, Wei Li, Jiao-long Wang, Zhi-guang Hu

School of Environmental Science & Engineering, North China Electric Power University (NCEPU), Baoding, China

Received 3 May 2016; Received in revised form 18 July 2016; accepted 23 August 2016

Abstract

Poly(aspartic acid-citric acid) copolymer (PAC) is a new product of poly(carboxylic acid) scale inhibitor. The study aims to develop a "green" water treatment agent for calcium phosphate scale. The article compares the efficiency of three polymeric antiscalants, poly(aspartic acid-citric acid) copolymer (PAC), polymaleic acid (HPMA) and a compound inhibitor (PAC-HPMA), for calcium phosphate scale prevention under varying experimental conditions. Inhibitor concentration, calcium concentration, system pH, temperature and experimental time were varied to determine their influences on inhibitor performance by the static scale inhibition method. The copolymer (PAC) was characterized by FTIR, ^{1}H NMR and ^{13}C NMR. The compound inhibitor was applied in the actual circulating cooling water system. An atomic force microscope (AFM), X-ray powder diffraction (XRD) and a scale formation process analysis were used to explore the scale inhibition mechanism. The results showed that scale inhibition rates of PAC, HPMA and PAC-HPMA against $Ca_3(PO_4)_2$ were, respectively, about 23%, 41.5% and 63% when the dosage was 8 mg/L in the experiment. The compound inhibitor showed the better inhibition performance than the above two kinds of monomers. Under the actual working conditions, the inhibition rate of compound inhibitor was close to 100% and completely met the actual application requirements of scale inhibitor in circulating cooling water systems. The main inhibition mechanism was the decomposition-chelation dispersion effect. The compound inhibitor can be used as an efficient "green" scale inhibitor for calcium phosphate.

Keywords: Poly(aspartic acid-citric acid) copolymer (PAC); Polymaleic acid (HPMA); Compound inhibitor (PAC-HPMA); Calcium phosphate; Inhibition rate

1. Introduction

Phosphorus scale inhibitors can prevent the formation of calcium carbonate and calcium sulfate scales; however, the phosphorous-based compounds, particularly the poly(phosphate)s, may produce orthophosphate in hydrolysis reactions and exacerbate phosphate scaling when water contains significant hardness (Snoeyink & Jenkins, 1980). Phosphorus-based inhibitors, which can serve as nutrients leading to eutrification difficulties. Phosphorus and heavy-metal discharges are regulated in many areas of the world, and permissible limits are decreasing (Hasson, Shemer, & Sher, 2011). Furthermore, reclaimed water widely used in the circulating cooling system usually contains trace amounts of phosphorus compounds, such as orthophosphates, poly(phosphate)s and organophosphates, which cannot be completely removed from raw wastewater by secondary or advanced treatment (Wang, Wang, & Hou, 2016) and may increase calcium phosphate deposition in the circulating cooling system. Moreover, increasing cooling systems are operating under the larger cycles at the higher temperatures, so $Ca_3(PO_4)_2$ scale has become common in cooling water systems (Feng et al., 2014).

The growth of calcium phosphate scale in industrial processes causes serious problems. Especially, calcium phosphate scale deposited on heat exchanger surfaces in industrial cooling water systems, boiler, oil and gas production, geothermal energy and distillation systems, leads to overheating and thermal loss of

* Corresponding author.
E-mail address: zhangyuling_hit@163.com (Y.-l. Zhang).
Peer Review under the responsibility of Universidad Nacional Autónoma de México.

http://dx.doi.org/10.1016/j.jart.2016.08.006

Please cite this article in press as: Zhang, Y. -l., et al. Application of poly(aspartic acid-citric acid) copolymer compound inhibitor as an effective and environmental agent against calcium phosphate in cooling water systems. *Journal of Applied Research and Technology* (2016), http://dx.doi.org/10.1016/j.jart.2016.08.006

systems (Wang, Shen, Li, & Wang, 2014). Undesirable scale deposits often cause numerous technical and economic problems (Belarbi, Gamby, Makhloufi, Sotta, & Tribollet, 2014). Calcium scaling from cooling water seriously affects the operation of recirculating cooling water facilities (Wang et al., 2014).

To prevent or minimize unfavorable events caused by scaling problems, it is necessary to add large quantities of scale inhibitors into cooling water systems (Lin & Singer, 2005; Zuhl & Amjad, 2010). Some polymers as scale inhibitors were synthesized to explore its inhibition effect. Zhang, Wang, Jin, and Zhu (2013) synthesized a polysaccharide sulfonate salt from a hetero-polysaccharide extracted from abandoned corn stalks and its scale inhibition rates against $CaSO_4$ and $Ca_3(PO_4)_2$ respectively reached 95% and 55%. Biodegradable polymers such as PASP and polyepoxysuccinic acid (PESA) have drawn much attention recently in view of environmental benefits (Liu, Dong, Li, Hui, & Lédion, 2012; Roweton, Huang, & Swift, 1997). Demadis and Stathoulopoulou (2006) reported that CMI, at a dosage of 4–6 mg/L, showed good inhibitory performance with regard to $CaCO_3$ and $CaSO_4$ scale formation. These polymers had the better anti-scaling performance for $CaCO_3$ and $CaSO_4$; nonetheless, their scale inhibition rate to $Ca_3(PO_4)_2$ was not outstanding, thus limiting their large-scale commercial applications (Xu, Zhang, Zhao, & Cui, 2013). Hence, it is necessary to develop environmentally friendly agent as efficient calcium phosphate scale inhibitor.

In the study, we firstly composited the compound inhibitor (PAC-HPMA) with aspartic acid-citric acid copolymer (PAC) and polymaleic acid (HPMA) according to a certain proportion. Then, following the static scale inhibition method, we compared the anti-scaling performances of PAC, HPMA, and PAC-HPMA with $Ca_3(PO_4)_2$ scale as the target and under different conditions (scale inhibitor dosage, pH, Ca^{2+} concentration, constant temperature and time). In addition, the compound inhibitor was applied in the actual circulating cooling water system. Atomic force microscope (AFM), X-ray powder diffraction (XRD) and scale formation process analysis were used to explore the scale inhibition mechanism.

2. Experimental

2.1. Reagents and instruments

HPMA (active component of 48%) was purchased from Taihe Chemical Reagent Co. Ltd. (Shandong, P.R. China). Poly(aspartic acid-citric acid) copolymer (PAC, *Mw*: 16,242; *Mn*: 11,255; PDI: 1.44; mole ratio of aspartic acid and citric acid is 9:1) and compound inhibitor (PAC-HPMA) were self-made in the laboratory.

Instruments used in the study included HH-S6 Digital constant temperature water bath pot, TP-214 electronic balance, UV-6000 PC spectrophotometer, CSPM5500 Perkin Elmer Spectrum 100 spectrometer (IR), Bruker Advance AV 50 MHz nuclear magnetic resonance spectrometer (NMR), atomic force microscope (AFM), and D8 Advance X-ray powder diffraction (XRD).

2.2. Synthesis and purification methods of PAC

The synthesis method was as follows: a certain amount of aspartic acid and citric acid were fully mixed. NaH_2PO_4 as catalyst and propylene carbonate (PC) as organic solvent were added into the above mixture to obtain suspension. The suspension reacted several minutes under microwave radiation to generate yellow fluffy product PSID called as intermediate. PSID was fully hydrolyzed by adding an appropriate amount of 6 mol/L NaOH solution. The color of the solution after hydrolyzation turned into red brown. The pH was adjusted to 3.84 by using hydrochloric acid, and then excess anhydrous ethanol was added into the solution. The object product (PAC) was obtained after filtering, drying and grinding.

Purification of PAC: excess anhydrous ethanol was added into 70% PAC solution to obtain the suspension. Then suspension was static settling for 30 min and the deposit was observed. After filtering, the deposit was added to excess anhydrous ethanol again. The above operation was repeated four times. High-purity PAC was gained after filtering, drying and grinding.

2.3. Determination of scale inhibition rate

$Ca_3(PO_4)_2$ inhibition tests were determined by the static scale inhibition method. According to the national standard of P.R. China concerning the code for the design of industrial circulating cooling water treatment (GB/T 22626-2008), after pH was adjusted to 9.0 using 1.0 g/L $Na_2B_4O_7{\cdot}10H_2O$, the testing solution containing 100 mg/L $CaCl_2$, 5 mg/L KH_2PO_4 and a certain amount of inhibitor was incubated at 80 °C for 10 h in water bath. The hot solution was filtered and the PO_4^{3-} concentration in the filtrate was detected by the ammonium molybdate spectrophotometric method. The inhibition rate of the scale inhibitor against $Ca_3(PO_4)_2$ scales was calculated according to Eq. (1):

$$\eta_{Ca_3(PO_4)_2} = \frac{\rho_1 - \rho_0}{\rho_2 - \rho_0} \times 100 \quad (1)$$

where ρ_1 and ρ_0 are the concentration of PO_4^{3-} in the supernatant after10 h test period in the presence and absence of the inhibitor, respectively; ρ_2 is the mass absorbance of all in to-be-tested solution.

2.4. Characterization of PAC

2.4.1. FTIR analysis

A small amount of purified samples were dried to constant weight in an oven at 60 °C, which were mixed with KBr and pressed onto disk. FTIR spectra in the range 400–4000 cm^{-1} of the copolymers were recorded by means of a Perkin Elmer Spectrum 100 spectrometer made in USA.

2.4.2. H NMR and ^{13}C NMR analysis

^{13}C NMR and ^{1}H NMR spectra of PAC were measured with a Bruker Advance AV 50 MHz NMR spectrometer made in Switzerland. 5 mg sample and 1 mL D_2O were used to measurement.

Please cite this article in press as: Zhang, Y. -l., et al. Application of poly(aspartic acid-citric acid) copolymer compound inhibitor as an effective and environmental agent against calcium phosphate in cooling water systems. *Journal of Applied Research and Technology* (2016), http://dx.doi.org/10.1016/j.jart.2016.08.006