



Development of green/biodegradable polymers for water scaling applications



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ABSTRACT

The usage of green polymers are widely increased from day-to-day as detergent builders, paper-sizing agents, flocculants, thickeners, emulsifiers, and scale inhibitors due to their friendly nature with the water systems. Minimizing the formation of inorganic scale deposits in processing industrial waters presents a challenge for water treatment systems. In the present investigation, we have developed water soluble green polymers based on malic acid (MA) and citric acid (CA) through a bulk-melt condensation process and applied as water scaling inhibitors. The copolymer of poly(malic acid-citric acid) (PMC) was synthesized by varying the ratio of MA and CA monomers with 1:3, 1:1, and 3:1, and studied their descaling property with carbonate, sulfate and phosphate ions. The scale inhibition property of the homopolymers was also investigated and compared with the copolymers. As the ratio of CA was increased in the copolymer formation, there was a greater influence on the scale inhibition. Interestingly, copolymers showed the highest phosphate inhibition (98%) and have no significant change with its homopolymers. The results indicate that the synthesized green copolymers PMC were water soluble, biodegradable, non-toxic and hence, have a good water descaling property without disturbing the taste, quality and purity of water. Characterization techniques such as Fourier Transform Infrared Spectroscopy (FTIR) analysis and Thermal Gravimetric Analysis (TGA) were performed in order to understand its thermal properties and copolymer confirmation.

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1. Introduction

Diminishing the formation of inorganic scale deposits in processing industrial waters presents a huge challenge for water treatment systems. Water hardness is known to be the presence of hard ions (e.g. Ca²⁺ or Mg²⁺) forming build up on water heaters, boiler feed water heaters, and other plumbing fittings, and is a problem faced by many countries, especially those with ground-water filtered by aquifers (Samia and Salem, 2009). In Barbados, limestone filters our groundwater, and in both industrial and domestic use, the hardness of the water can pose huge problems to plumbing, water treatment and cooling equipment. Along with the presence of calcium and magnesium ions, the presence of

carbonates, nitrates, phosphates and even zinc in water can impose stress on industrial water cooling and treatment facilities (He et al., 1995; Littlejohn et al., 2000; Yu et al., 2002, 2003; Buffi et al., 2002; Loy et al., 2004; Macadam and Parsons, 2004; Demadis, 2004). Sparingly soluble mineral salts such as calcium sulfate in the form of gypsum can cause a decline in the efficiency of industrial water systems, geothermal energy, oil and gas production and desalination (Uchymiak et al., 2008).

Scaling causes a number of problems like an increase of energy being used, equipment shutting down or malfunctioning and impedance of heat transfer (Yang et al., 2001). The sparingly soluble species such as CaCO₃ and CaSO₄ present in raw or natural water are concentrated and precipitated during desalination process and leads to scale deposition on flow surfaces that eventually damage the performance of the desalination system (Kaysar et al., 1994; Hasson et al., 1998). According to Chapman (1992), chemical weathering cause the 50% contribution of carbonate and bicarbonate salts found in natural water. In other areas these salts can

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also stem from the atmosphere and soil containing carbon dioxide. Carbonic acid produces carbonate and bicarbonate salts when small amounts of carbon dioxide dissolve into water.

Control of scale formation on heat transfer surfaces is also considered a serious problem in the distillation processes. Scaling can be controlled by the use of chemical additives that diminish the adherence of solids to different surfaces (Hasson et al., 1996). Antiscalant chemicals involve the inhibition of crystal growth by retarding the nucleation and weakening the tenacity of the scale thus distorting the crystal structure (Zhou, 2002; Hasson and Semiat, 2006). Polyelectrolytes and organophosphorous compounds are two types of inhibitors extensively used (Amjad and Hooley, 1986; Amjad, 1988; Xyla et al., 1992). Polyamino Polyether methylenephosphonate (PAPEMP) was developed by Gill (1999), and is capable of controlling both calcium carbonate and calcium sulfate scales in water desalination. Tang et al. (2008) tested the efficiency of three inhibitors such as Polyacrylic acid (PAA), Aminotrimethylenephosphonic acid (ATMP) and PAPEMP for the inhibition of CaCO₃ scaling. Phosphonates (HERA, 2004) such as Aminotris(methylenephosphonic acid) (ATMP or AMP), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), are used to inhibit the formation of scales and control steel corrosion in industry and domestic (Amjad and Zuhl, 2004). Synthetic polymers such as Polyacrylates, Polymethylacrylates and Polyacrylamide are used in prolonging the life and usage of phosphonates and are referred to as scale control polymers. The function of these polymers is to keep the scale particles suspended in the bulk fluid or prevent scale formation (dispersant or antiscalant). Since the synthetic polymers are not biodegradable, therefore these are not considered as an environmental-friendly option due to its sludge present in waste water.

The day-to-day usage of green polymers has greatly increased due to their minimal impact on water systems (Roweton et al., 1997). Unlike some of its predecessors, green polymers are good scale inhibitors which do not disturb the taste, quality or purity of water. As they are also water soluble polymers, they can be used as detergent builders, paper-sizing agents, flocculants, thickeners and emulsifiers (Ramesh Babu et al., 2010). In recent years, these polymers have showed the extent of their usability within water treatment applications, such as cooling water treatment, boilers, evaporators, RO (Reverse osmosis) membranes, secondary oil recovery, as well as, deposit control agents for scale inhibition (Weijnen and van Rosmalen, 1986; Amjad, 1989; Yeboah et al., 1994; Uchymiak et al., 2008). This is mainly due to the high decomposition temperature and thermal stability of such polymers. For example, malic acid a water soluble chemical is becoming increasingly significant in a number of industries such as pharmaceuticals, the cosmetic industry, building materials, the food industry and textiles. In this respect, malic acid is being incorporated into polymers in hopes of replacing less environmentally-friendly polymers such as polyacrylics. The efficacy of green polymers such as thermal polyaspartate (TPA) and polymaleic acid (PMA) have been studied as biodegradable alternatives to polyacrylates.

This research investigates the anti-scaling application of copolymers of malic acid and citric acid PMCs and homopolymers PMA and PCA, synthesized by melt condensation method with various composition ratios. The synthesized copolymers and homopolymers are biodegradable and water soluble materials, which are thought to have anti-scaling effects. The anti-scaling efficacies of the polymers are tested against the carbonate, sulphate and phosphate ions. Inhibition assays are also investigated by the effect of time, pH, temperature and copolymer dose. Further, the synthesized copolymers are characterized by Fourier transform

spectroscopy (FTIR) and Thermal gravimetric analysis (TGA) to understand the physical and thermal properties.

2. Materials and methods

2.1. Materials

ACS grade Monomers, DL-Malic acid (MA) and Citric Acid (CA) were purchased from Sigma Aldrich Co., USA. Chemicals obtained from Aldrich Chemicals in order to prepare salt solutions include Calcium chloride (CaCl₂·2H₂O), Sodium bicarbonate (NaHCO₃), Sodium chloride (NaCl), Sodium sulphate (Na₂SO₄), Zinc sulphate (ZnSO₄·7H₂O), Potassium hydrogen phosphate (KH₂PO₄), and Ammonium Molybdate also obtained from Sigma Aldrich Chemical Co. Ltd., USA. Deionised (DI) water obtained from the laboratory was used throughout this work.

2.2. Synthesis of copolymers and homopolymers

Various ratios of Poly(malic acid-citric acid) (PMC) copolymers were prepared by mixing different weight ratios of DL-malic acid (MA) and citric acid (CA) via thermal condensation process. The weight ratios of both monomers utilized in the polymer synthesis and the resulting copolymer yield were presented in Table 1 along with its melting point. The reactants MA and CA were placed in a ceramic crucible following polymerization in a thermal furnace (Barnstead Thermolyne-FA1630-1, USA). A standardized protocol was followed carefully to obtain the condensed copolymers. The temperature programme utilized within this process consisted of two steps. In the first step, the mixture of monomers in the ceramic crucible was heated to 100 °C for 2 h following which the temperature was raised to 120 °C for 10 min where the reaction mixture started melting. Next, the reaction mixture was heated to 130 °C for nine hours until the mass attained a yellowish-cream color. In second step, the temperature was increased to 200 °C for five hours in order to facilitate the complete polymerization of the monomers to the polymeric state at which the color was changed from dark brown to light black. The samples were removed from the furnace after reaching to room temperature and washed with distilled water several times. As a result, the copolymers were obtained and thus able to be used as the anti-scaling material for the present investigation. The same procedure was applied for the preparation of homopolymers PMA (Polymalic acid) and PCA (Polycitric acid). The copolymers were labeled as PMC1, PMC2 and PMC3 for the ratio of MA and CA 3:1, 1:1 and 1:3.

2.3. Characterization studies

The synthesized copolymers were characterized by various techniques such as Fourier Transform Infrared Spectroscopy (FTIR) and Thermal Gravimetric Analysis (TGA). FTIR spectra of the copolymers and homopolymers were recorded in a Shimadzu IR Affinity-1 spectrometer over the wave range 4000–400 cm⁻¹. The samples were prepared as KBr discs. Thermo-oxidative stability of

Table 1
Masses of monomers and % yield of copolymer PMC at various ratios.

Ratio of MA:CA	Weight of MA (g)	Weight of CA (g)	Yield (%)	Melting point (°C)
1:0	15.00	0	32	296–306
0:1	0	15.00	69	86–166
1:1	12.50	12.50	67	246–260
1:3	3.75	11.25	57	172
3:1	11.25	3.75	30	270–273

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