Journal of the Taiwan Institute of Chemical Engineers 60 (2016) 445–452

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Fouling mitigation on heat exchanger surfaces by EDTA-treated MWCNT-based water nanofluids

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ARTICLE INFO

Article history:
Received 20 May 2015
Revised 5 November 2015
Accepted 13 November 2015
Available online 11 December 2015

Keywords:
Calcium carbonate
Crystallization fouling
Fouling mitigation
MWCNT-based water
EDTA

ABSTRACT

Fouling can be defined as adherent deposits of unwanted compounds that are formed by the precipitation of soluble salts from water and crystal growth on the surfaces of processing equipment. The deposition layer becomes an insulating layer that deteriorates the heat transfer efficiency and shortens the service life. The development of functionalized nanomaterial leads to multi-functionality, such as the ability to adsorb scaling cations with high thermal conductivity, which is very important for heat transfer applications to manage the fouling problems. The purpose of this study was to evaluate the mitigation of calcium carbonate scaling by applying EDTA-treated MWCNT-based water nanofluids on heat exchanger surfaces. A set of fouling experiments was conducted by using additive EDTA-treated MWCNT-based water nanofluids (benign to the environment) to verify the additives' retardation of the fouling rate of deposition. Fouling solution for deposit analysis was prepared by using 300 mg/L of artificially-hardened calcium carbonate solution. Also the assessment of the deposition of calcium carbonate on the heat exchanger surface with respect to the inhibition of crystal growth was conducted by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectrometry (EDS). The results showed that the formation of calcium carbonate crystals can be retarded significantly by adding MWCNT-EDTA additives to the solution.

1. Introduction

Fouling refers to unwanted materials being deposited and accumulated on the surfaces of processing equipment [1–3]. In cooling circuit, these deposits generally are $CaCO_3$, $CaSO_4$, silica, *etc*., which seriously deteriorates the capacity of the surface to transfer heat. In addition, the cross sectional area is reduced, which causes an increase in pressure drop across the apparatus [4–6]. Therefore, fouling has been described as the major unresolved problem in heat transfer, and, thus, many efforts have been made to solve this problem [7,8].

Scale deposition occurs when water contains ions of low-solubility salts. Process conditions create supersaturation in presence of one or more of the sparingly-soluble salts which impose the potential for their precipitation as scale. Crystallization fouling is one of the most common and detrimental fouling mechanisms in a wide range of industrial applications [9,10]. Supersaturation of dissolved salts appears due to evaporation of solution which precipitates on pipes and other equipment as fouling layer [11].

Dealing with hard water in cooling circuit is one of the major concerns in an industrial environment. A solution of an inverted-solubility salt in contact with a hot surface can attain supersaturation by the inverted-solubility effect causing deposition of scale on the hot surface which generates some serious problems by reducing the performance of the heat exchangers. Thus, efforts are given to mitigate fouling by reducing the free ions of components of the dissolved salts in the heat exchanging liquids [12–14].

Fouling mitigation can be achieved by using natural chemical additives [15], modifying the surface of the heat exchanger [16], modifying the operational parameters of the heat exchanger [17], and adding particles and natural fibre to the fouling liquids [18]. Various chemical additives can be used to curb scaling, but those that are used at present introduce hazards to the environment [19,20]. So investigators have tried to explore green additives, such as carboxyl methyl cellulose (CMC), cationic inulin polymer (cations), poly-allylamine hydrochloride (PALAM), and more environmentally benign additives [21].

Additives are found to act in different ways [22], such as (i) threshold agents, (ii) crystal modifiers, (iii) sequestering agents, and (iv) dispersants. EDTA (a sequestering agent), polyphosphonates (threshold agents), polyphosphates, and polycarboxylic acid and its derivatives (sequestering and threshold treatment) could be

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http://dx.doi.org/10.1016/j.jtice.2015.11.006
1876-1070/

considered as some of the common additives. EDTA is a sequestering agent that forms a strong complex with scaling cations, such as Ca^{2+}, Mg^{2+}, and Cu^{2+} in exchange with Na^{+}, thus preventing scaling as well as removing any previously-formed scale. In heat exchanging liquids that thermal conductivities of the common base fluids (water and ethylene glycol) are not suitable. To solve this problem, the use of carbon-based nanoparticles, such as carbon nanotubes (CNTs) and graphene, can be used due to their high surface area and potential for improving the thermal conductivity of the base fluids [23–25]. In the varieties of carbon nanostructures, CNTs are the most promising materials since they are economically viable for replacing metallic nanoparticles and graphene [26,27]. According to the previous studies, CNTs have high thermal conductivity [24,25,28] and sufficient potential for creating thermally-conductive nanofluids. These properties, along with their high surface areas for sequestering cations, such as Ca^{2+}, Mg^{2+}, and Cu^{2+} and their low cost, suggest that CNTs could be used effectively as an additive in heat exchanging liquids. Thus, they are suitable candidates for use in different thermal equipment, such as two-phased closed thermosyphons [29–33]. Despite some promising applications of CNT in the field of nanofluids, several issues have limited their thermal applications, such as their tendency to aggregate in the base fluids and their strong van der Waals interactions have led to the formation of bundles.

Covalent modification has been suggested as a viable solution for developing interactivity [24,25]. In order to enhance the dispersibility of CNTs in pure water along with inhibiting the formation of large crystals, covalent functionalization by using EDTA could be a method for getting promising results. From covalent alteration the crystal organization is distorted, and the formation of large crystals is inhibited by the crystal modifying agents (*e.g.*, polycarboxylic acid). The distorted crystals remain suspended in the bulk solution and do not settle on the heat transfer surface. However, particulate fouling may occur if their concentration increases beyond a certain limit. This is prevented either by using techniques to minimize particulate fouling or by using dispersing agents along with crystal-modifying agents. The resulting crystalline deposits are different from those formed in the absence of any additives. The layer can be removed easily as it loses its strength.

In the field of solid sorption, additives are vitally important for enhancing heat and mass transfer. Mitigation of deposits and enhancement of heat transfer by adding additives are common in principle [34]. The addition of a small quantity of surfactant reduces surface tension significantly and enhances heat transfer. Efforts have been made to develop chemicals that are extremely benign to the environment. The present work reports the retardation of fouling rates on heat exchanger surfaces in the presence of a biodegradable additive (MWCNT-EDTA). This finding has not been reported earlier and it is an environmentally-friendly approach for mitigation of fouling which could be used in heat exchanger liquids operated at low temperatures.

2. Methodology

2.1. Materials, functionalization and preparation of nanofluids

Hydroxyl-functionalized multi-walled carbon nanotubes (MWCNT-OH) with an outer diameter of 8–15 nm, lengths of 30 nm, and purity > 95% were obtained from Nanostructured & Amorphous Materials, Inc. (NanoAmor). All analytical grade chemicals were purchased from the Sigma-Aldrich Co. Recently, a new mechanism for the direct esterification of carboxylic acids and alcohols catalyzed by zirconium(IV) salts was suggested by Ishihara et al.[35].

Regarding the synthesis of MWCNT-EDTA, in a typical experiment, MWCNT-OH (50 mg), $ZrCl_4$ (0.2 mol%), and EDTA (50 mg) were poured into an agate mortar and ground for 5 min. Then, the mixture was poured into a vessel filled with 200 ml of THF and sonicated for

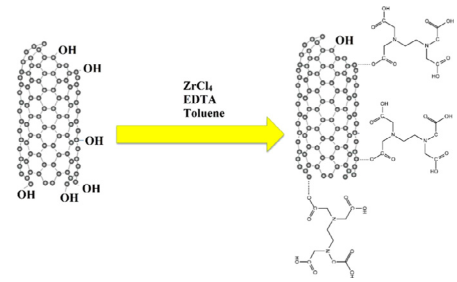

Fig. 1. Schematic layout functionalization procedure of MWCNT with EDTA.

2 h at 50 °C until a uniform suspension was obtained. During the sonication, 5 ml of toluene were added drop by drop to the suspension to complete the esterification reaction. Subsequently, the mixture was placed on a stirrer and continuously agitated at 80 °C for 24 h. After the mixture cooled to room temperature, it was centrifuged and washed more than 20 times with water, THF, and methanol to remove any unreacted materials.

To prepare EDTA-treated MWCNT-based water nanofluid, the functionalized MWCNT with EDTA in a known amount of water as a base fluid was sonicated for nearly 30 minutes using a sonicator. Unsurprisingly, the MWCNT-EDTA was dispersed easily in water. Fig. 1 shows the functionalization procedure of MWCNT-OH with EDTA. The easily-miscible EDTA functionalities can explain the higher dispersion of the functionalized MWCNT. MWCNT-EDTA-based water nanofluid with weight concentrations of 0.015, 0.030, and 0.045% were synthesized.

2.2. Test set-up

Fig. 2 shows the experimental setup used in this study. The experimental setup, equipment, instruments, and the experimental procedure are discussed in this section. The setup consisted of flow meter, thermostatically-controlled hot water bath with pump, temperature-regulated solution bath, chiller, thermocouples, and data acquisition system [12].

2.3. Test specimens

Each of the experimental test pipes was 105 mm long and had a wall thickness of 2 mm and an outer diameter of 15 mm. Metal pipes (stainless steel SS-316) with the same dimensions were used throughout the experiment. The smooth test specimens were cleaned by rubbing with a water-soaked cloth and flushed with hot water to remove any deposits of oil, grease, or other impurities before being installed in the test rig. Stainless steel coupons that were 10 mm long were installed in the middle of the test pipes. The coupons were characterized before and after the scaling tests.

2.4. Experimental procedures

Experiments were conducted by varying the parameters to determine the fouling rates, fouling resistances, and heat transfer rates for SS316 heat exchanger surfaces. In addition, we studied the effective of the MWCNT-EDTA additive (benign to the environment) in retarding the rate of deposition. Leakage tests were conducted prior to the experimental runs to ensure smooth flow conditions. To ensure reproducibility of the system, the experimental test rig was cleaned by circulating chemical cleaning agents and distilled water after each experimental run. In order to accelerate the scaling effect, a supersaturated solution of salts in water was prepared and used in all of the tests. Artificial hard water was prepared by dissolving a mixture of sodium bicarbonate ($NaHCO_3$) and calcium chloride ($CaCl_2$) powders