

Teng, KH, Amiri, A, Kazi, SN, Bakar, MA, Chew, BT, Al-Shamma'a, A and Shaw, A

**Retardation of heat exchanger surfaces mineral fouling by water-based diethylenetriamine pentaacetate-treated CNT nanofluids**

<http://researchonline.ljmu.ac.uk/id/eprint/6314/>

#### Article

**Citation** (please note it is advisable to refer to the publisher's version if you intend to cite from this work)

**Teng, KH, Amiri, A, Kazi, SN, Bakar, MA, Chew, BT, Al-Shamma'a, A and Shaw, A (2017) Retardation of heat exchanger surfaces mineral fouling by water-based diethylenetriamine pentaacetate-treated CNT nanofluids. *Applied Thermal Engineering*. 110. pp. 495-503. ISSN 1359-4311**

LJMU has developed [LJMU Research Online](http://researchonline.ljmu.ac.uk/) for users to access the research output of the University more effectively. Copyright © and Moral Rights for the papers on this site are retained by the individual authors and/or other copyright owners. Users may download and/or print one copy of any article(s) in LJMU Research Online to facilitate their private study or for non-commercial research. You may not engage in further distribution of the material or use it for any profit-making activities or any commercial gain.

The version presented here may differ from the published version or from the version of the record. Please see the repository URL above for details on accessing the published version and note that access may require a subscription.

For more information please contact [researchonline@ljmu.ac.uk](mailto:researchonline@ljmu.ac.uk)

<http://researchonline.ljmu.ac.uk/>



## Research Paper

## Retardation of heat exchanger surfaces mineral fouling by water-based diethylenetriamine pentaacetate-treated CNT nanofluids

K.H. Teng<sup>a, b, \*</sup>, Ahmad Amiri<sup>c, \*</sup>, S.N. Kazi<sup>a, \*</sup>, M.A. Bakar<sup>a</sup>, B.T. Chew<sup>a</sup>, A. Al-Shamma'a<sup>b</sup>, A. Shaw<sup>b</sup><sup>a</sup> Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia<sup>b</sup> School of Built Environment, Liverpool John Moores University, Byron Street, Liverpool L3 3AF, United Kingdom<sup>c</sup> Department of Chemical Engineering, Engineering Faculty, Ferdowsi University of Mashhad, Mashhad, Iran

## ARTICLE INFO

## Article history:

Received 16 April 2016

Received in revised form 8 July 2016

Accepted 27 August 2016

Available online xxx

## Keywords:

Calcium carbonate  
Crystallization fouling  
Fouling mitigation  
MWCNT-based water  
DTPA

## ABSTRACT

Mineral scale deposition on heat exchanging surfaces increases the thermal resistance and reduces the operating service life. The effect is usually intensified at higher temperatures due to the inverse temperature solubility characteristics of some minerals in the cooling water. Scale formation build up when dissolved salt crystallize from solution onto the heated surface, forming an adherent deposit. It is very important for heat transfer applications to cope with the fouling problems in industry. In this present study, a set of fouling experiments was conducted to evaluate the mitigation of calcium carbonate scaling by applying DTPA-treated MWCNT-based water nanofluids on heat exchanger surfaces. Investigation of additive DTPA-treated MWCNT-based water nanofluids (benign to the environment) on fouling rate of deposition was performed. 300 mg L<sup>-1</sup> of artificially-hardened calcium carbonate solution was prepared as a fouling solution for deposit analysis. 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). The results showed that the formation of calcium carbonate crystals can be retarded significantly by adding MWCNT-DTPA additives as inhibition in the solution.

© 2016 Published by Elsevier Ltd.

## Nomenclature

$W_s$	weights of the deposited scale (g)
$W_f$	weights of the fouled coupon (g)
$W_i$	weights of the initial coupon (g)
$R_f$	fouling resistance (m <sup>2</sup> K/W)
$U_{\text{fouled}}$	overall heat transfer coefficient for the fouled case (W m <sup>-2</sup> K <sup>-1</sup> )
$U_{\text{initial}}$	overall heat transfer coefficient for the initial case (W m <sup>-2</sup> K <sup>-1</sup> )
$Q$	rate of heat gain (W)
$A$	total heat transfer surfaces (m <sup>2</sup> )
$\Delta T_D$	temperature difference which was determined from average temperature at the surface and bulk solution (K)
$T_s$	surface temperature (K)
$T_B$	bulk temperature (K)
$M$	solution mass flow rate (kg/s)
$C_p$	specific heat capacity constant ((kJ/(kg K))
$T_o$	outlet temperature (K)
$T_i$	inlet temperature (K)

\* Corresponding authors at: Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia (K.H. Teng).  
Email addresses: alex\_teng1989@hotmail.com (K.H. Teng); ahm.amiri@gmail.com (A. Amiri); salimnewaz@um.edu.my (S.N. Kazi)

## 1. Introduction

The formation of scale deposits is a complex process, which involves besides the nucleation and growth the formation layer of particles that deposit through sedimentation of particles that either shortly after their formation or through collision adhere on the wall in contact with the aqueous fluids. This mechanism of scale formation, initiated and sustained by sedimentating particles is known as “Fouling” [1–3]. Heat exchangers are an important part of industrial processes as they handle a major portion of total energy consumption. Water is the most common fluid used in these process and power industries. It is used as a cooling medium, as a process fluid, and even as a solvent. Many industries tend to locate where an easy access to water is available. The major sources of water include rivers, lakes, oceans, etc. However, because of water is a universal solvent, it dissolves everything it come to contact with including Ca<sup>2+</sup> and Mg<sup>2+</sup> and other mineral found in earth. When this water bond mineral are exposed to different physical influences, such as heat transfer, friction and pressure change, they can revert back into natural solid stage against with one another and always lead to the formation of deposits on the surfaces and causing fouling problems [4–6]. Therefore, many efforts have been made to solve this problem [7,8]. Scale deposition can form with the presence of sparingly salts such as CaCO<sub>3</sub>, CaSO<sub>4</sub> and CaC<sub>2</sub>O<sub>4</sub>.

Scale is a solid layer attached to equipment surfaces and piping systems in which some materials, originally dissolved in fluids, are

deposited on the surfaces under certain conditions. The formation of scale occurs during several industrial operations such as Crystallization, distillation, evaporation, mixing, cooling, or heating of liquids. The permanent scale formation results in serious industrial problems including reduced thermal efficiency of heat exchanger, induced under-deposit corrosion, increased pressure drop and upstream pressure in piping, cavitation and flow blockage [9]. The cost of scaling has been very high for industrial sector, which comprises various components such as special designs and construction of equipments, energy loss, maintenance costs and lost production [10,11]. At present, water fouling can be considered as a manageable problem, but at a high cost and usage of chemicals hazardous to environment. An environmental approach essential needed to overcome this fouling problem without use of hazardous chemicals. The research and development on fouling has progressed significantly in the last 15 years. The fouling mechanisms are now described in terms of processes associated with the formation, transportation, deposition, and removal mechanism. Major technical issues still remain before water fouling can be recognized as a solved problem [12].

There are four essential methodologies for  $\text{CaCO}_3$  scale control: (a) support of low operational pH (b) utilization of sequestrates (c) upkeep of low cycles of focus, and (d) utilization of scale inhibitors [13]. Utilization of corrosive acid is a powerful approach to avoid calcium carbonate fouling development by keeping up a low pH. However, it raises worries because of its hazardous nature and the capability of accelerating metal erosion. The utilization of sequestering specialists is too excessive for open recycling water applications. Keeping up low cycles of focus prompts exorbitant waste water treatment in cutting edge. Scale inhibitor used is a generally acknowledged practice and includes expansion of moment measures of scale inhibitors in the recycling water [14]. These added substances contain phosphonate and/or carboxylate amasses, and can be monomeric or polymeric. They work at threshold levels, since the inhibitor concentration ratio is extremely high [15]. It is believed that they perform "threshold inhibition" by a surface adsorption mechanism involving Langmuir adsorption. Adsorption onto the  $\text{CaCO}_3$  crystal surface(s) causes inhibition (or delay) of crystal growth at the very early stages.

On the topic of scale inhibition mechanism, three possible inhibitor mechanism involved in scale inhibition were summarized by Liu et al. [16] as shown in Fig. 1.

Scale inhibitors are a group of chemical that are capable of reducing the rate of scale formation and precipitation. The function of scale inhibitors is to prevent the scale mineral crystal growth [17]. Application of scale inhibitors is by far the major scale control technique, the overall goal of the inhibitor treatment is to provide the longest possible protection against scale formation before another treatment is necessary [18]. As reported by Davey and Garside [19], the growth morphology can be affected by supersaturation, solvent, temperature and additives. The inhibitors can alter crystal surface properties and influence the electrical double layers causing change in nucleation, growth retardation, agglomeration, and morphology [20]. Each face of the crystal has a different surface lattice structure and a different distribution of adsorption sites. The additives absorb onto the crystal surface, changing the charge of surface and the associated electrical double layer, which in turn alters the dispersion properties. This varies the shape of the growing crystals [21]. The attractive features of these chemical additives such as ease of handling, relatively low cost, low dose rates, avoidance of corrosion problems arising from the use of mineral acids, and ability to impact on hard scale formation have made their use widespread [22].

Several chemical additives can be used to control scaling, but those that are used at present introduce hazards to the environment [23,24]. 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 [25]. A comprehensive study done by Hoang et al. [26] of nine organic additives which including EDTP, NTMP NDPA, HEDP, HEDP, NPDA, EDTA, NTA, citric acid and tartaric acid on the formation of calcium sulphate in a pipe system using a multiple flow system. The results revealed that low concentration of additives can retard the growth of calcium sulphate scale on the pipe walls.

Covalent modification has been suggested as a viable solution for developing interactivity [27,28]. In order to enhance the dispersibility

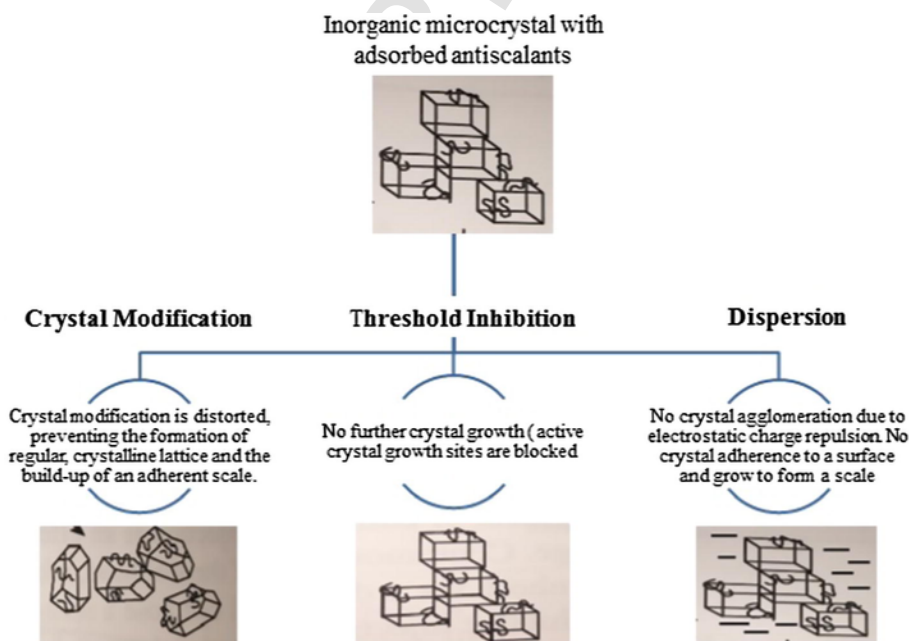


Fig. 1. Summary of primary chemical scale inhibition mechanism.

of CNTs in pure water along with inhibiting the formation of large crystals, covalent functionalization by using diethylenetriamine pentaacetate (EDTA) proven a method for getting promising results [29]. From covalent alteration the crystal organisation 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 strong sorption, added substances are essentially vital for mitigate fouling on heat exchanger. Moderation of stores and improvement of heat exchange by incorporating additives are basic on a fundamental level [9]. The present work reports the impediment of fouling rates on heat exchanger surfaces in the vicinity of a biodegradable added substance (MWCNT-DTPA). This finding has not been accounted for before and it is a naturally amicable methodology for alleviation of fouling which could be utilized as a part of heat exchanger fluids worked at low temperatures.

## 2. Experimental

### 2.1. Reactants and sample preparation

Hydroxyl-functionalized multi-walled carbon nanotubes (MWCNT-OH) with an outer diameter of 8–15 nm, lengths of 30 nm, and purity > 95% were purchased from Nanostructured & Amorphous Materials, Inc. (NanoAmor). MWCNT-OH has a very low stability in water and settled immediately. All analytical grade chemicals were purchased from the Sigma-Aldrich Co. A direct esterification of carboxylic acids and alcohols was suggested by Ishihara et al. [30] is applied with slight modification to synthesize DTPA-treated MWCNT.

For synthesis of DTPA-treated MWCNT, typically, MWCNT-OH (50 mg),  $\text{ZrCl}_4$  (0.2 mol%), and DTPA (50 mg) were poured into an agate mortar and ground thoroughly. Then, the obtained gray powder was poured into a glass bottle filled with 200 ml of THF and sonicated for 6 h until a uniform suspension was obtained. Toluene (5 ml) were added drop by drop to the suspension during the sonication for completing the esterification reaction. To complete reaction, the mixture was placed on a stirrer and agitated at 80 °C for 24 h. After cooling at room temperature, the mixture was centrifuged, washed with water, THF, and methanol to remove any unreacted materials and dried at 60 °C. For preparing the DTPA-treated MWCNT-based water nanofluids with weight concentration of 0.015, 0.030 and 0.045 wt%, respectively, 150, 300 and 450 mg of DTPA-treated MWCNT were typically added in 1 lit of water and sonicated for nearly 30 min. The easily-miscible DTPA functionalities may explain the suitable stability of the DTPA-treated MWCNT in water. MWCNT-EDTA-based water nanofluid with weight concentrations of 0.015%, 0.030%, and 0.045% were synthesized.

### 2.2. Functionalization analysis

Fig. 2 presents the Fourier transform infrared spectroscopy (FTIR) spectra of MWCNT-OH as pristine material and DTPA-treated MWCNT. FTIR spectroscopy (Bruker IFS 66/S) and Raman spectroscopy (Renishaw confocal spectrometer at 514 nm) are used to study the functional groups attached to MWCNT-OH. The infrared spectra were evaluated in the range of 400–4000  $\text{cm}^{-1}$  and all samples were

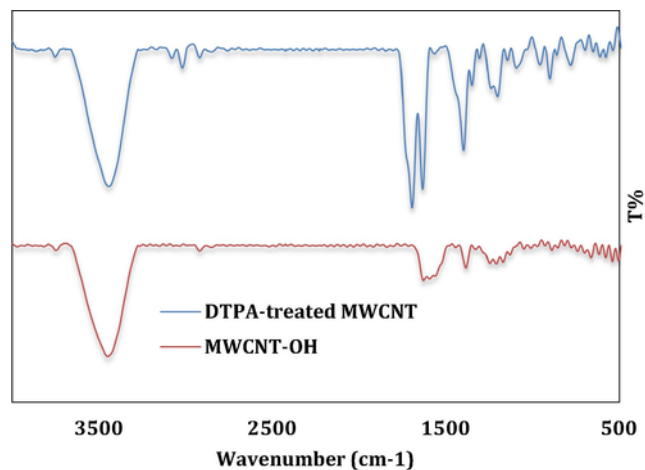


Fig. 2. Fourier transform infrared spectroscopy (FTIR) spectra of MWCNT-OH and DTPA-treated MWCNT.

placed on KBr pellets at room temperature. Also, the detailed list of peaks along with their interpretations are given in Table 1. It can be seen that both of the materials illustrate significant peaks in their spectra, however the number of peaks increases after functionalization procedure.

The FT-IR spectra of both materials show some similar peaks around 3442, 1627, 1203 and 1093  $\text{cm}^{-1}$ , which were attributed to the O—H, C=O, C—O and C—C stretching vibrations on the MWCNT generated by the attachment of the —OH groups. After MWCNT with DTPA, some new peaks are appeared in the spectrum of DTPA-treated MWCNT. The main peak at 1695.63  $\text{cm}^{-1}$  can be assigned to C=O stretching vibration after esterification. Also, the peak at 1305.85  $\text{cm}^{-1}$  is corresponded to the stretching vibration of C—N. In addition, two other peaks, one at 3018.62  $\text{cm}^{-1}$  and one at 3079.61  $\text{cm}^{-1}$ , are consistent with the  $\text{sp}^3$  C—H and  $\text{sp}^2$  C—H, respectively, which resulted from MWCNT decoration with DTPA. It can be seen that a peak at 1349.00  $\text{cm}^{-1}$ , which was attributed to the C—H bending vibration.

Raman characterization is a strong measurement for analyzing structure,  $\text{sp}^2$  and  $\text{sp}^3$  hybridized carbon atoms in carbon-based nanomaterials, functionalization, and exfoliation by following alterations in hole and electron doping [31,32]. The Raman spectra of the MWCNT-OH and DTPA-treated MWCNT are presented in Fig. 3. While the MWCNT-OH is weak in terms of D intensity, the fairly strong D

Table 1  
Fourier transform infrared interpretation of the MWCNT-OH and MWCNT-EDTA.

MWCNT-OH	DTPA-treated MWCNT	Interpretation
3448.56	3441.53	O—H stretching vibration
	3018.62 and 3079.61	C—H stretching vibration
	1695.63	C=O stretching vibration (ester band)
1629.88	1634.6	C=O stretching vibration (carboxylic acid)
1384.07	1397.75	O—H bending vibration
	1349.00	CH <sub>2</sub> bending vibration
	1305.85	C—N stretching vibration
1247.75	1203.29	C—O stretching vibration
1210.88	1146.03	C—O stretching vibration
1171	1093.84	C—C stretching vibration



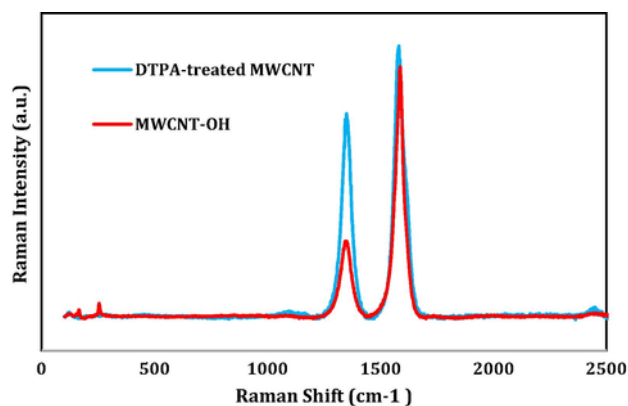


Fig. 3. Raman spectra of MWCNT-OH and DTPA-treated MWCNT.

bands in the DTPA-treated MWCNT sample can be seen at  $1350$  and  $1578\text{ cm}^{-1}$ , respectively. The ratio of the intensities of the D-band to those of the G-band ( $I_D/I_G$ ) is the amount of  $\text{sp}^3$ -hybridized carbon relative to  $\text{sp}^2$ -hybridized carbon. In functionalization of carbon-

based materials, the higher intensity ratio of  $I_D/I_G$  indicates the higher disordered carbon. The  $I_D/I_G$  ratio of DTPA-treated MWCNT was relatively higher than that of MWCNT-OH, which confirmed the successful functionalization via a DTPA.

TEM images of the DTPA-treated MWCNT are shown in Fig. 4. In these images, one can see multi-walled CNT (few-walled CNT) with relatively cylindrical shape and diameter less than  $15\text{ nm}$ . It can also be seen that there is no unzipping with low-diameter MWCNT.

### 2.3. Test set-up

Fig. 5 demonstrates the experimental setup employed in this research work. Discussion on the equipment and instruments, experimental setup and the experimental procedure are presented in this section. The experimental setup consisted of two rotary flow meter, Wise-Circu refrigerated bath circulator with temperature controlled, hot water bath circulator, K-type thermocouples, solution tank made of Perspex material, test specimens with coupon (SS-316) and data acquisition system (Graphtec Midi Logger GL220) [32].

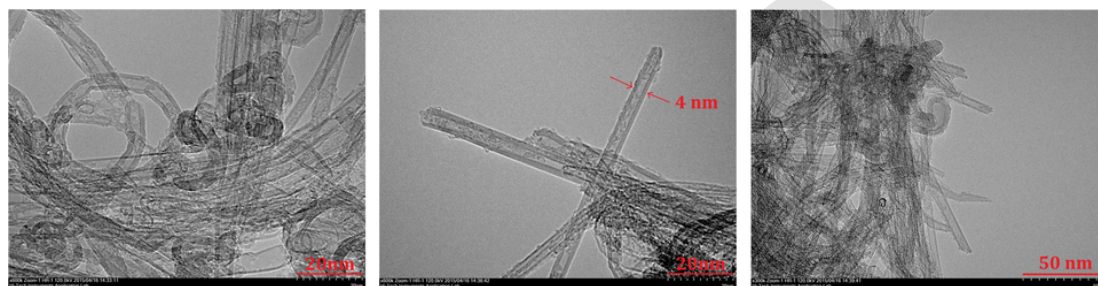


Fig. 4. TEM images of DTPA-treated MWCNT.

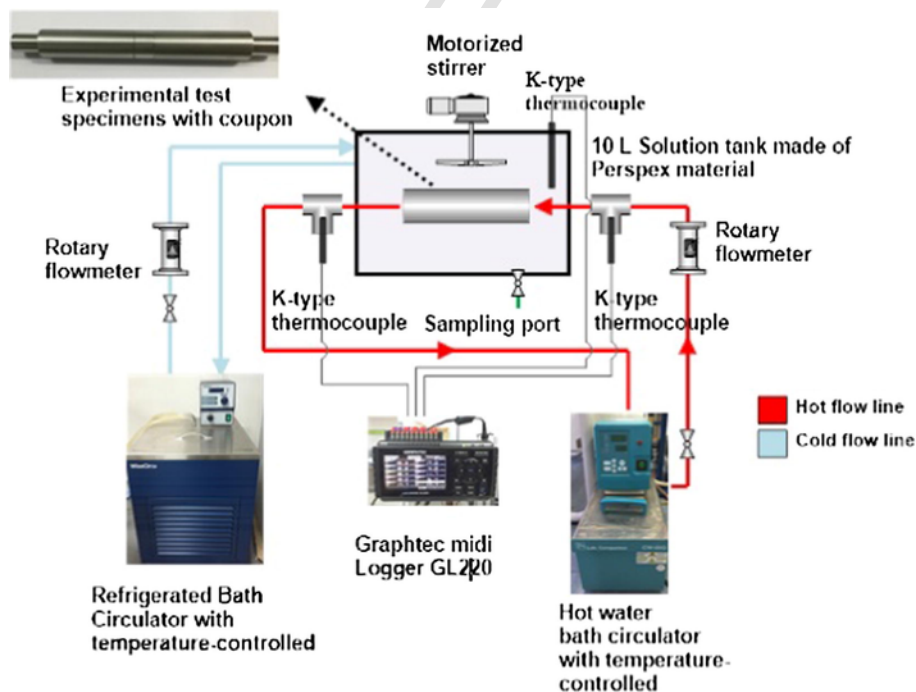


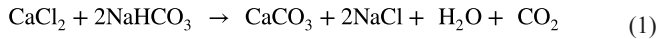
Fig. 5. Schematic diagram of the experimental set-up.

## 2.4. Test specimens

Every single of the experimental test tubing was 105 mm in total length and with 11 mm and 15 mm for inner and outer diameter respectively. Same dimensions of metal pipes (stainless steel SS-316) were used throughout the experiment. Cleaning of the smooth test specimens were performed in first place by rubbing with a water-soaked cloth and flushed with hot water in order to remove any deposited of grease, oil 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. Characterized on the coupons were performed before and after the scaling tests to understand the fouling deposition rate.

## 2.5. Experimental procedures

Experiments were conducted to identify the fouling rates, fouling resistances, and heat transfer rates for SS316 heat exchanger surfaces. Furthermore, the effectiveness of the MWCNT-DTPA additive (environment-friendly means) in mitigating the fouling deposition rate was studied in this research. Leakage tests were conducted prior to the experimental runs to ensure smooth flow conditions. The experimental test rig was cleaned by incorporating chemical cleaning agents and distilled water after each of the experimental run to ensure reproducibility data of the system. 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 calcium chloride ( $\text{CaCl}_2$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) powders in distilled water. Calcium carbonate was formed by the reaction of  $\text{CaCl}_2$  with  $\text{NaHCO}_3$ , as shown in Eq. (1).



The temperatures of the flow loops were set at 60 °C and the bulk temperature of 7 L of solution fluid remained at 25 °C by regulating the chiller. EDTA complexometric titration method was used to maintaining the constant hardness of the solution throughout the experimental process. The stirrer was regular at 200 rpm to ensure good mixing and 5 min intervals of the data recording accomplished by the data acquisition system.

## 2.6. Measurement and characterization

All of the stainless steel coupons were weighed before and after the scaling tests. The measurement of deposited calcium carbonate scale on the coupon was calculated by using the accompanying Eq. (2):

$$W_s = W_f - W_i \quad (2)$$

where  $W_s$ ,  $W_f$ , and  $W_i$  are the weights of the deposited scale, the fouled coupon, and the initial coupon, respectively. The morphologies of the scale deposits were characterized by scanning electron microscopy (SEM), and the elemental analysis was determined by energy dispersive spectroscopy (EDS). Photographic and optical images were obtained to visually differentiate the effect of the additives on the scaling that occurred on the surfaces.

## 2.7. Fouling characteristics

A number of experiments were performed to study the effect of MWCNT-DTPA concentration on  $\text{CaCO}_3$  crystallization fouling. The fouling resistance  $R_f$  on the SS316 surfaces under all cases were calculated using the Eq. (3).

$$R_f = \frac{1}{U_{fouled}} - \frac{1}{U_{initial}} \quad (3)$$

where  $U_{fouled}$  is the overall heat transfer coefficient for the fouled case, while  $U_{initial}$  is the overall heat transfer coefficient for the initial clean condition. These overall coefficients of heat transfer were calculated using the Eq. (4).

$$Q = U A \Delta T_D \quad (4)$$

where  $\Delta T_D$  (Eq. (5)) is the temperature difference which was determined from average temperature at the surface ( $T_s$ ) and bulk solution ( $T_B$ ):

$$\Delta T_D = T_s - T_B \quad (5)$$

$$Q = M C_p (T_o - T_i) \quad (6)$$

where  $Q$  is the rate of heat gained by the solution,  $M$  is the solution mass flow rate,  $T_i$  and  $T_o$  are the inlet and outlet temperature respectively and  $C_p$  is the specific heat of the solution [33].

## 3. Results and discussion

### 3.1. Effect of the concentration of the MWCNT-DTPA

Fig. 6 indicates the effect of an additive on fouling deposition. The results obtained were comparing to results from EDTA and MWCNT-EDTA additives. It is showed that fouling was reduced as the percentage of the additive was increased in the fouling solution without corrosion effects. According to E. Altay, EDTA in which containing four carboxylic and two amine groups is a well-known complexing agent of  $\text{Ca}^{2+}$  and its presence in solution would consequently lower the amount of free ions thus decreasing the driving force towards nucleation [34]. In these research works, DTPA with five carboxylic and three amine centres groups was considered as the fouling retardation additives. As a chelating agent, DTPA wraps around a metal ion by forming up to eight bonds.

The conjugate base of DTPA has a high affinity for metal cations. In this manner, the penta-anion  $\text{DTPA}^{5-}$  is potentially an octadentate ligand assuming that every nitrogen centre and each  $\text{COO}^-$  group counts as a centre for coordination. The formation constants for its complexes are about 100 greater than those for EDTA [35]. It was obvious that DTPA could perform much more better than EDTA and had a promising ability to sequester metal ions, such as  $\text{Fe}^{3+}$  and  $\text{Ca}^{2+}$  [36]. Hence, effort on decorated MWCNT-OH with DTPA was introduced. The water soluble product obtained was being bound by DTPA and sequestering  $\text{Ca}^{2+}$ , thus reducing in the decreased reactivity of the  $\text{Ca}^{2+}$  ions.

Moreover, it can be clearly seen that there is a descending connection between weight depositions under effect of MWCNT-DTPA ad-

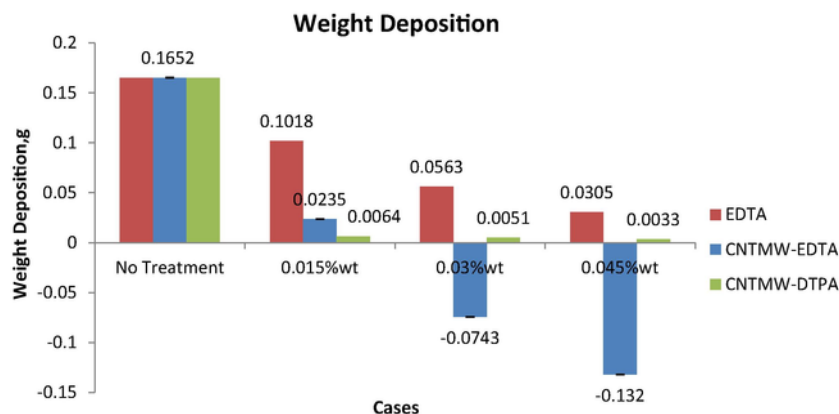


Fig. 6. Deposition of fouling under effect of concentration at inlet temperature of 60 °C for MWCNT-DTPA.

ditives concentration. The higher amount of DTPA functionalities (or active chain for sequestering  $\text{Ca}^{2+}$ ) in the presence of higher MWCNT-EDTA concentration can clarify the above-mentioned reduction in the weight of scale deposited. These findings are supported by several investigations which indicated that the induction period of crystallization could be prolonged by having high degree of carboxyl group due to the ability of the anionic carboxylate groups to adsorb  $\text{Ca}^{2+}$ . The nuclei remain subcritical and eventually disappear through dissolution consequences of rapidly adsorption of the inhibitor ions.

It concluded that increasing of the concentration of DTPA-treated MWCNT could provide more carboxylate group with the effect of higher probability of sequestering  $\text{Ca}^{2+}$  without corrosion effect is observed in these experiments findings.

### 3.2. Fouling resistance

Fig. 7 demonstrates the results of the fouling test that were found by using a water hardness of 300 mg  $\text{L}^{-1}$  and different concentrations of additives. Agreeing to Yang et al., the induction period can be well-defined as the time required for stable crystal nucleation to take place and to gradually spread out along the side until the heat transfer surface is completely covered with scale deposits [37]. A straight horizontal line at the outset of the fouling curve is normally used to portray this phenomenon.

In this present study, we obviously observed that the induction period was dramatically increased by the increased concentration of additives due to the high absorption ability of the additives. The additives sequestered vast numbers of calcium ions, modified the crystal structure and retarded the formation of calcium carbonate crystals. Without the additive, there was a step increase in fouling resistance in the first 12 h of operation, which indicated the precipitation of  $\text{CaCO}_3$  and its adherence to the heat transfer surfaces. It was observed visually that the stainless steel tubes became fully covered in the first 6 h of the test, and the fouling resistance began to increase gradually in 12 h, reaching an asymptotic level, indicating significant deposition on the surfaces. In the tests without additives, a fouling layer of thick, white deposits was observed visually, but the thickness of the deposits was not measured.

When the additives were used, very low fouling resistance curves were observed for difference concentrations of additives and the induction period took a longer time and had a nearly zero asymptotic value. It is understood that the additives had a significant role in retarding the formation of  $\text{CaCO}_3$  on the surface.

As mentioned above, the results showed a reduction in fouling with the increase of the concentration of MWCNT-DTPA in the fouling solution. According to the previous results [38], EDTA and MWCNT-EDTA capable in sequestering metal ions. However, MWCNT-EDTA reported a corrosion phenomenon. At present, DTPA-treated

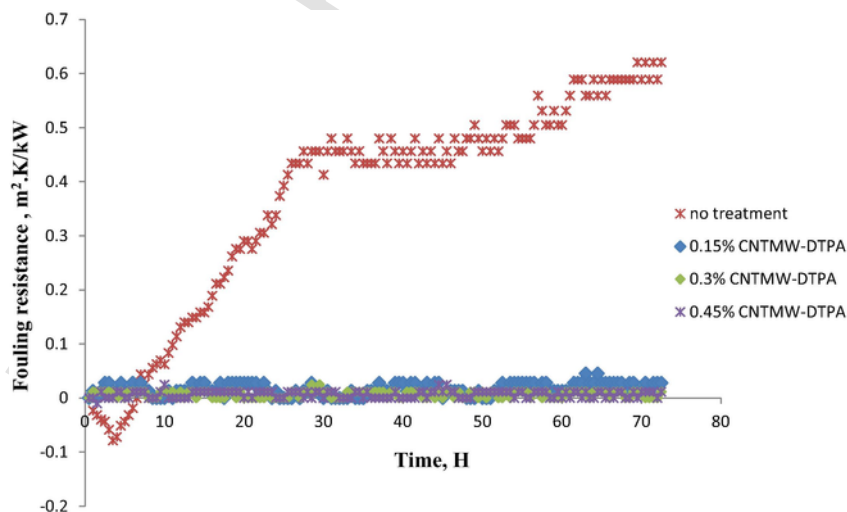


Fig. 7. Fouling resistance under influence of additive at inlet temperature of 60 °C with 300 mg  $\text{L}^{-1}$   $\text{CaCO}_3$ .

MWCNT was used to sequester  $\text{Ca}^{2+}$  ions by diminishing their reactivity without any corrosion on the heat exchanger surfaces. MWCNT-DTPA loading in a base fluid, such as water, has two advantages, i.e., (i) enhancement of heat transfer rate by increasing the thermal conductivity of the base fluid and subsequently enhancing convective heat transfer [39,40] and (ii) diminishing the reactivity of heavy metal ions, such as  $\text{Ca}^{2+}$ , which results in the mitigation of fouling on the surfaces of heat exchangers without corrosion effect. Based on the results, higher weight concentrations of DTPA-treated MWCNT in the base fluid can enhance the probability of sequestering a larger quantity of  $\text{Ca}^{2+}$  ions.

### 3.3. Effect of MWCNT-DTPA on the scale morphology of $\text{CaCO}_3$ crystal

#### 3.3.1. Comparison between treatment and no treatment case

Fig. 8 shows SEM images of the  $\text{CaCO}_3$  scale formed on the surface under no treatment condition. The amorphous  $\text{CaCO}_3$  appear to be metastable and aggregate into larger spherical particles (about 20  $\mu\text{m}$ ). The crystals simultaneously grow larger and accumulation to form a layer a  $\text{CaCO}_3$  fouling layer.

Fig. 9 shows SEM images of the  $\text{CaCO}_3$  scale formation under effect of 0.015 wt% MWCNT-DTPA additive. With the additives treatment, it can be seen clearly, the crystal morphology is distorted, irregular shape and relative smaller crystal size (about 10  $\mu\text{m}$ ) is ob-

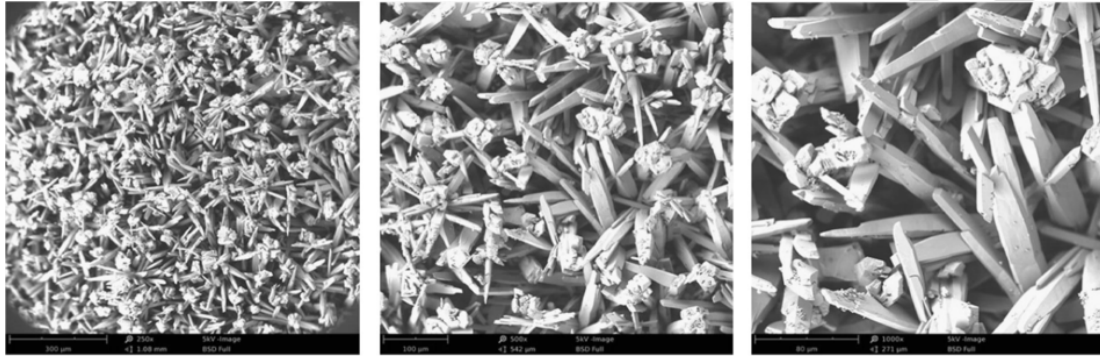


Fig. 8. SEM images of 250–1000x of calcium carbonate crystal under no treatment case.

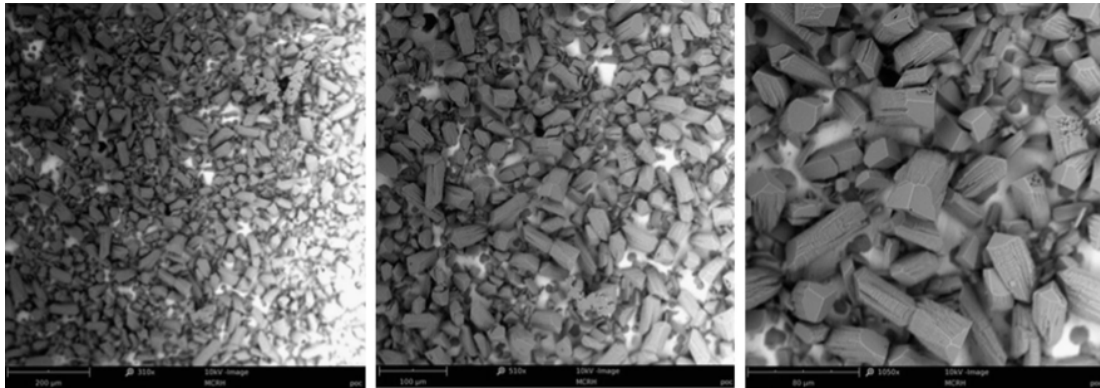


Fig. 9. SEM images of 250–1000x of calcium carbonate crystal under effect of 0.015 wt% MWCNT-DTPA.

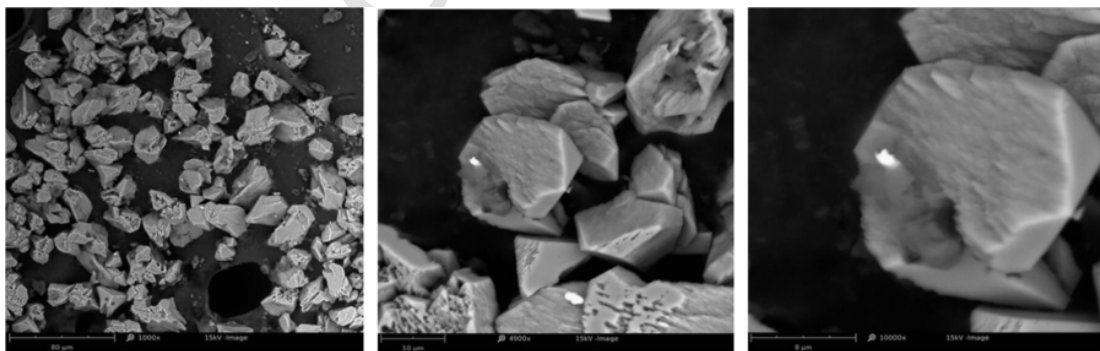


Fig. 10. Crystal morphology of  $\text{CaCO}_3$  under effect of 0.03 wt% additives concentration.



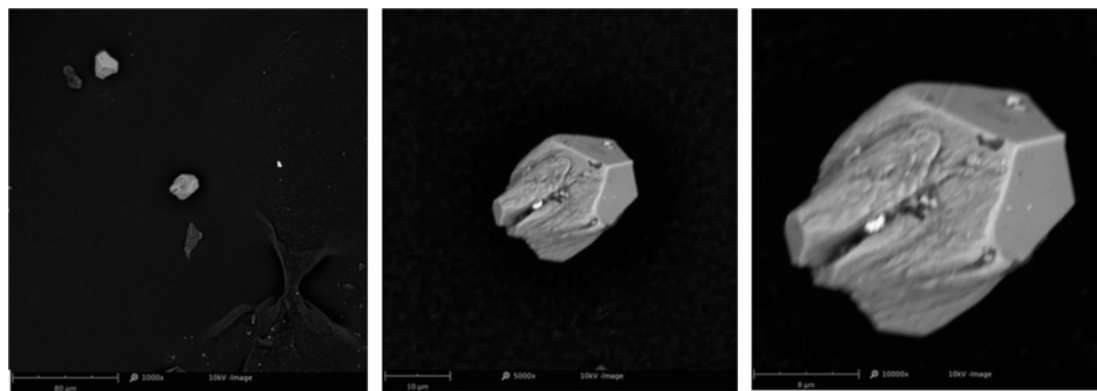


Fig. 11. Crystal morphology of  $\text{CaCO}_3$  under effect of 0.045 wt% additives concentration.

served. As a consequence of inhibition by MWCNT-DTPA, new crystal faces were developed and the crystals became more distorted.

These SEM images indicated that the additives affecting the crystals growth and microstructure. Incorporated additives resulted in an accumulation of distorted and small-sized crystallites, prominently indicating that the growth rate when additives were used was relatively slow compared to the case without additives [41]. In addition, it is preventing the formation of a regular, crystalline lattice and the build-up of an adherent scale. Related findings have been stated in the literature regarding the practice of additives for the drive of mitigating fouling [42–45].

### 3.3.2. Effect of additives concentration

Crystals formed during the  $\text{CaCO}_3$  fouling experiments in the no-additives and presence of the additives cases. Fig. 10 illustrates that  $\text{CaCO}_3$  crystals are  $<20\ \mu\text{m}$  in size, defect near the crystal wall structure in 0.03 wt% concentration. When 0.045 wt% additives concentration incorporating in the inhibited system, it was observed crystal structure are fewer in number, most are  $<10\ \mu\text{m}$  and significantly distorted as seen in Fig. 11. Most importantly that it was observed no corrosion effect on all the test specimen for 3 different concentrations.

## 4. Conclusions

In these experiments, the comparing of fouling mitigation by using additive EDTA, MWCNT-EDTA and MWCNT-DTPA were studied systematically. Artificial hard water was prepared and used in this experimental setup to accelerate the occurrence of fouling. EDTA is a common chelating agent used to retard the rate of fouling. However, the efficiency is limited due to the corrosion effect because of high concentration of additives of the solution. MWCNT-DTPA was incorporated in the system to mitigate fouling. A promising result with no corrosion effect is observed. Hence, the use of MWCNT-DTPA additive in the solution potentially retarded the formation of calcium carbonate crystals on the surface of the heat exchanger. These findings could be extended for use in designing systems and heat exchangers with enhanced performance and diminished adverse environmental consequences, which are topics that should be addressed in future research.

## Conflict of interests

The authors declare that there is no conflict of interest regarding the publication of this paper.

## Acknowledgements

The authors gratefully acknowledge High Impact Research Grant UM.C/625/1/HIR/MOHE/ENG/45 and UMRG RP012A-13AET, University Malaya Postgraduate Research Fund (PPP) (e.g., PG109-2015A) and University of Malaya, Malaysia for support to conduct this research work.

## References

- [1] T.R. Bott, *Fouling of Heat Exchangers*, Elsevier, 1995.
- [2] K.-J. Hwang, C.-Y. Liao, Effects of membrane morphology and operating conditions on microfiltration particle fouling, *J. Taiwan Inst. Chem. Eng.* 43 (2012) 46–52.
- [3] Y.-C. Juang, D.-J. Lee, J.-Y. Lai, Fouling layer on hollow-fibre membrane in aerobic granule membrane bioreactor, *J. Chin. Inst. Chem. Eng.* 39 (2008) 657–661.
- [4] M.-S. Hans, C4 fouling of heat exchanger surfaces, In: *VDI Heat Atlas*, Springer, Berlin, Heidelberg, 2010, pp. 79–104.
- [5] S.S. Al-Jaroudi, A. Ul-Hamid, J.A. Al-Matar, Prevention of failure in a distillation unit exhibiting extensive scale formation, *Desalination* 260 (2010) 119–128.
- [6] G.G. Duffy, S.N. Kazi, X.D. Chen, Heat transfer and pressure drop characteristics of suspensions of synthetic and wood pulp fibres in annular flow, *Appl. Therm. Eng.* 31 (2011) 2971–2980.
- [7] T.R. Bott, Fouling in heat transfer equipment, *Chem. Eng.* (1971) 391–395.
- [8] K.H. Chan, E.T. Wong, M. Irfan, A. Idris, N.M. Yusof, Enhanced Cu(II) rejection and fouling reduction through fabrication of PEG-PES nanocomposite ultrafiltration membrane with PEG-coated cobalt doped iron oxide nanoparticle, *J. Taiwan Inst. Chem. Eng.* 47 (2015) 50–58.
- [9] C. Wang, C. Xu, Z. Cao, H. Di, Investigation on minerals migration during co-firing of different straw/coal blending ratios, *Energy Convers. Manage.* 74 (2013) 279–285.
- [10] D.-H. Zhao, Y.-L. Zhang, Y.-P. Wei, H.-W. Gao, Facile eco-friendly treatment of a dye wastewater mixture by in situ hybridization with growing calcium carbonate, *J. Mater. Chem.* 19 (2009) 7239–7244.
- [11] M. Markowski, M. Trafczynski, K. Urbaniec, Validation of the method for determination of the thermal resistance of fouling in shell and tube heat exchangers, *Energy Convers. Manage.* 76 (2013) 307–313.
- [12] J. Mansouri, S. Harrison, V. Chen, Strategies for controlling biofouling in membrane filtration systems: challenges and opportunities, *J. Mater. Chem.* 20 (2010) 4567–4586.
- [13] M. Schoenitz, L. Grundemann, W. Augustin, S. Scholl, Fouling in microstructured devices: a review, *Chem. Commun.* 51 (2015) 8213–8228.
- [14] F. Zhang, Z. Hou, K. Sheng, B. Deng, L. Xie, Crystallization of calcium carbonate on polyethylene [gamma]-radiation-grafted with acrylic acid, *J. Mater. Chem.* 16 (2006) 1215–1221.
- [15] G. Rubasinghege, V.H. Grassian, Role(s) of adsorbed water in the surface chemistry of environmental interfaces, *Chem. Commun.* 49 (2013) 3071–3094.
- [16] X. Liu, T. Chen, P. Chen, H. Montgomerie, T.H. Hagen, B. Wang, X. Yang, Understanding mechanisms of scale inhibition using newly developed test method and developing synergistic combined scale inhibitors, In: *SPE International Conference on Oilfield Scale*, Society of Petroleum Engineers, 2012.
- [17] Z. Amjad, Influence of natural and synthetic additives on calcium carbonate precipitation and crystal morphology, *Tenside Surface. Det.* 43 (2006) 184–191.

- [18] W.W. Frenier, N. Ziauddin, Formation, Removal, and Inhibition of Inorganic Scale in the Oilfield Environment.
- [19] J.G.R. Davey, From Molecules to Crystallizers: An Introduction to Crystallization, Oxford, 2000.
- [20] D. Hasson, H. Shemer, A. Sher, State of the art of friendly “Green” scale control inhibitors: a review article, *Ind. Eng. Chem. Res.* 50 (2011) 7601–7607.
- [21] J.J. De Yoreo, P.G. Vekilov, Principles of crystal nucleation and growth, *Rev. Min. Geochem.* 54 (2003) 57–93.
- [22] A. Kavitha, T. Vasudevan, H.G. Prabu, Evaluation of synthesized antiscalants for cooling water system application, *Desalination* 268 (2011) 38–45.
- [23] H. Müller-Steinhagen, M.R. Malayeri, A.P. Watkinson, Heat exchanger fouling: environmental impacts, *Heat Transfer Eng.* 30 (2009) 773–776.
- [24] S.N. Kazi, G.G. Duffy, X.D. Chen, Mineral scale formation and mitigation on metals and a polymeric heat exchanger surface, *Appl. Therm. Eng.* 30 (2010) 2236–2242.
- [25] Z. Amjad, R. Zuhl, An Evaluation of Silica Scale Control Additives for Industrial Water Systems, NACE International, New Orleans, 2008.
- [26] T.A. Hoang, H.M. Ang, A.L. Rohl, Effects of organic additives on calcium sulfate scaling in pipes, *Aust. J. Chem.* 62 (2009) 927–933.
- [27] A. Amiri, M. Shanbedi, H. Eshghi, S.Z. Heris, M. Baniadam, Highly dispersed multiwalled carbon nanotubes decorated with Ag nanoparticles in water and experimental investigation of the thermophysical properties, *J. Phys. Chem. C* 116 (2012) 3369–3375.
- [28] S.S.J. Aravind, P. Baskar, T.T. Baby, R.K. Sabareesh, S. Das, S. Ramaprabhu, Investigation of structural stability, dispersion, viscosity, and conductive heat transfer properties of functionalized carbon nanotube based nanofluids, *J. Phys. Chem. C* 115 (2011) 16737–16744.
- [29] K.H. Teng, A. Amiri, S.N. Kazi, M.A. Bakar, B.T. Chew, Fouling mitigation on heat exchanger surfaces by EDTA-treated MWCNT-based water nanofluids, *J. Taiwan Inst. Chem. Eng.*
- [30] K. Ishihara, M. Nakayama, S. Ohara, H. Yamamoto, Direct ester condensation from a 1:1 mixture of carboxylic acids and alcohols catalyzed by hafnium (IV) or zirconium (IV) salts, *Tetrahedron* 58 (2002) 8179–8188.
- [31] A. Amiri, G. Ahmadi, M. Shanbedi, M. Savari, S. Kazi, B. Chew, Microwave-assisted synthesis of highly-crumpled, few-layered graphene and nitrogen-doped graphene for use as high-performance electrodes in capacitive deionization, *Sci. Rep.* 5 (2015).
- [32] A. Amiri, M. Shanbedi, H. Yarmand, H.K. Arzani, S. Gharehkhani, E. Montazer, R. Sadri, W. Sarsam, B. Chew, S. Kazi, Laminar convective heat transfer of hexylamine-treated MWCNTs-based turbine oil nanofluid, *Energy Convers. Manage.* 105 (2015) 355–367.
- [33] H. Baig, M.A. Antar, S.M. Zubair, Performance evaluation of a once-through multi-stage flash distillation system: impact of brine heater fouling, *Energy Convers. Manage.* 52 (2011) 1414–1425.
- [34] E. Altay, T. Shahwan, M. Tanoğlu, Morphosynthesis of  $\text{CaCO}_3$  at different reaction temperatures and the effects of PDDA, CTAB, and EDTA on the particle morphology and polymorph stability, *Powder Technol.* 178 (2007) 194–202.
- [35] J.R. Hart, Ethylenediaminetetraacetic acid and related chelating agents, In: Ullmann’s Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
- [36] D.H. Troup, J.A. Richardson, Scale nucleation on a heat transfer surface and its prevention, *Chem. Eng. Commun.* 2 (1978) 167–180.
- [37] Q. Yang, Y. Liu, A. Gu, J. Ding, Z. Shen, Investigation of induction period and morphology of  $\text{CaCO}_3$  fouling on heated surface, *Chem. Eng. Sci.* 57 (2002) 921–931.
- [38] J.R. Hart, Ethylenediaminetetraacetic acid and related chelating agents, In: Ullmann’s Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
- [39] M. Shanbedi, S.Z. Heris, A. Amiri, M. Baniadam, Improvement in heat transfer of a two-phased closed thermosyphon using silver-decorated MWCNT/water, *J. Dispers. Sci. Technol.* 35 (2014) 1086–1096.
- [40] M. Shanbedi, S.Z. Heris, A. Amiri, H. Eshghi, Synthesis of water-soluble Fe-decorated multi-walled carbon nanotubes: a study on thermo-physical properties of ferromagnetic nanofluid, *J. Taiwan Inst. Chem. Eng.* (2015).
- [41] A. Verch, D. Gebauer, M. Antonietti, H. Colfen, How to control the scaling of  $\text{CaCO}_3$ : a “fingerprinting technique” to classify additives, *Phys. Chem. Chem. Phys.* 13 (2011) 16811–16820.
- [42] H. El-Shall, E.A. Abdel-Aal, B.M. Moudgil, Effect of surfactants on phosphogypsum crystallization and filtration during wet-process phosphoric acid production, *Sep. Sci. Technol.* 35 (2000) 395–410.
- [43] S.-T. Liu, G.H. Nancollas, The crystal growth of calcium sulfate dihydrate in the presence of additives, *J. Colloid Interface Sci.* 44 (1973) 422–429.
- [44] F. Manoli, J. Kanakis, P. Malkaj, E. Dalas, The effect of aminoacids on the crystal growth of calcium carbonate, *J. Cryst. Growth* 236 (2002) 363–370.
- [45] D. Volkmer, M. Fricke, T. Huber, N. Sewald, Acidic peptides acting as growth modifiers of calcite crystals, *Chem. Commun.* (2004) 1872–1873.