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Experimental study of catalytic effect of different forms of zinc on ferrous iron oxidation in a bubble column reactor using ionic, oxide, and oxide nanopowder of zinc

Manizhe Moradi Shahre Babak[a,b], Ataallah Soltani Goharrizi[a,*], Mohammad Mirzaei[c]

[a]*Technical Faculty, Chemical Engineering Department, Shahid Bahonar University, Jomhuri Blvd., Kerman, Iran*
Email: a.soltani@mail.uk.ac.ir
[b]*Pars Oil and Gas Company, Tehran, Iran*
[c]*Chemistry Department, Shahid Bahonar University, Kerman, Iran*

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ABSTRACT

In this investigation, catalytic effect of zinc compounds (in ionic, oxide, and oxide nanopowder forms) on oxidation of ferrous iron by aeration in a bubble column reactor was studied experimentally. Effects of various zinc forms were compared with each other. As experimental results showed, zinc oxide nanopowder is the most effective form on oxidation reaction; which oxidation yield at 20 ppm of zinc and time 70 min increases about 17% compared to no using of zinc. Also zinc oxide and ionic zinc, respectively, enhance the oxidation rate. In addition, oxidation rate of ferrous iron increases with increasing concentration of each forms of zinc.

Keywords: Catalytic effect; Ferrous iron; Nanoparticle; Oxidation rate; Zinc

1. Introduction

Iron is one of the major components of Earth's crust and has a very important role in the chemistry of natural waters and ground waters. Groundwater is slightly acidic and has only low levels of dissolved oxygen for oxidation [1]. The guideline for maximum iron content in drinking water defined by the World Health Organization for iron is 0.3 mg/L. Another source for dissolved iron in drinking water in distribution networks may be the pipelines through which water flay [2]. Physicochemical treatment methods have been used to remove soluble ferrous iron and insoluble ferric iron from the water. Iron removal by aeration and separation is a common method. Alternative processes, such as ion-exchange [3], oxidation with oxidizing agents including chlorine and potassium permanganate [4], filtering with activated carbon and other filtering materials [5], supercritical fluid extraction [6], bioremediation [7], and treatment with limestone [8], have been proposed in order to removal of high amounts of iron. Oxidation has been determined to be effective in eliminating both forms of iron. There are several methods of oxidation: chlorination, ozonation, and aeration. Of the three, aeration is the most economical that requires no chemicals, especially when the ferrous iron concentration is high. In addition, groundwater commonly contains elevated concentrations of dissolved CO_2. Aeration has long been used in active water treatment because it can add O_2, increase the mixing, and degas CO_2.

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*Corresponding author.

An airlift reactor has been used that provides several advantages, such as good mixing due to the enhanced liquid circulation, high mass transfer rates, and low operating and maintenance costs due to the absence of internals [9]. The transport of the gas to the liquid frequently limits the rate of these reactions. Antonucci et al. [10], Dudukovic and Mills [11], Dudukovic et al. [12], Scholten et al. [13], and Vleeming et al. [14] demonstrated that the wettability or the external contacting efficiency of the catalyst support is an important particle property for trickle-bed and slurry reactors.

The stoichiometry of ferrous iron oxidation into ferric iron can be summarized as follows:

$$4Fe^{2+} + O_2 + 4H_3O^+ \rightarrow 4Fe^{3+} + 6H_2O \quad (1)$$

$$4Fe^{3+} + 12OH^- \rightarrow 4Fe(OH)_3 \quad (2)$$

Azher et al. [15] experimentally observed that the presence of ferric hydroxide induces obviously a strong autocatalytic effect on ferrous iron oxidation.

Zinc oxide is a well-known catalytic material in a large number of industrial processes. The catalytic activity of zinc oxide is very much dependent on the method of its preparation [16,17].

The enhancement of gas–liquid mass transfer of the oxygen is due to the adsorption of oxygen on the particles in the mass transfer zone close to the gas–liquid interface and the subsequent desorption and redistribution of the oxygen in the liquid bulk. The enhancement of gas absorption rate in the colloid is caused by the grazing effect (the so-called grazing effect). The grazing effect is the transfer phenomenon of a gas from the gas–liquid interface to the bulk of the liquid. Vinke [18] reported that the hydrogen absorption rate into an aqueous solution was enhanced by the presence of fine particles. According to the reports by Alper et al. [19] and Quicker et al. [20], the enhancement of gas absorption rate in the colloid is caused by the grazing effect. Kang et al. [21] found that the mass transfer enhancement is much more significant than the heat transfer in the binary nanofluids with Fe and CNT. Catalytic effect of copper nanoparticles on ferrous iron oxidation also was investigated [22].

It is observed that small particles may cover the bubble surface, thus preventing coalescence of bubbles and resulting in smaller bubbles and an increased specific surface. The effect of an increase in specific surface is enhanced further by the fact that smaller bubbles have lower rising velocities, which leads to increasing gas hold-up. Specific surface increases directly with the decrease of particles size and thus benefits the liquid–solid mass transfer. Some existing works assumed that irregular Brownian motion of nanoparticles is one of the main factors being contributed to the enhancement of energy transport [23,24]. Krishnamurthy et al. [25] experimentally calculate the effective mass diffusivity of the dye in both deionized water and nanofluid.

The present work focused on waters exhibiting iron typically between 5 and 20 mg/L. In this case, multiphase gas–liquid reactors similar to bubble columns are used which is usually the best way to carry out the aeration. Here, in addition to the influence of operation parameters such as aeration rate, initial ferrous iron concentration, and pH, catalytic effect of zinc and grazing effects of zinc oxide and zinc oxide nanopowder are investigated and compared.

2. Materials and methods

In this work, an airlift reactor consisting of a Plexiglas tube 9 cm in internal diameter and 150 cm height was used. The experimental setup is shown in Fig. 1. The experiments were carried out at room temperature, which was 25˚C. Total pressure of the system was atmospheric pressure. Experiments were carried out under semi-batch flow conditions. Synthetic water was prepared using deaerated tap water (the properties of the water are reported in Table 1). Nitrogen bubbling was used for water deoxygenation. The dissolved oxygen levels were recorded using a DO meter (Aqualytic Dissolved Oxygen Meter model AL20Oxi,

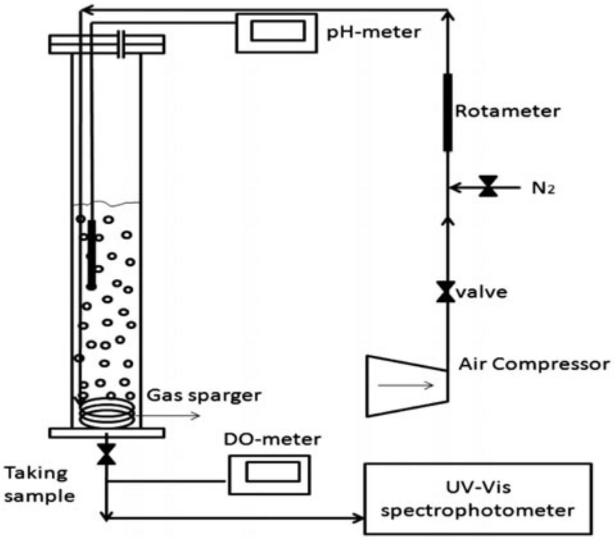

Fig. 1. Experimental setup.

Table 1
Synthetic water composition

Ionic comps.	Ca	Fe	Na	Cr	Sb	Cd	Mn	Pb	Cu	SO_4^{2-}	NO_3^-	Cl^-	F^-
Conc.	26.50 ppm	0	61.32 ppm	1.5 ppb	0.3 ppb	1.5 ppb	0.5 ppb	0	6 ppb	77.33 ppm	11 ppm	89.79 ppm	0.38 ppm

Germany). The initial ferrous iron concentration $[Fe^{2+}]_0$ was adjusted on 20 mg/L by the addition of iron (II) sulfate ($FeSO_4 \cdot 7H_2O$, Merck). Iron (II) sulfate was chosen because sulfate anions are a common constituent of most groundwater and acid mine waters. Additionally, sulfate anions have already been reported to decrease the rate constant. Compressed air was injected into the reactor and controlled using a glass tube rotameter. Aeration rate varied from 2 up to 8 L/min.

During the aeration, CO_2 is driven off, pH increases, and the concentration of dissolved O_2 increases until saturation with respect to the atmosphere, then Fe (II) oxidation rate increases. For the preparation of zinc ionic solution, zinc (II) sulfate ($ZnSO_4 \cdot 7H_2O$, Merck) was used; also zinc oxide (Merck, particle size ≤160 μm) and zinc oxide nanopowder (Sigma–Aldrich, particle size ≤50 nm, specific surface 10.8 m^2/g) were used the preparation of desired solutions. The desired ferrous sulfate was added to the tap water only when dissolved oxygen levels were below 1.0 mg/L. For measuring the iron (II) concentration, samples were obtained from the outlet flow. Then, samples were mixed with a 25% H_2SO_4 aqueous solution in order to limit further ferrous iron oxidation and stored for subsequent analysis. Measurements were carried out using a spectrophotometric determination (Varian Cary 50 UV–vis Spectrophotometer) with 1,10-phenanthroline [15].

3. Results and discussion

3.1. Effects of air flow rate and pH

As the aeration rate increases, the circulation of the fluid inside the reactor increases, so the mass transfer increases. The effect of aeration flow rate on the iron oxidation is shown in Fig. 2. This figure shows that the concentration of iron (II) decreases with increasing the aeration rate. The concentration curves at various flow rates are close to each other. Therefore, it can be concluded that the aeration rate does not have a strong effect on the conversion yield. In all of the subsequent experiments, the aeration rate is considered to be 6 L/min.

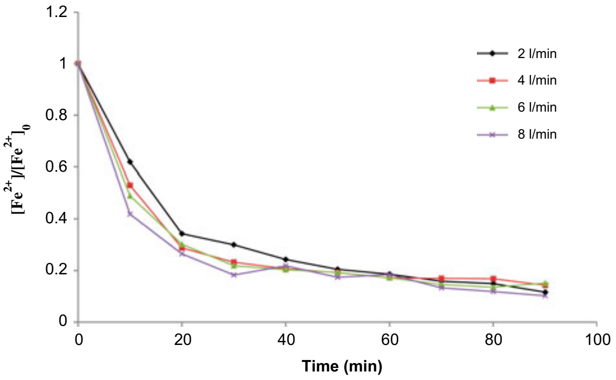

Fig. 2. Effect of aeration rate on iron (II) oxidation at pH 5.8 and initial ferrous iron concentration $[Fe^{2+}]_0 \approx 20$ mg/L.

By increasing the pH, the reaction rate will increase, so the concentration of iron (II) will decrease. The effect of pH on iron oxidation is shown in Fig. 3. As shown in this figure, the iron (II) oxidation strongly depends on the pH. Consequently, the time required to achieve 80% yield when pH is 5.3, 5.8, and 6.7 is about 90, 70, and 18 min, respectively. Because

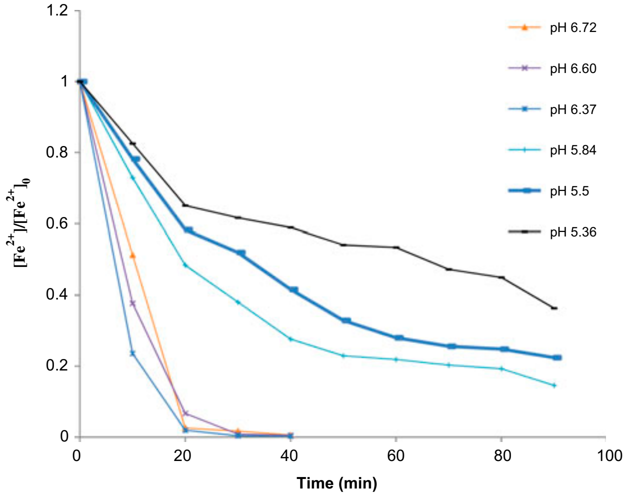

Fig. 3. Effect of pH on iron (II) oxidation at aeration rate of 6 L/min for $[Fe^{2+}]_0 \approx 20$ mg/L.

groundwaters are mildly acidic and basic waters are corrosive, pH 5.8 was considered for subsequent experiments.

3.2. Effect of zinc ions

Zinc (II) is an efficient catalyst in many oxidation reactions. Its catalytic effect has been shown in Fig. 4. By experimental results, the time required to achieve 80% yield when zinc (II) concentration is 0 (tap water), 2, 5, 10, and 20 ppm is about 70, 60, 59, 54, and 47 min, respectively. As it is seen from these experiments, concentration of iron (II) decreases slowly with increasing the concentration of zinc (II) ions. Also as it has been shown in Fig. 4 and following figures, lines are in the same extent at the beginning and diverges after some time. This divergence occurs because of autocatalytic effect of produced $Fe(OH)_3$ [15]. As Ferric hydroxide produces, it catalyze oxidation reaction and as a result, the rate of reaction increases.

3.3. Effect of zinc oxide

Fig. 5 shows that the ferrous iron oxidation rate increases with increasing the particle concentration. According to these results, the time required to achieve 80% yield when zinc oxide concentration is 2, 5, 10, and 20 ppm is about 49.67, 48.53, 45.07, and 44.06 min, respectively.

3.4. Effect of zinc oxide nanoparticles

The effect of zinc oxide nanoparticles on ferrous iron oxidation has been shown in Fig. 6. As results show, the time required to achieve 80% yield when zinc oxide nanopowder concentration is 2, 5, 10, and 20 ppm is about 49.18, 42.45, 39.36, and 37.23 min, respectively. Stochastic Brownian motion of suspended nanoparticles and the induced microscopic convection of fluid around the nanoparticles are two important factors that enhance the mass transport process inside the nanofluid. Adding more fine particles (typically below 0.6%) could result in smaller bubbles. Smaller bubbles have lower rising velocities and increase gas hold-up, so the oxidation of ferrous iron increases. As expected, increasing the nanopowder concentration will increase the oxidation rate.

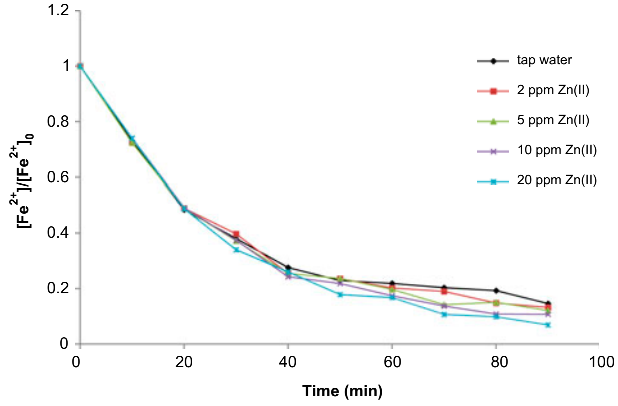

Fig. 4. Catalytic effect of zinc (II) ions on oxidation reaction at pH 5.8 and aeration rate of 6 L/min for $[Fe^{2+}]_0 \approx 20$ mg/L.

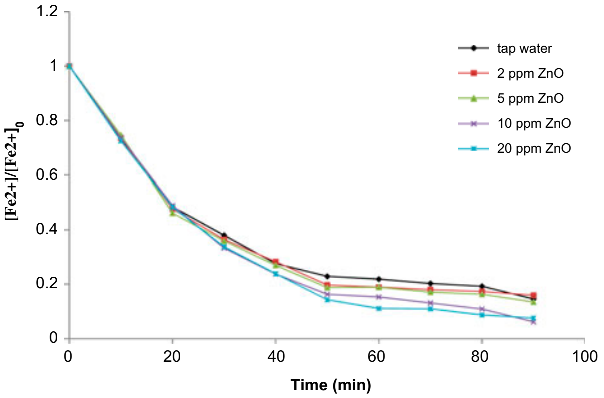

Fig. 5. Catalytic effect of zinc oxide on oxidation reaction at pH 5.8 and aeration rate of 6 L/min for $[Fe^{2+}]_0 \approx 20$ mg/L.

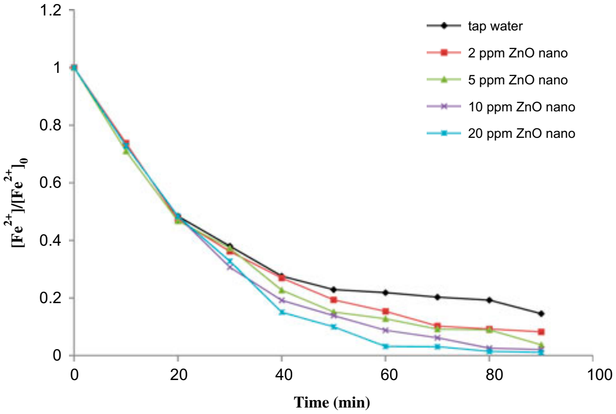

Fig. 6. Catalytic effect of zinc oxide nanopowder on oxidation reaction at pH 5.8 and aeration rate of 6 L/min for $[Fe^{2+}]_0 \approx 20$ mg/L.

Due to relatively high marketing price of nanopowders, this process may not be effective in comparison to aeration process, but if nanopowders are produced with lower cost, this process could be economical because zinc oxide nanoparticles have considerable effect in decreasing the aeration time.

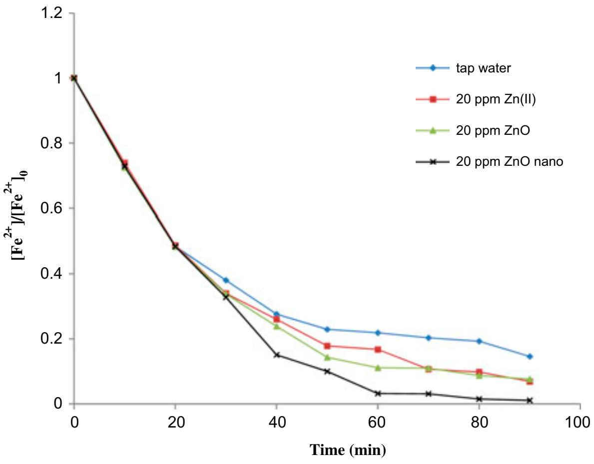

Fig. 7. Comparison of effects of zinc compounds at pH 5.8 and aeration rate of 6 L/min for $[Fe^{2+}]_0 \approx 20$ mg/L.

3.5. Comparison of effects of various forms of zinc

A comparison of various zinc forms effects on iron oxidation is shown in Fig. 7. According to the experimental results, oxidation yield at 20 ppm concentration of zinc and time 70 min is about 79.7% for tap water, 89% for zinc (II), 89% for zinc oxide, and 96.88% for zinc oxide nanopowder. Also it is seen that the finer particles have more enhancements. Zinc oxide nanoparticles have considerable effect on oxidation by playing catalytic role, thus enhancing the oxygen absorption with affecting mass transfer rate. Indeed, nanoparticles work better than zinc oxide because of its finer particle size. Zinc oxide and ionic zinc approximately have the same performance. This result could be because of grazing effect of zinc oxide, while soluble ionic zinc increases oxidation by acting as a chemical catalyst.

4. Conclusions

Zinc oxide is a well-known catalytic material in a large number of processes. The conversion yield of zinc oxide nanopowder is much better than zinc oxide. Suspended nanoparticles enhance the mass transport process inside the nanofluid. The micro motion and stirring of suspended nanoparticles enhanced the mass transport process. Such enhancement in the mass diffusivity depends upon the size/shape of particles, properties of the base fluid/particle, and the concentration of the particles. Experimental data showed that as the particle size decreases or the volume fraction of nanoparticles increases, the conversion yield increase. So, zinc oxide nanopowder has greater effect than zinc oxide. The results showed that in the nanofluid, containing only a small amount of nanoparticles, grazing effect is dominant. In ionic zinc solution, the chemical catalyzing is the only oxidation enhancement.

References

[1] S. Piche, F. Larachi, Oxidation kinetics of iron (II) complexes of trans-1,2-diaminocyclohexanetetraacetate (cdta) with dissolved oxygen: Reaction mechanism, parameters of activation and kinetic salt effects, Chem. Eng. Sci. 61 (2006) 3452–3462.

[2] P. Sarin, V.L. Snoeyink, J. Bebee, K.K. Jim, M.A. Beckett, W.M. Kriven, J.A. Clement, Iron release from corroded iron pipes in drinking water distribution systems: Effect of dissolved oxygen, Water Res. 38 (2004) 1259–1269.

[3] K. Vaaramaa, J. Lehto, Removal of metals and anions from drinking water by ion exchange, Desalination 155 (2003) 157–170.

[4] D. Ellis, C. Bouchard, G. Lantagne, Removal of iron and manganese from groundwater by oxidation and microfiltration, Desalination 130 (2000) 255–264.

[5] R. Munter, H. Ojaste, J. Sutt, Complexed iron removal from groundwater, J. Environ. Eng. 131 (2005) 1014–1020.

[6] W.C. Andersen, T.J. Bruno, Application of gas–liquid entraining rotor to supercritical fluid extraction: Removal of iron (III) from water, Anal. Chim. Acta 485 (2003) 1–8.

[7] P. Berbenni, A. Pollice, R. Canziani, L. Stabile, F. Nobili, Removal of iron and manganese from hydrocarbon contaminated groundwaters, Bioresour. Technol. 74 (2000) 109–114.

[8] H.A. Aziz, M.S. Yusoff, M.N. Adlan, N.H. Adnan, S. Alias, Physico-chemical removal of iron from semiaerobic landfill leachate by limestone filter, Water Manage 24 (2004) 353–358.

[9] Y. Chisti, M. Moo-Young, Air lift reactors: Characteristics, applications and design consideration, Chem. Eng. Commun. 60 (1987) 195–242.

[10] P.L. Antonucci, V. Alderucci, N. Giordano, H. Kim, On the role of surface functional groups in Pt carbon interaction, J. Appl. Electrochem. 24 (1994) 58–65.

[11] M.P. Dudukovic, P.L. Mills, Contacting and hydrodynamics in trickle bed reactors, in: N.P. Cheremisinoff (Ed.), Encyclopedia of Fluid Mechanics, Gulf, Houston, TX, 1986, p. 969 (Chapter 32).

[12] M.P. Dudukovic, F. Larachi, P.L. Mills, Multiphase reactors—Revisited, Chem. Eng. Sci. 54 (1999) 1975–1995.

[13] J.J.F. Scholten, R.A. van Santen, P.W.N.M. van Leeuwen, J.A. Moulijn, Catalysis and Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis, second revised and enlarged edition, Elsevier Science B.V, Amsterdam, 1999.

[14] J.H. Vleeming, B.F.M. Kuster, G.B. Marin, Effect of platinum particle-size and catalyst support on the platinum-catalyzed selective oxidation of carbohydrates, Catal. Lett. 46 (1997) 187–194.

[15] N. El Azher, B. Gourich, C. Vial, M. Belhaj Soulami, M. Ziyad, Study of ferrous iron oxidation in Morocco drinking water in an air lift reactor, Chem. Eng. Proc. 47 (2008) 1877–1886.

[16] S. Chauvin, J. Saussey, J.C. Lavalley, G. Djega-Mariadassou, Definition of polycrystalline ZnO catalytic sites and their role in CO hydrogenation, Appl. Catal. 25 (1986) 59–68.
[17] G. Sengupta, S.P. Sen, Catalytic Properties of ZnO and ZnO Modified HZSM-5 Zeolite, Proceedings of the Sixth National Symposium on recent advances in Catalysis 10 and Catalytic Reaction Engineering, Pune (India), Oral and Poster Presentation, February 5–7, 1983, p. 343.
[18] H. Vinke, The effect of catalyst particle to bubble adhesion on the mass transfer in agitated slurry reactors, PhD thesis, Municipal University of Amsterdam, 1992.
[19] E. Alper, B. Wichtendahl, W.D. Deckwer, Gas absorption mechanism in catalytic slurry reactors, Chem. Eng. Sci. 35 (1980) 217–228.
[20] G. Quicker, E. Alper, W.D. Deckwer, Gas absorption rates in a stirred cell with plane interface in the presence of fine particles, Can. J. Chem. Eng. 67 (1989) 32–45.
[21] Y.T. Kang, H.J. Kim, K.I. Lee, Heat and mass transfer enhancement of binary nanofluids for H_2O/LiBr falling film absorption process, Int. J. Ref. 31 (2008) 850–856.
[22] M.M. Shahre Babak, A. Soltani Goharrizi, M. Mirzaei, E. Roayaei, An experimental study for enhancing the catalytic effects of various copper forms on the oxidation of ferrous iron, Environ. Technol. 34 (2013) 1–6.
[23] Y. Xuan, Q. Li, W. Hu, Aggregation structure and thermal conductivity, AIChE J. 49 (2003) 1038–1043.
[24] R.S. Prasher, P. Bhattacharya, P.E. Phelan, Thermal conductivity of nanoscale colloidal solutions (nanofluids), Phys. Rev. Lett. 94 (2005) 025901–025914.
[25] S. Krishnamurthy, P. Bhattacharya, P.E. Phelan, R.S. Prasher, Enhanced mass transport in nanofluids, Nano Lett. 6 (2006) 419–423.