

Removal of chlorobenzene using cordierite coated with zero-valent iron under microwave irradiation

Chien-Li Lee¹ and Chih-Ju George Jou^{2,*}

¹Research and Development Center for Water Resource and Conservation
National Kaohsiung First University of Science and Technology
Kaohsiung 811, Taiwan

²Department of Safety, Health and Environmental Engineering
National Kaohsiung First University of Science and Technology
Kaohsiung 811, Taiwan

Key Words: ZVI-coated cordierite, zero-valent iron, Freundlich isotherm, Langmuir isotherm

ABSTRACT

In this research, microwave energy was applied to enhance chlorobenzene (CB) removal using zero-valent iron (ZVI) coated cordierite as the dielectric media. Laboratory data demonstrate that when 30 W of microwave energy is applied for 300 s, the CB removal efficiency is improved by 2.3 times (43 vs. 18%) for ZVI-coated cordierite particles. Hence, applying the microwave induced cordierite coated with ZVI can potentially decompose toxic organic substances as demonstrated in this laboratory study.

INTRODUCTION

Nano-scale zero-valent iron (ZVI) particles are effective in decomposing chlorine-containing organic compounds found in wastewater or groundwater [1-3]. In addition to high Miller Index or stepped surface and high surface energies [4-6], other factors that affect the capacity of ZVI particles to decompose organic compounds include the chemical properties and surface activity of ZVI particles [7,8].

Microwave (MW) is an electro-magnetic radiation with frequencies ranging from 300 MHz to 300 GHz [9,10]. The MW energy absorbed by the solution of an organic matter will cause non-thermal reduction of the activation energy that weakens the chemical bonds of the organic matter [10-12]. The MW technology depends on selecting appropriate media for treating organic matter, e.g., MW energy combined with granular activated carbon or ZVI particles for treating pentachlorophenol [13-15], chlorobenzene, CB [16-21], heavy oil contaminated sand [22] and improving the efficiency of TiO₂ photocatalyst [13] for savings energy while improving efficiencies.

Cordierite is a porcelain material consisting of MgO-Al₂O₃-SiO₂ with regular internal structures through a simple sintering process [23]. It has small expansion coefficient with superb thermal, volumetric,

and thermal stabilities as well as desiccating nature. When subject to high temperature, cordierite particles do not deform easily so that they are an excellent carrier [23,24] to support precious metal catalysts such as platinum and palladium. Additionally, cordierite has low dielectric constant and high electrical resistance; it is also used in integrated circle board as semiconductor carrier [25].

Because cordierite does not contain carbon in its chemical composition, it does not show carbonization phenomenon and pore enlargement problem under high temperature. Thus, problems such as refraction and arc production caused by MW energy as observed in surface pores of other carriers do not occur with cordierite so that the effectiveness of using cordierite as a dielectric medium does not diminish. In this research, cordierite is used as a carrier to support ZVI and dielectric medium to enhance the absorption and thermal decomposition of chlorine-containing organic matter under MW irradiation. Evaluation of this new technology that combines unique characteristics of cordierite as a carrier to support ZVI and also as a dielectric medium to produce heat energy from MW irradiation for ZVI to catalyze the thermal destruction of chlorine-contained organic matter was evaluated in this study.

MATERIALS AND METHODS

*Corresponding author
Email: george@nkfust.edu.tw

1. Preparation of ZVI Particles and ZVI-Coated Cordierite

The ZVI particles were synthesized by adding 0.75 M NaBH₄ (Lancaster, 98%) aqueous solution dropwise to a 0.135 M FeCl₃·6H₂O (SHOWA, 97%) aqueous solution. Without drying, the prepared ZVI particles were directly used in the subsequent CB decomposition experiment. The stock solution that contains 2000 mg L⁻¹ CB was prepared by dissolving 905 μL of 99.9% pure CB (GR Reagent, TEDIA, USA) in 99.9% methanol (GR Reagent, TEDIA, USA). 200 μL of the stock solution was then diluted with de-ionized water (18.2 MΩ cm, Millipore, USA) to form the 100 mg L⁻¹ CB working solution. The ZVI-coated cordierite particles were prepared by boiling cordierite particles in an acid solution containing 37% HCl and 100 mL 10% oxalic acid for 0.5, 1 and 1.5 h. They are rinsed with de-ionized water several times, agitated in ultrasonic vibrator for 30 min, and then immersed in boiling water for 30 min. These procedures were repeated for several times until the cordierite particle surface becomes neutral before the washed cordierite particles were dried in 150 °C oven for 24 h. The cordierite particles were then submerged in FeCl₃·6H₂O solution, and the mixture was shaken at 200 rpm in a water bath for 4 h while the temperature was maintained at 60 °C. The ferric ion adsorbed on cordierite surface was converted to ZVI with the addition of NaBH₄ solution; the un-reacted ferric chloride, the residual NaBH₄ and the un-adsorbed ZVI were rinsed off with de-ionized water. The cordierite particles were then dried in a vacuum oven, and the quantity of ZVI adsorbed on the surface of cordierite particles was determined.

2. Methods

Background information on CB decomposition without MW irradiation was obtained by adding 1 g each of ZVI, cordierite, and ZVI covered cordierite (ZVI/cordierite) to three sets of 40 mL solutions containing 100 mg L⁻¹ CB placed in a series of brown bottles sealed with Teflon-lined screw caps. The decomposition experiment was carried out at 25 °C up to 240 min. For the experiment on CB decomposition with MW irradiation, 1 g each of ZVI, cordierite, and ZVI/cordierite was added to 50 mL of 100 mg L⁻¹ CB solution in a series of boron-silicate glass bottle reactors sealed with Teflon-lined screw caps. The reactor was placed in a MW oven to be irradiated intermittently for 300 s using two levels of MW power output (30 or 250 W). The MW was applied for 20 s followed by no irradiation for 120 s. The cycle was repeated 15 times, and the intermittent pattern of MW irradiation eliminates the problem of physical loss of CB due to higher solution temperature during the treatment process. Such MW treatment procedure

will cause the final CB solution temperature to vary between 36.0 and 36.2 °C so that only less than 0.1% of CB, which is negligible, is lost due to slightly higher solution temperature.

3. Analyses

The cordierite permittivity and permittivity loss factor were analyzed using Impedance Analyzer (Agilent, 4291B) at 25 °C with 1.75 GHz frequency. The cordierite have 3.08 F m⁻¹ permittivity loss factor. IR thermography (T360, Flir Systems, USA) was used to measure temperature variations of the media during the reaction process. An HP 6890 gas chromatography (GC) coupled with an HP 5973 mass selective detector (MSD) and a capillary column (HP-5MS, 30 m x 0.25 mm x 0.25 μm) was used for the identification of intermediates and degradation products. Flow rate of the carrier gas (He) was maintained constant at 1.5 mL min⁻¹. The oven temperature was programmed from 70 to 260 °C (held for 5 min) at a ramp rate of 30 °C min⁻¹. The GC and MSD injector temperatures were 250 and 320 °C, respectively.

RESULTS AND DISCUSSION

1. Cordierite Acid Washing and Zero-valent Iron Coverage

Cordierite has 47-62 pores cm⁻² surface area; the acid washing increases its effective surface area and pore diameter [26] so that more ZVI can be adsorbed. In this study, oxalic acid and hydrochloric acid were used to wash the cordierite that is to be used as the carrier. Figure 1 shows that the quantity of ZVI covered on the treated cordierite increases with longer acid washing time. Additionally, the ZVI coverage is proportional to the degree of acid washing, or the weight difference between the original cordierite and the treated cordierite. The acid washing raises the original cordierite surface area 5.4 times from 14 to 75 m² g⁻¹. The highest ZVI coverage of 13.3 wt% can be obtained if the cordierite is boiled in 37% HCl for 1.5 h. This procedure is used to prepare ZVI/cordierite particles for all subsequent studies.

2. Sorption of CB by Cordierite under Room Temperature

In the study, both the Freundlich and Langmuir adsorption isotherm models were used to evaluate the concentration of adsorbates interacting with composite media [5,6,27-30]. The isotherm experiment sorption study was carried out by mixing 1 g of cordierite with 40 mL of 100 mg L⁻¹ CB solution in brown bottle covered with Teflon-lined screw cap submerged in a constant-temperature bath

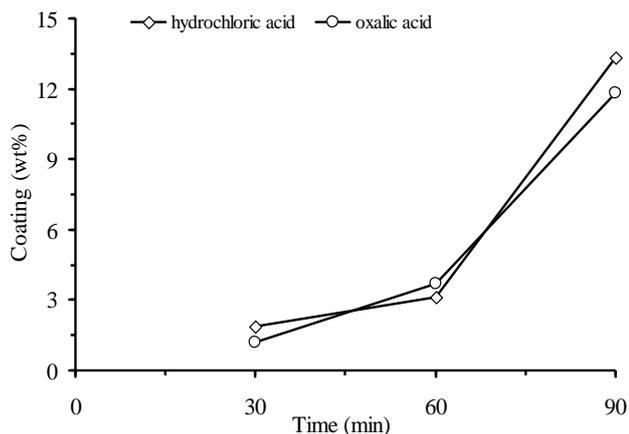


Fig. 1. Relationship between acid washing time and zero-valent iron coverage for cordierite washed with 37% HCl and 10% oxalic acid.

with the temperature maintained at 25 °C up to 240 min for batch study. Data reveal that saturated sorption of CB by cordierite is approached at 210 min, and the maximum quantity of 5.3 mg CB is adsorbed at 240 min.

The quantity of CB adsorbed (C_e) per unit weight of cordierite (Q_e), C_e/Q_e at equilibrium, versus Q_e is fitted with Langmuir isotherm. The equilibrium adsorption equation is $y = 81.7x - 7890$ with the least R^2 value of 0.599 and the adsorption constant K value of 0.0104. If the $\ln Q_e$ is plotted with the $\ln C_e$, the Freundlich isotherm equation of $y = -69.0x + 317$ is obtained with the least R^2 of 0.898 and adsorption constant K of 0.0145. Based on the R^2 value, Freundlich isotherm fits the adsorption of CB better than Langmuir isotherm. This is because that many realistic assumptions, e.g., mutual attraction among the molecules to be adsorbed and multiple layers of adsorption have been considered in the development of Freundlich isotherm so that it better delineates the adsorption of CB by cordierite.

3. Influence of MW Irradiation on Cordierite Temperature

When a dielectric medium is subject to MW irradiation, internal ionic migration and dipole rotation cause the dielectric molecules to vibrate thus generating heat to raise the internal temperature. Additionally, the polarization of a substance depends on the composition and the frequency of externally applied electrical field [31]. Under constant electric field, the heating of a substance is controlled by the dielectric characteristics of the substance subject to MW irradiation. Hence, when media of different dielectric constants are subject to MW irradiation, those with higher dielectric loss factor will preferentially couple with MW energy [32]. Increasing MW energy causes higher internal ionic

migration and dipole rotation so that more MW energy is absorbed and converted into heat energy [23]. Under similar MW irradiation conditions of 250 W power output and 240 s irradiation time, temperature variations of 1 g cordierite, 50 mL water, and 1 g cordierite submerged in 50 mL are shown in Fig. 2. The final temperatures are 39 °C for 1 g cordierite, 68 °C for 50 mL water and 66 °C for 1 g cordierite in 50 mL water. The dielectric constants of cordierite and water at 25 °C at 1.75 GHz are 3.08 and 26.5 $F m^{-1}$, respectively. MW energy is directly transported via the mutual reaction between molecules and electromagnetic field to convert the electromagnetic energy into heat energy. When a substance is exposed in the entire MW irradiation field, a relatively uniform and rapid heat is transported internally within the substance [32] to produce obvious thermal effect. On the other hand, cordierite has low dielectric constant, low expansion coefficient, high electric resistant and higher thermal conductivity so that it is capable of transmitting the heat generated in aqueous solution rapidly to cordierite particles.

4. Decomposition of CB by Cordierite under MW Irradiation

When a dielectric medium is placed in electric or magnetic fields, the medium is subject to transformation of polarization so that polar molecules experience vigorous rotation and displacement to generate frictional heat that causes the temperature to rise rapidly. The vigorous movement of polar molecules causes them to be at higher excited state to increase the molecular impact frequency and hence the decomposition of the adsorbed pollutant [4]. The MW heating is dependent on the dielectric loss of a substance that is related to the polarization of the substance because electromagnetic MW reacts with substances via energy to produce heat and store electric energy [10,31]. When 1 g blank cordierite is placed in 50 mL of 100 $mg L^{-1}$ CB solution and subject to 30 W irradiation for 300 s, the results shown in Fig. 2a indicate that CB concentrations decreases with irradiation time, and the CB removal efficiency is 15% at 300 s. Under similar conditions, the MW irradiation removes 8% CB without cordierite. Data reveal that the maximum quantity of CB adsorbed by cordierite is 5.3 mg. Hence, when subject to 30 W MW irradiation for 300 s, the removal of CB by MW irradiation is almost negligible ($14.8 - 8.3 - 5.3 = 1.2\%$).

5. Comparison of CB Removal by Cordierite, ZVI/Cordierite and ZVI

When ZVI iron is used to decompose CB, the organic substance first contacts the ZVI and is then trans-

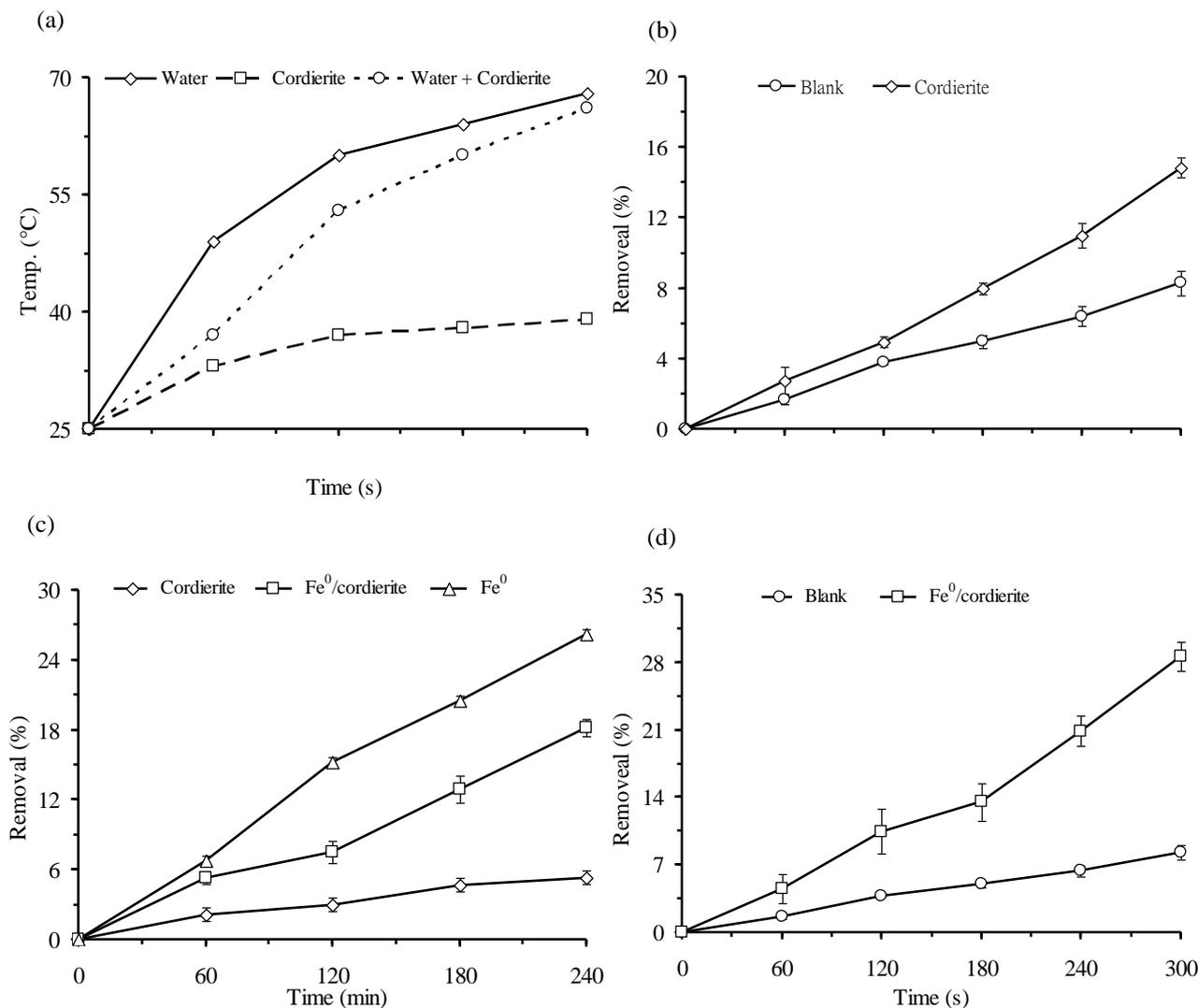


Fig. 2. Effects of the reaction time on the removal of chlorobenzene in aqueous solution. (a) Water, cordierite and cordierite in aqueous solution temperature variations, microwave power 250 W, (b) cordierite and blank (chlorobenzene solution only without addition of cordierite), microwave power 30 W, (c) cordierite, Fe⁰/cordierite and Fe⁰ (without microwave irradiation) and (d) Fe⁰/cordierite and blank (chlorobenzene solution only without addition of cordierite), microwave power 30 W.

ported to the iron particle surface where the organic substance is directly reduced and decomposed through electron transfer [33]. Hence, the surface reactions include transfer of organic CB from the bulk of solution to the surface of ZVI particle surface, adsorption on active sites, and then reductive de-chlorination [31]. Results of decomposing 40 mL of 100 mg L⁻¹ CB using cordierite, Fe⁰/cordierite, and Fe⁰ at 25 °C for 240 min reaction time are shown in Fig. 2b. The CB removal efficiencies are 26% for ZVI and only 18% for Fe⁰/cordierite. As discussed in above sections that cordierite under normal temperature is capable of decomposing 5.3 mg CB. If the amount of adsorbed CB is deducted, the actual CB decomposition efficiency is 13% for Fe⁰/cordierite. The difference in CB decomposition efficiencies is related to the efficiency of diffusion of CB to the

surface of ZVI particle surface [34]. The nano-scale ZVI particle suspended in solution has more exposed surface than the ZVI particle spread on the cordierite surface. The total quantity of ZVI on fully-covered cordierite particles is only 0.1 g. Additionally, cordierite particles are in cylindrical shape, they have limited surface to contact the CB solution so that Fe⁰/cordierite has worse CB removal efficiencies than ZVI particles.

6. Influence of MW Irradiation on CB Decomposition by Fe⁰/Cordierite

Under MW irradiation, vigorous rotation and displacement of polar molecules generates friction heat that causes the solution temperature to rise rapidly and the molecule to be at higher excited state

so that CB decomposition is greatly enhanced [4,9]. The MW activation process can be illustrated based on non-thermal and thermal models. In non-thermal activation, the reactant and MW involve through molecular vibration or molecular rearrangement to store the absorbed energy that changes the thermodynamic function or enthalpy of the system. This leads to lowering the solution activation energy and weakening the various chemical bonds [10,11,35]. On the other hand, in the thermal de-chlorination reaction, ZVIs are reduced to Fe^{+2} exothermally by releasing electrons. The reaction rate increases with higher temperature. Hence, the MW irradiation enhances the CB decomposition both thermally and non-thermally. Figure 2c shows the influence of applying 30 W MW irradiation for 300 s on the removal of CB from 50 mL of 100 mg L⁻¹ solution with and without the use of 1 g Fe⁰/cordierite as the dielectric media. Under similar MW irradiation, the CB solution alone shows 8% removal efficiency with the final temperature of 36.2 °C. In the presence of 1 g Fe⁰/cordierite, the CB removal efficiency is raised to 43% with the final solution temperature of 36 °C. At such temperature, the physical loss of CB due to evaporation is less than 0.1% that is negligible.

CONCLUSIONS

The cordierite crystal structure is loose with relatively large internal gases that allow ample space for thermal vibration without causing significant expansion. Hence, cordierite has relatively low thermal expansion coefficient, low dielectric constant, high resistance and higher thermal conductivity. At room temperature, the maximum adsorption of CB is 5.3 mg and the adsorption can be fitted with the Freundlich isotherm. Under similar reaction conditions, e.g., reaction temperature of 25 °C for 240 min, nano-scale ZVI particles have better CB removal efficiency than ZVI/cordierite (26 vs. 13%). This is because that the former is easily suspended in the solution to greatly increase the contact surface area, and that only 0.1 g ZVI covers the ZVI/cordierite. MW irradiation enhances the CB decomposition both thermally and non-thermally. With MW irradiation, the use of ZVI/cordierite as dielectric media will increase the CB removal from 8 to 43%.

REFERENCES

- Lin, C.J. and S.L. Lo, Effects of iron surface pretreatment on sorption and reduction kinetics of trichloroethylene in a closed batch system. *Water Res.*, 39(6), 1037-1046 (2005).
- Oh, S.Y., P.C. Chiu, B.J. Kim and D.K. Cha, Enhanced reduction of perchlorate by elemental iron at elevated temperatures. *J. Hazard. Mater.*, 129(1-3), 304-307 (2006).
- Chiu, Y.C., H.S. Chou and C.J. Lu, Interaction between zero-valent iron and hydrogen in anaerobic degradation of tetrachloroethylene. *Sustain. Environ. Res.*, 22(2), 107-111 (2012).
- Chen, J.L., S.R. Al-Abed, J.A. Ryan and Z.B. Li, Effects of pH on dechlorination of trichloroethylene by zero-valent iron. *J. Hazard. Mater.*, 83(3), 243-254 (2001).
- Shiue, A., C.M. Ma, R.T. Ruan and C.T. Chang, Adsorption kinetics and isotherms for the removal methyl orange from wastewaters using copper oxide catalyst prepared by the waste printed circuit boards. *Sustain. Environ. Res.*, 22(4), 209-215 (2012).
- Lai, C.H., S.H. Yeh, M.J. Chen, H.C. Huang, L.J. Huang and L.H. Cheng, Adsorptive characteristics in a system consisting of iron-coated sands, arsenic and humic acid. *Sustain. Environ. Res.*, 22(3), 135-141 (2012).
- Cheng, S.F. and S.C. Wu, The enhancement methods for the degradation of TCE by zero-valent metals. *Chemosphere*, 41(8), 1263-1270 (2000).
- Su, C.M. and R.W. Puls, Kinetics of trichloroethene reduction by zerovalent iron and tin: Pretreatment effect, apparent activation energy, and intermediate products. *Environ. Sci. Technol.*, 33(1), 163-168 (1999).
- Chang, Y.Y., Y.L. Yan, C.H. Tseng, J.Y. Syu, W.Y. Lin and Y.C. Yuan, Development of an innovative circulating fluidized-bed with MW system for controlling NO_x. *Aerosol Air Qual. Res.*, 12(3), 379-386 (2012).
- Woo, M.H., A. Grippin, C.Y. Wu and J. Wander, Microwave-irradiation-assisted HVAC filtration for inactivation of viral aerosols. *Aerosol Air Qual. Res.*, 12(3), 295-303 (2012).
- Zhang, Z., Y. Shan, J. Wang, H. Ling, S. Zang, W. Gao, Z. Zhao and H. Zhang, Investigation on the rapid degradation of Congo Red catalyzed by activated carbon powder under microwave irradiation. *J. Hazard. Mater.*, 147(1-2), 325-333 (2007).
- Lin, Y.C., J.F. Lin, Y.H. Hsiao and K.H. Hsu, Soybean oil for biodiesel production assisted by a microwave system and sodium methoxide catalyst. *Sustain. Environ. Res.*, 22(4), 247-254 (2012).
- Jou, C.J., Degradation of pentachlorophenol with zero-valence iron coupled with microwave energy. *J. Hazard. Mater.*, 152(2), 699-702 (2008).
- Jou, C.J. and C.R. Wu, Granular activated carbon coupled with microwave energy for treating pentachlorophenol-containing wastewater. *Environ. Prog.*, 27(1), 111-116 (2008).
- Lee, H.Y., C.L. Lee and C.J.G. Jou, Comparison degradation of pentachlorophenol using microwave-induced nanoscale Fe⁰ and activated

- carbon. *Water Air Soil Pollut.*, 211(1-4), 17-24 (2010).
16. Lee, C.L., C.J.G. Jou and H.G. Huang, Degradation of chlorobenzene in water using nanoscale Cu coupled with microwave irradiation. *J. Environ. Eng. ASCE*, 136(4), 412-416 (2010).
 17. Lee, C.L., C.J.G. Jou and H.P. Wang, Enhanced degradation of chlorobenzene in aqueous solution using microwave-induced zero-valent iron and copper particles. *Water Environ. Res.*, 82(7), 642-647 (2010).
 18. Jou, C.J.G., S.C. Hsieh, C.L. Lee, C.T. Lin and H.W. Huang, Combining zero-valent iron nanoparticles with microwave energy to treat chlorobenzene. *J. Taiwan Inst. Chem. Eng.*, 41(2), 216-220 (2010).
 19. Jou, C.J.G., C.R. Wu and C.L. Lee, Application of microwave energy to treat granular activated carbon contaminated with chlorobenzene. *Environ. Prog.*, 29(3), 272-277 (2010).
 20. Lee, C.L. and C.J.G. Jou, Reduced degradation of chlorobenzene in cosolvent solution using nanoscale zero valent iron with microwave irradiation. *Environ. Eng. Sci.*, 28(3), 191-195 (2011).
 21. Lee, C.L. and C.J.G. Jou, Degradation of chlorobenzene with microwave-aided zero valent iron particles. *Environ. Eng. Sci.*, 29(6), 432-435 (2012).
 22. Chang, H.J., C.J.G. Jou and C.L. Lee, Treatment of heavy oil contaminated sand by microwave energy. *Environ. Eng. Sci.*, 28(12), 869-873 (2011).
 23. Yamuna, A., R. Johnson, Y.R. Mahajan and M. Lalithambika, Kaolin-based cordierite for pollution control. *J. Eur. Ceram. Soc.*, 24(1), 65-73 (2004).
 24. Acimovic, Z., L. Pavlovic, L. Trumbulovic, L. Andric and M. Stamatovic, Synthesis and characterization of the cordierite ceramics from nonstandard raw materials for application in foundry. *Mater. Lett.*, 57(18), 2651-2656 (2003).
 25. El-Shobaky, H.G. and Y.M. Fahmy, Nickel cuprate supported on cordierite as an active catalyst for CO oxidation by O₂. *Appl. Catal. B-Environ.*, 63(3-4), 168-177 (2006).
 26. Vergunst, T., F. Kapteijn and J.A. Moulijn, Preparation of carbon-coated monolithic supports. *Carbon*, 40(11), 1891-1902 (2002).
 27. Halim, A.A., H.A. Aziz, M.A.M. Johari, K.S. Ariffin and M.J.K. Bashir, Semi-aerobic landfill leachate treatment using carbon-minerals composite adsorbent. *Environ. Eng. Sci.*, 29(5), 306-312 (2012).
 28. Cheng, W.H. and S.C. Tsai, Competition among mixed adsorbates affecting the adsorption of gaseous methyl ethyl ketone by hydrophobic molecular sieve. *Aerosol Air Qual. Res.*, 7(2), 205-220 (2007).
 29. Cheng, W.H., Adsorption characteristics of granular activated carbon and SPME indication of VOCs breakthrough. *Aerosol Air Qual. Res.*, 8(2), 178-187 (2008).
 30. Prasad, A.L. and T. Santhi, Adsorption of hazardous cationic dyes from aqueous solution onto *Acacia nilotica* leaves as an eco friendly adsorbent. *Sustain. Environ. Res.*, 22(2), 113-122 (2012).
 31. McLoughlin, C.M., W.A.M. McMinn and T.R.A. Magee, Physical and dielectric properties of pharmaceutical powders. *Powder Technol.*, 134(1-2), 40-51 (2003).
 32. Venkatesh, M.S. and G.S.V. Raghavan, An overview of microwave processing and dielectric properties of agri-food materials. *Biosyst. Eng.*, 88(1), 1-18 (2004).
 33. Xiong, G., X. He and Z. Zhang, Microwave-assisted extraction or saponification combined with microwave-assisted decomposition applied in pretreatment of soil or mussel samples for the determination of polychlorinated biphenyls. *Anal. Chim. Acta*, 413(1-2), 49-56 (2000).
 34. Noubactep, C., Processes of contaminant removal in "Fe⁰-H₂O" systems revisited: The importance of co-precipitation. *Open Environ. J.*, 1, 9-13 (2007).
 35. Al-Harabsheh, M., S. Kingman and S. Bradshaw, The reality of non-thermal effects in microwave assisted leaching systems? *Hydrometallurgy*, 84(1-2), 1-13 (2006).

Discussions of this paper may appear in the discussion section of a future issue. All discussions should be submitted to the Editor-in-Chief within six months of publication.

Manuscript Received: March 13, 2013

Revision Received: April 29, 2013

and Accepted: May 31, 2013