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Integrating Suspended Copper/Iron Bimetal Nanoparticles and Microwave Irradiation for Treating Chlorobenzene in Aqueous Solution

Chien-Li Lee[1] & Chih-Ju G Jou[2]

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

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

Correspondence: Chih-Ju G. Jou, 2, Juoyue Road, Nantsu District, Kaohsiung 811, Taiwan. Tel: 886-7-601-1000 ext. 2316. E-mail: george@ccms.nkfust.edu.tw

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Abstract

Microwave irradiation is combined with copper/iron bimetal (Cu/Fe) nano-particles suspended in aqueous chlorobenzene solution for reducing chlorobezene activation energy to enhance its decomposition. When the metal particles are suspended in solution, the total surface area to absorb the MW energy will increase so that the heat converted from the absorbed MW energy will be distributed evenly in the solution to enhance CB decomposition. Laboratory results show that when 250 W of microwave energy is applied for 300 sec to irradiate 100 mg L^{-1} of CB solution containing 1 g of suspended Cu/Fe bimetallic particles, the CB removal rate is improved by 1.3 times (95.0% vs. 76.2%), and the activation energy is lowered by 3 to 6%. The integrated suspended copper/iron bimetal nano-particle and Microwave Irradiation system is confirmed to be an effective method to treat chlorobenzene.

Keywords: chlorobenzene, Microwave irradiation, copper-iron bimetal

1. Introduction

Studies conducted in recent years show that electrons generated by zero-valent iron (ZVI or Fe^0) are effective in dechlorating and treating organic chlorine-containing matter contained in wastewater or groundwater (Lin & Lo, 2005; Clark II et al., 2003). For example, zero-valent iron was implemented successfully for treating various groundwater and soil contaminated by various organic contaminants, e.g., halogenated organics solvents, azoaromatics and nitroaromatics (Xu et al., 2005a, 2005b, 2006; Lien & Zhang, 2007), and inorganic pollutants, e.g., arsenic, chromium and copper. The end products of zero-valent iron treatment are carbon hydrogen, chloride and ferric oxides, among the many others (Janda et al., 2004; Lin et al., 2004; Liou et al., 2005). Two major disadvantages are associated with the use of plain zero-valent iron nano-particles: 1) Iron oxides are easily formed on the nano-particle surface so that the particle surface reactivity is greatly reduce, and high iron surface activity is difficult to maintain; and 2) Irons of different sources may have various activities (Lin et al., 2004; Zhang et al., 1998). If zero-valent iron nano-particles are covered with a second metal, e.g. Pt, Ag, Ni or Cu, the metal-covered iron particles, or double metal catalyst, are more effective in treating chlorine-containing organic pollutants with faster reaction rate than zero-valent iron nano-particles alone (Lin et al., 2004). The advantages of metal-covered ZVI particles include: (1) effectively lowering the activation energy of the pollutants, increasing the reaction rate of de-chlorinaton reactions, and reducing the formation of secondary products (Liou et al., 2005), (2) alleviating the problem of forming oxides on the iron particle surface, and (3) rapidly releasing electrons from zero-valent iron nano-particles (Cheng & Wu, 2000). Additionally, the process of using the double-metal catalyst requires relatively simple equipment to achieve rapid and complete dechlorination (Lien and Zhang, 2007) by increasing the iron particle surface area, and surface activity to reduce the formation of by-products (Clark II et al., 2003; Zhang et al., 1998).

Microwave (MW) is a multiple frequency (300 MHz to 600 MHz) electro-magnetic radiation (Jones et al., 2002; Appleton et al., 2005; Yuan et al., 2006), it induces dipole orientation (dipole rotation) and ionic conduction to

generate internal heat in the media irradiated (Hidaka et al., 2007), and also reduces the solution activation energy by weakening chemical bonds (Zhang et al., 2007). Recently, the microwave heating technology has attracted much interest in various fields because of the rapid homogeneous heating that is capable of enhancing reaction kinetics (Menéndez et al., 2002; Park et al., 2002; Takashima et al., 2008). The microwave is also combined with granular activated carbon or zero-valent iron nano-particles for treating pentachlorophenol (Jou, 2008; Jou & Wu, 2008; Lee et al., 2010a), chlorobenzene (Lee et al., 2009a, 2010b; Jou et al., 2010a, 2010b) and improving the efficiency of TiO_2 photocatalyst (Jou et al., 2008) for savings energy while improving efficiencies (Liu et al., 2004). In this study, the unique characteristics of nano-scale bi-metal catalysts, e.g. enhanced surface area and reactivity, and the rapid heating of microwave are combined into a new integrated method for treating aqueous chlorobenzene solution. The bimetal particles will absorb microwave energy within the particles. When they are suspended throughout chlorobenzene solution and irradiated with microwave, each nano-particles will produce heat so that the heat is more rapidly produced and evenly distributed throughout the bulk of the chlorobenzene solution. The influence of microwave irradiation on reducing chlorobenzend activation energy and increasing the removal efficiency is investigated.

2. Materials and Methods

2.1 Reagent

The chlorobenzene solution was prepared by dissolving 905 μL of chlorobenzene (99.9% purity GR Reagent, TEDIA, USA) in methanol (99.9% purity, GR Reagent, TEDIA, USA) with the final concentration of the stock solution adjusted to 20000 mg L^{-1}. When needed, 250 μL of the stock solution was dissolved in de-ionized water (18.2 MΩ, Millipore Co, USA) with the final volume adjusted to yield 100 mg L^{-1} chlorobenzene.

2.2 Preparation of Cu/Fe Bimetal Nano-particles

Raw Fe^0 and Cu^0 nano-particles were purchased from Conyuan Biochemical Technology Ltd. The Cu/Fe bimetal particles were produced using the wet reduction method by adding 1 g zero-valent iron nano-particles to each of 5 test tubes containing 5, 10, 50, and 100 mL of 1000 mg L^{-1} copper dichloride solution. The Cu^{+2} ions rapidly convert to Cu^0 to release ferric ions; the converted Cu^0 deposits on the surface of zero-valent iron nano-particles. Completion of the reaction is seen by the solution color changing from the original blue to light yellow. Nearly all Cu^{+2} ions are converted to Cu^0 to deposit on the zero-valent iron nano-particle surface although a tiny quantity of Cu^{+2} remains in the solute due to chemical equilibrium. Subsequently, the Cu^0 coated zero-valent iron nano-particles (Cu/Fe bi-metal particles) are separated from the liquid; ratios of Cu/Fe are 0.5, 1, 5 and 10% of Cu/Fe (w/w) with the reduced element copper (Cu^0) lodged in the surface structure of the iron particles. Specific surface areas of nano-scale Fe^0, Cu^0 and Cu/Fe particles are 55.8, 44.8 and 43.43 m^2 g^{-1}, respectively, as measured using a BET surface analyzer.

2.3 Experimental Methods

The study was carried out using 40 mL of 100 mg L^{-1} CB solution placed in 3 sets of boron-silica glass column reactors. Three sets of reactor containing chlorobenzene aqueous solution were added with 1 g of Fe^0, Cu^0 and Cu/Fe nano-particles, respectively. The CB decomposition study was carried out at various constant temperatures for 30, 60, 120, 150, 180, 210 and 240 min.

For the microwave irradiation study, a 2.45 GHz microwave with a max power of 650 W was used to generate microwave energy. An 80-mL boron-silica glass column reactor that is made of low-energy-loss and heat-resistant was used to hold the sample; the reactor was placed in the microwave oven for carrying out the MW irradiation experiment. The top of the reactor was connected to a vacuum gas collecting bag for capturing all organic substances that may escape with the tail gas during the reaction period. Constant microwave energy of 250 W was used to irradiate CB samples for 20 sec followed by interruption of no irradiation for 120 sec as one cycle; the experiment was repeated for 15 cycles. Triplicate samples were used in all studies; the average was used to calculate the CB removal efficiency.

2.4 Analyses

Chemical analyses of organic intermediates and final products matter was performed with HP 6890 gas chromatography (GC) using the HP-5MS capillary column; the chromatography is equipped with an HP 5973 mass selective detector (MSD). The constant carrying gas (He) flow rate was maintained at 1.5 mL min^{-1}. The oven temperature was programmed to vary from 70 ^oC to 260 ^oC at an increasing rate of 30 ^oC min^{-1} to remain at 260 ^oC for 5 more min. Changes of nano-particle surface were detected using Scanning Electron microscopic (Hitachi, S-2500) images. Samples were scanned with Fourier Transformation Infra Red (FTIR, NICOLET-is10) using KBr window between 400 to 4000 cm^{-1} for 8 times to result in images with 0.5 resolution.

3. Results and Discussion

3.1 The Optimal Quantity of Cu Deposited

Deposition of copper on the iron particle surface will generate numerous localized galvanic cells that promote the iron corrosion to facilitate release of electrons (Lin et al., 2004; Lien & Zhang, 2001), and favor the thermodynamic reactions ($\Delta E0 = + 0.784$ V) (Eq. 1~3).

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \qquad E = 0.447 \text{ V} \tag{1}$$

$$+) \; Cu^{2+} + 2e^- \rightarrow Cu^0 \qquad E = 0.337 \text{ V} \tag{2}$$

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0 \qquad E = 0.784 \text{ V} \tag{3}$$

The data obtained on 100 mg L^{-1} CB solution treated with 0.5, 1, 5, and 10% of 1 g Cu/Fe particles without microwave irradiation are shown in Figure 1 and Figure 2. Laboratory results indicates that at room temperature (25 ^oC), the chlorobenzene reaction rate constants after 240 min are 1.4×10^{-3} min^{-1} for 0.5% of Cu/Fe (w/w), 1.8×10^{-3} min^{-1} for 1% of Cu/Fe (w/w), 3.4×10^{-3} min^{-1} for 5% of Cu/Fe (w/w), and 1.5×10^{-3} min^{-1} for 10% of Cu/Fe (w/w) with removal efficiency of 27.9%, 36.8%, 62.0% and 32.7%, respectively. The iron nano-particles with various quantities of Cu deposited show different reaction rates and efficiencies of CB removal. When the quantity of Cu deposited is smaller than 5%, both reaction rate constant and CB removal efficiency increase with higher Cu deposited until the optimum 5% level of Cu deposit is reached. If the quantity of Cu deposited exceeds 5% the efficiency will not be further enhanced or even reduced. Results of t-test carried out on curves plotted in Figure 2 confirm that the 5% Cu deposit curve is much better than all other curves for 0.5%, 1% and 10% of Cu deposits. These observations are similar to those made by Liou et al. (2005) when using nano-scale Cu/Fe particles to carry out the reduction of nitrate. They reported that the Cu/Fe (w/w) of 5% has the optimum removal efficiency whereas Cu/Fe (w/w) exceeding 5% will not further enhance the removal efficiency. In another study using the Ru/Fe bi-metal to decompose Trichloroethylene, Lin et al. (2005) observed that the quantity of Ru deposited greater than 1.5% will cause higher reaction rate constants with increasing quantity of Ru deposited until 5% of Ru deposit is reached. Their results seem to be somehow comparable with the observations made in this study.

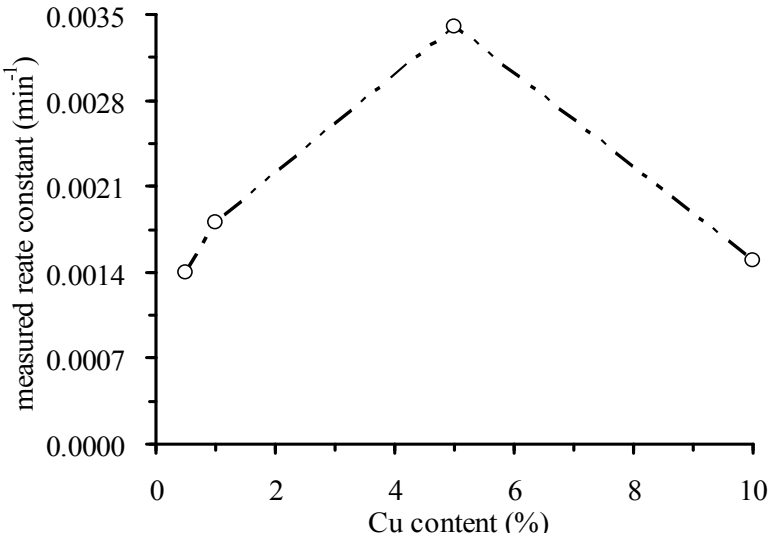


Figure 1. Relationship between the Cu content in the Cu/Fe bi-metal nanoparticles and the measured reaction rate constant

The XRD of X-ray diffraction of the nano-scale bi-metal particles shows that obvious peaks occur at 2θ of 44.9 and 65.2Cu/Fe (Figure 3a) indicating the existence of crystal zero-valent iron at 2θ of 35.9 and 44.9 (Figure 3b).

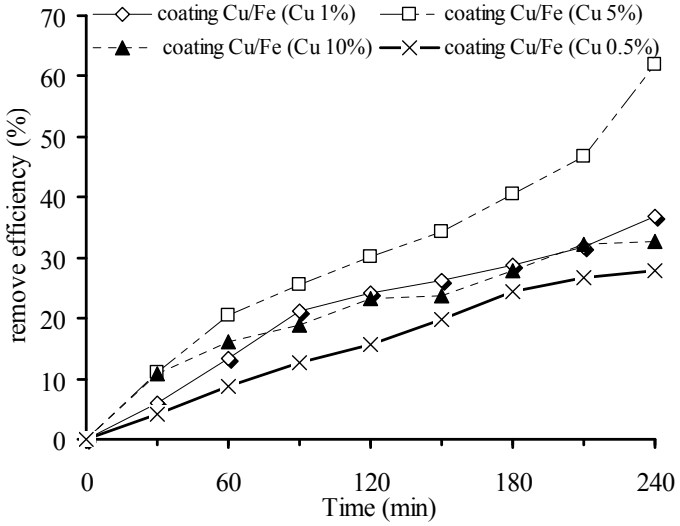


Figure 2. Chlorobenzene removal efficiencies for the Cu/Fe bi-metal nanoparticles containing various Cu Content at different reaction times (without microwave irradiation)

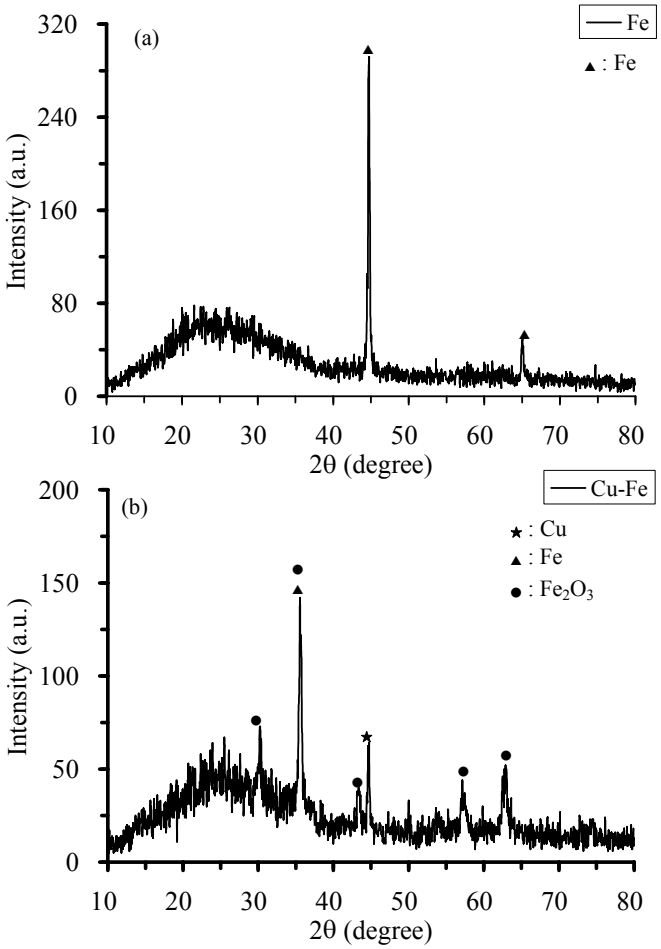


Figure 3. Cu/Fe (w/w) = 0.5% and Fe XRD

3.2 CB Degradation for Nano-scale Particles of Cu/Fe, Fe^0 and Cu^0

Copper has a small electropotential than iron; when copper is deposited on the surface of nano-scale Fe^0 particles (Cu/Fe bi-metal particles), the electropotential difference between these two metals causes the release of

electrons to enhance the corrosion and reactivity of Fe^0 particles. Comparison of the CB decomposition rates using nano-scale particles of Cu/Fe bi-metal, zero-valent Fe, and zero-valent copper with microwave irradiation are shown in Figure 4. Results of t-test confirm that the 5% Cu/Fe curve is obviously different from those for 0.5%, 1% and 10% Cu/Fe curves. When the Cu/Fe (w/w) ratio is 5% in the bi-metal particle, the CB removal efficiency is 62.0% whereas using Fe^0 and Cu^0 removes only 18.1%, and 19.5% of CB, respectively. A metal with lower hydrogen over-voltage (Fe^0) will be more easily oxidized than the metal with higher hydrogen over-voltage (Cu^0) that stays mostly in element form. The metal oxidation releases hydrogen in atomic form, which favors the reduction of organic matter (Su & Puls, 1999). The observed slightly higher CB removal efficiency for Cu^0 than Fe^0 (19.5 vs. 18.1%) is caused by a higher hydrogen over-voltage for Cu^0 (0.584 V) than Fe^0 (0.557 V). The results also show a significant improvement of CB removal with the nano-scale Cu/Fe paraticles (62.0 vs. 19.5 % or 18.1%). The major functions of Cu^0 deposited on the surface of nano-scale Fe^0 particles are: (1) catalytically accelerating the CB dechloration rate, (2) preventing the oxidizing membrane from forming on the surface of Fe^0 particles and retention the reactivity of Fe^0 particles, (3) enhancing CB reduction by rapid release of electrons due to the electropotential difference between of Fe^0 and of Cu^0 (Su and Puls, 1999).

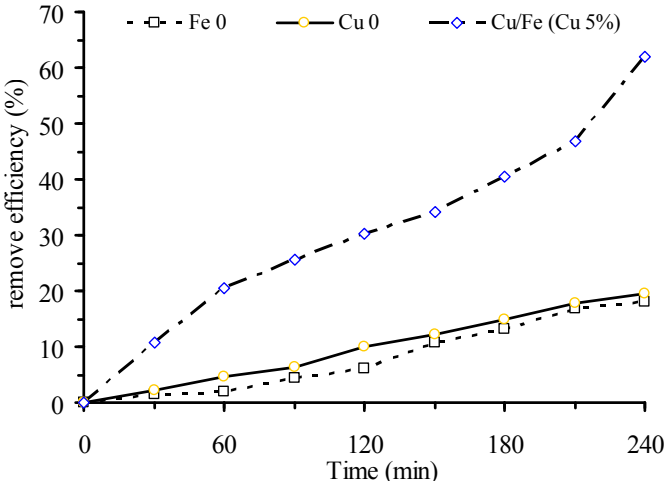


Figure 4. Comparison of chlorobenzene removal efficiencies for the nano-scale Cu/Fe, Fe^0, and Cu^0 particles at various treatment times (without microwave irradiation)

3.3 Activation Energy of CB Degradation by Using Cu/Fe, Fe^0 and Cu^0

For heterogeneous reactions, the effect of temperature on reaction rates reveals whether the rate-limiting step is to due chemical reactions at the surface, or the diffusion of the reactant in question (Lien & Zhang, 2001) because a slower reaction step requires more activation energy (Ea). Lower Ea values are usually associated with the rate-limiting step that is a reactant diffusion, or diffusion-controlled process. Higher Ea values show that the process is chemical-controlled (Su and Puls, 1999). The activation energies for diffusion-controlled reactions in solution are generally between 10-20 kJ/mol (Liou et al., 2005). Rates of CB degradation with Cu/Fe, Fe^0 and Cu^0 particles at various temperatures are well fitted with linear plot of the Arrhenius equation expressed as (Su & Puls, 1999):

$$\ln ksa = \ln A - Ea/RT \quad (4)$$

Where: lnksa is the observed rate constant (h^{-1}); Ea is activation energy (kJ mol^{-1}); R is the molar gas constant (8.314 J mol^{-1} K^{-1}); T is the absolute temperature (K); and A is a pre-exponential factor (L $h^{-1}\cdot m^{-2}$). Therefore, straight lines are obtained when lnk is plotted versus 1/T; the slope is the negative ratio of the activation energy to the ideal gas constant (-Ea/R), and the y-axis intercept is lnA. Figure 5 gives the Arrhenius plots of ln ksa versus 1/T for the CB dechlorination with Cu/Fe, Fe^0 and Cu^0 nano-particles. The Arrhenius behavior is seen by the linear plot for the temperature range 25, 40, 50 and 60 ^oC, and the the activation energies of dechlorination degradation are 9.8 kJ/mol for Cu /Fe, 21.9 kJ/mol for Fe^0 nano-particles and 21.4 kJ/mol for Cu^0 nano-particles. For Cu/Fe bi-metal particles, the reduction of CB activated energy is lower than 20 kJ/mol. This indicates that the rate-limiting step of CB degradation reaction begins to shift from surface reaction to mass transfer whereas the CB degradation limiting steps for both Cu^0 and Fe^0 are typical surface reaction.

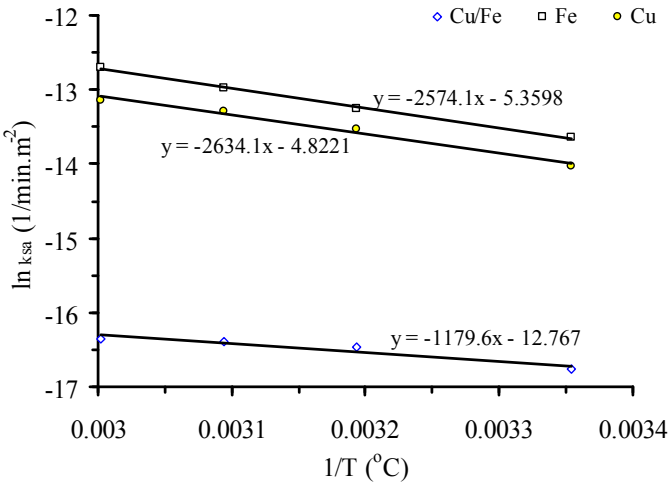


Figure 5. Linear plots of $\ln k_{sa}$ vs. 1/T for chlorobenzene degradation using Cu/Fe bimetal particles (□ solid line), Fe^0 particles (□ solid line), and Cu^0 particles (○ solid line) particles at 25 °C, 40 °C, 50 °C and 60 °C

3.4 Effect of MW Radiation on CB Degradation by Using Cu/Fe, Fe^0 and Cu^0 as MW Absorbing Media

MW irradiation will induce ion migration and dipole rotation causing the polar molecules in the solution to vibrate thus producing heat to raise the solution temperature (Lien and Zhang, 2007; Parida and Parija, 2006; Horikoshi and Serpone, 2009). The heat changes the thermodynamics characteristics as well; it reduces the activation energy of the reaction system, and weakens the molecular chemical bonds of the various substances in the solution. The existence of MW absorbing dielectric media will enhance the MW absorption to augment the influence of microwave on the degradation of solutes in the solution (Menéndez et al., 2002). The experiment on the influence of MW irradiation on CB degradation with Fe^0, Cu^0 and Cu/Fe added to CB solution as MW absorbing media was carried out by fixing the MW output at 250 W for a total irradiation time of 300 sec. The results shown in Figure 6 reveal that when exposed to MW radiation, the Cu/Fe bi-metal particles have better CB removal efficiency than either Cu^0 or Fe^0 particles during the first 80 sec. of total treatment time. This reveals that Cu^0 molecules added to the zero-valent Fe^0 particles behave as a catalyst to raise the CB removal efficiency. On the other hand, a substance that has more dielectric loss is better capable of converting MW energy into heat energy (Bilbao-Sáinz et al., 2007). The magnitude of dielectric loss is 38.2 for nano-scale Fe^0 particles, 30 for Cu/Fe particles and 9.7 for nano-scale Cu^0 particles; hence, the order of the capacity to absorb MW and convert it into heat energy is Fe^0 > Cu/Fe > Cu^0. The same order is reflected by the results shown in Figure 6 that under similar MW irradiation, the CB removal efficiency is 82.8% for Fe^0, 76.2% for Cu/Fe and 72.1% for Cu^0.

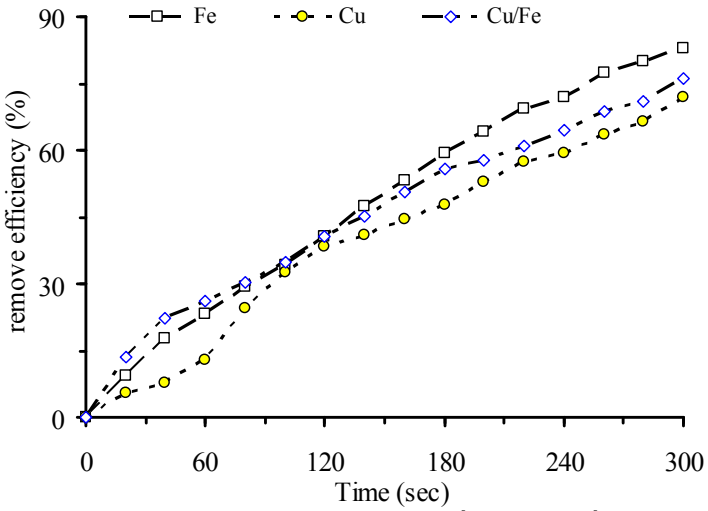
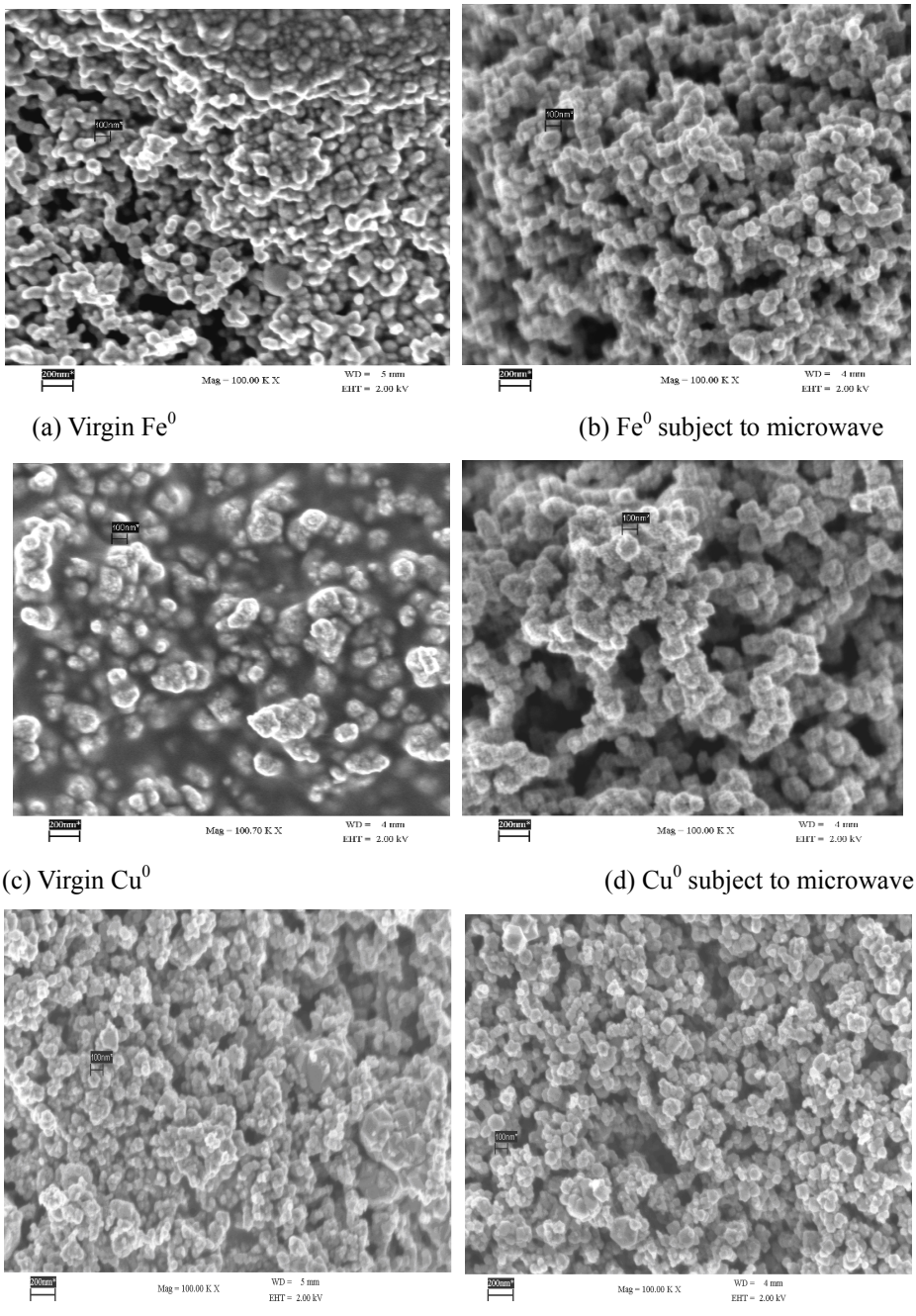


Figure 6. Chlorobenzene removal efficiencies for Cu/Fe (◊), Fe^0 (□) and Cu^0 (○) particles (with microwave irradiation)

Changes of the particle surface before and after CB decomposition have been observed with scanning electron microscope (SEM). As shown in Figure 7 (a) and (b), the appearance of Fe^0 particles do not show obvious changes except that the microwave irradiated Fe^0 nano-particles appear not as dense as they were before the irradiation. Figures 7 (c), (d), (e), and (f) show the same observations for Cu^0 and Cu/Fe particles.



(a) Virgin Fe^0 (b) Fe^0 subject to microwave

(c) Virgin Cu^0 (d) Cu^0 subject to microwave

(e) Virgin Cu/Fe (f) Cu/Fe subject to microwave

Figure 7. SEM images (Mag = 100 KX) showing changes of surface structure for Fe^0 and Cu^0 before and after being used as the medium in the microwave (250 W MW energy for 300 sec) treatment for chlorobenzene

3.5 Suspension of Cu/Fe in CB Solution

The suspension of Cu/Fe particles in CB solution will result in relatively larger Cu/Fe particle surface area to absorb more microwave energy for generating more heat evenly distributed in the solution. Additionally, based on the principle of "non-thermal activation", the microwave energy will behave as the vibrating energy to agitate

or align CB molecules so that the CB molecule activation energy is significantly reduced (Al- Harahsheh et al., 2006). When irradiated by microwave energy, Cu/Fe particles absorb the MW energy that reaches the particle surface. The large particle surface area enhances the oxidation rate, and increases the active sites on the particle surface; the vigorous reaction re-suspends the particles that have settled to the bottom until all Cu/Fe particles are fluidized in the solution. The Cu/Fe particles thus suspended in CB solution will provide more solid/liquid contact area, absorb more MW energy, enhance CB degradation rate, and raise CB removal efficiency. Figure 8 shows that the suspended Cu/Fe particles reduce the CB activation energy from 13.9 to 13.4 kJ mol^{-1}, and remove 18.8% more CB (95.0% vs. 76.2%) than un-fluidized Cu/Fe particle. The difference between these two curves is confirmed by the t-test results.

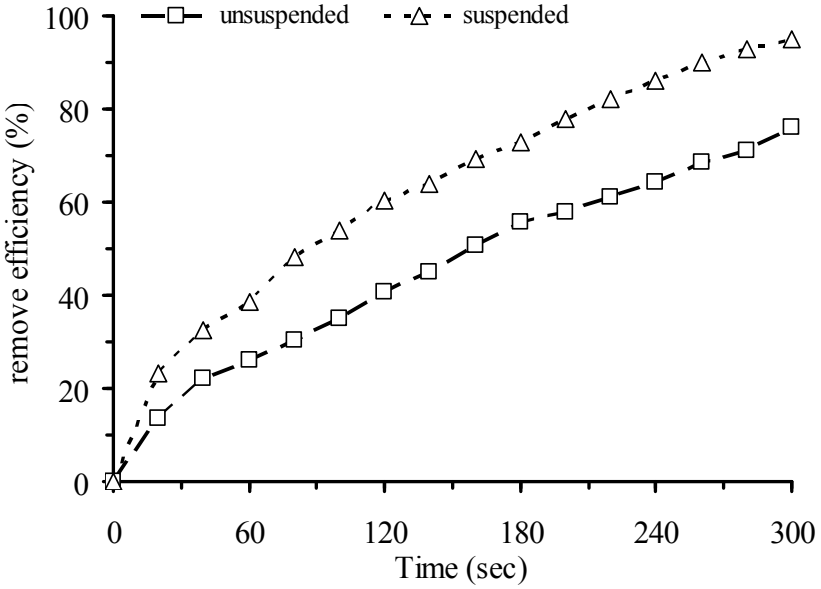


Figure 8. Enhanced chlorobenzene removal efficiency achieved by suspended Cu/Fe particles (with microwave irradiation)

3.6 Analyses of End-products

Samples of the tail gas generated when the CB solution suspended with Cu/Fe particles is irradiated using 250 W for 300 sec are collected and analyzed using GC/MSD. Results of qualitative analyses indicate the presence of benzene compounds. The samples are further subject to FTIR (Fourier Transform Infrared) analyses to identify the end product. The results shows a major peak is seen to occur between 2320~2380 cm^{-1}; other minor peaks obviously occur between 665~670, 3598~3630, and 3703~3730 cm^{-1}, and hence CO_2 is identified to be the major end product. Relatively wider absorbing peaks are also observed 1030~1032 cm^{-1}, 1340~1455 cm^{-1}, 2708~3060 cm^{-1} and 3730~3833 cm^{-1}; CH_3OH that comes from the solvent used to prepare CB solution is identified. Additionally, the strong absorbance in 1375~1875 cm^{-1} and 3600~3925 cm^{-1} indicate the presence of water originated from the aqueous solution. The chloride ion concentration in the treated chlorobenzene solution, measured with a chloride electrode, increases from 2.9 to 6.2 ppm, and the solution pH increases from 6.8 to 8.2

4. Conclusion

Embedding copper in the surface structure of nano-scale Fe^0 particles will favor the iron oxidation to release electrons under the influence of different electropotentials of Fe^0 and the embedded copper. Under similar experimental conditions, i.e. 25 ^oC and 240 minute reaction time, the order of CB removal efficiencies are 62.0% for Cu/Fe particles, 19.5 % for zero-valent copper nano-particles, and 18.1% for zero-valent iron nano-particles. Additionally, a substance with higher dielectric loss is more capable of absorbing MW energy and converting it into heat energy. The order of magnitude for dielectric loss is nano-scale Fe^0(38.2) > Cu/Fe (30) > nano-scale Cu^0 (9.7) that indicates the order of magnitude of the capacity in absorbing and converting MW energy being nano-scale Fe^0> Cu/Fe > nano-scale Cu^0. Laboratory results confirm that under similar MW irradiation (i.e. 250-W MW for 300 sec), Cu/Fe has better CB removal rate that either Fe^0 or Cu^0 indicating that the copper added to Fe^0 plays the role of catalyst to result in better treatment efficiency for the bi-metal Cu/Fe particles. The ultimate CB removal efficiencies are 82.8% for Fe^0 nano-particles 76.2% for Cu/Fe nano-particles, and 72.1%

for Cu^0 nano-particles.

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