The Reaction of Nano-scale Iron Fluidized in Microwave Radiation Field to Treat Chlorobenzene

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Abstract- Microwave (MW) is applied to enhance chlorobenzene (CB) removal using micron iron (μ-Fe) particles, nanoscale iron particles freshly prepared in our lab (nP-Fe^0), and commercial nanoscale iron particles (nC-Fe^0) as the dielectric media. The results show that when the CB solution is irradiated with 250 W MW for 150 sec, better CB removal can be achieved than without MW irradiation. The MW radiation increases the iron oxidization rate, surface activity, and hence the CB removal rate. The MW-induced iron particles are capable of removing 13.6 times (61.2% vs. 4.5% for μ-Fe), 2.8 times (76.5% vs. 27.5% for nP-Fe^0) and 3.6 times (65.4% vs. 18.1% for nC-Fe^0) more CB, and the CB activation energy is decreased 16.8 kJ/mol (μ-Fe), 3.2 kJ/mol (nP -Fe^0) and 3.5 kJ/mol (nC-Fe^0). Using the microwave induced Nano-scale Iron Fluidized is effective in decomposing toxic organic substances as demonstrated in this laboratory study.

Keywords: Microwave-Induced; Zero valent Iron; Chlorobenzene (CB); Activation energy (Ea)

1. INTRODUCTION

Nano-scale zero-valent iron (ZVI) particles are effective in decomposing chlorine-containing organic compounds found in wastewater or groundwater [1, 2]. These organic compounds include pentachlorophenol, azo-dyestuff [3, 4], pesticides [5], polychlorinated biphenyls [6], herbicides [7] and aromatic nitric compounds [8]. Nano-particles have higher Miller Index or more stepped surface [9], and higher surface energies than micro-scale particles [10]. The factors that affect the capacity of ZVI particles to decompose organic compounds include the chemical properties, and surface activity of ZVI particles [11, 12].

Microwave (MW) is an electro-magnetic radiation with frequencies ranging from 300 MHz to 300 GHz [13]. The MW absorbed by a solution will cause the polar molecules in the solution to rotate rapidly leading to obvious thermal effect that will reduce the activation energy of the organic chemicals dissolved in the solution and weaken their chemical bonds [14]. Selecting an appropriate medium to absorb the MW energy is important to integrating the MW technology. For example, the MW radiation may be combined with granular activated carbon or ZVI for treating pentachlorophenol [15, 16] to improve the efficiency of TiO2 photocatalyst [17]. However, little information is available in literature on the microwave irradiation technique integrated with nano-scale ZVI particles to accelerate the dechlorination of chlorinated organic compounds in the liquid system.

The objectives of this study are to: (1) compare the efficiencies of different type of micron iron (μ-Fe), nanoscale iron particles freshly prepared in our lab (nP-Fe0), and commercial nanoscale iron particles (nC-Fe0) to treat aqueous chlorobenzene solution with and without MW irradiation; and (2) study the effect of particle size and surface activity on the removal of chlorobenzene dissolved in aqueous solution in the presence of MW.

2. MATERIALS AND METHODS

2.1 MATERIALS

The working solution containing 100-mg/L chlorobenzene was prepared by dissolving 905 μL of 99.9% pure chlorobenzene (GR Reagent, TEDIA, USA) in 99.9% methanol (GR Reagent, TEDIA, USA) to form a 2000-mg/L stock solution. Two hundred micro liters (μL) of the stock solution was then diluted with de-ionized water (18.2 MΩ, Millipore Co., USA) to form the 100-mg/L chlorobenzene working solution. Micro Fe was purchased from Riedel-deHaën (99.9%, < 212 μm) and Commercial Fe0 nanoparticles were obtained from Conyuan Biochemical Technology Ltd. Company (99.9%, < 60 nm).

2.2 METHODS AND ANALYSIS

A modified household microwave oven operated at 2.45 GHz with a max power of 650 W was used for generating the microwave energy. It was slightly modified by installing a programmable PID (Proportional-Integral-Derivative) controller. The MW energy was controlled by programming the PID controller for maintaining a constant pre-selected MW energy level. The sample was held in 40 mL low-energy-loss boron-silica serum bottles with Teflon coated screwed caps for carrying out the experiment.

The study was initiated by placing 40 mL of 100 mg/L CB solution in the bottle. After adding 1 g of μ-Fe, nP-Fe0 or

nC-Fe0, the sample was stirred in a constant-temperature shaker at 100 rpm to complete the CB decomposition study at various constant temperatures, i.e. 25, 40, 50 and 60 oC for different reaction periods, i.e. 30, 60 ... and 240 min. If the microwave energy was used, it was set at 250 W to irradiate the prepared samples according to the following operating conditions: MW irradiation time = 10 sec, MW interruption irradiation time = 120 sec, total irradiation time = 150 sec, number of cycle = 15.

Qualitative analyses was done with a HP 6890 gas chromatography (GC) coupled with an HP 5973 mass selective detector (MSD). An HP capillary column (HP-5MS, 30 m × 0.25 mm × 0.25 μm) was used for the identification of intermediates and degradation products. The carrier gas (He) flow rate was kept at 1.5 ml/min (constant flow). The oven temperature was programmed from 35 °C (maintain for 1 min) to 130 °C at a ramp rate of 5 °C /min. IR (Raytek, Raynger 3i) was used to measure temperature variations of the media during the reaction process.

3. Results and Discussion

3.1 Effect of Surface Area on CB Degradation

The degradation of chlorinated organic solvents by ZVI is a surface-mediated reaction; there is enough evidence to suggest that adsorption of chlorinated organic compounds at the Fe0 surface indeed occurs [18]. The rate of degradation of chlorinated solvents by Fe0 is a pseudo-first-order reaction with respect to the contaminant residual concentration [2, 12].

Fig. 1 indicates that at room temperature (25 oC), the chlorobenzene removal efficiencies after 240 min are 4.5% for μ-Fe, 27.5% for nP-Fe0 and 18.1% for nC-Fe0 particles with reaction rate constants of 2.0 × 10-4, 1.3 × 10-3 and 9.0 × 10-4 min-1, respectively.

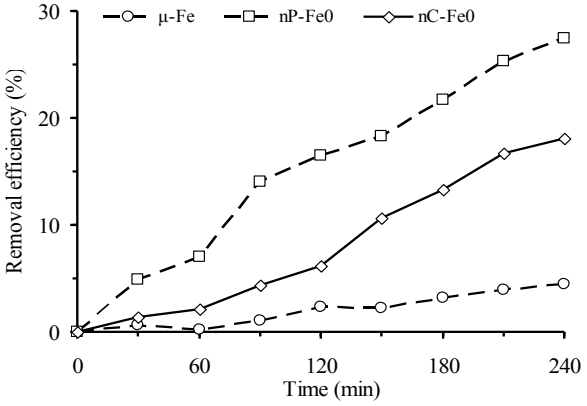

Fig. 1. CB removal efficiency for μ-Fe, nP-Fe0, and nC-Fe0 (at 25 oC, iron/liquid rate was 1 g/50 mL and CB concentration 100 mg/L).

3.2 Effect of MW Radiation on CB Degradation

When microwave irradiation is combined with some suitable microwave absorbents as the catalysts in the integrated system, the microwave can weaken the chemical bond intensities of various molecules, and reduce the activation energy of the reaction system. Commercial nano iron particles have smaller surface area to absorb more MW than the nano particle particles prepared in the laboratory. However, the former tend to agglomerate in the solution and thus absorb less MW energy to result in less efficiency of CB decomposition. In contrast, the prepared nano iron particles are used directly in wet form; they are thus evenly suspended in the CB solution. This leads to larger surface areas to absorb more MW energy than the particles that have settled to the bottom as in the case of the commercial nano-scale iron particles. Hence, the un-dried, laboratory prepared nano-scale iron particles (nP-Fe0) exhibit better CB removal efficiency than either commercial nano-scale iron particles (nC-Fe0) or micro-scale iron particles (μ-Fe0). Fig. 2 shows that applying 250 W MW for 150 sec will remove 76.5% CB for nP-Fe0, 65.4% CB for nC-Fe0, and 61.2% CB for μ-Fe0. The activated energy levels are 32.7 kJ/mol for μ-Fe, 18.6 kJ/mol for nP-Fe0, and 18.3 kJ/mol for nC-Fe0.

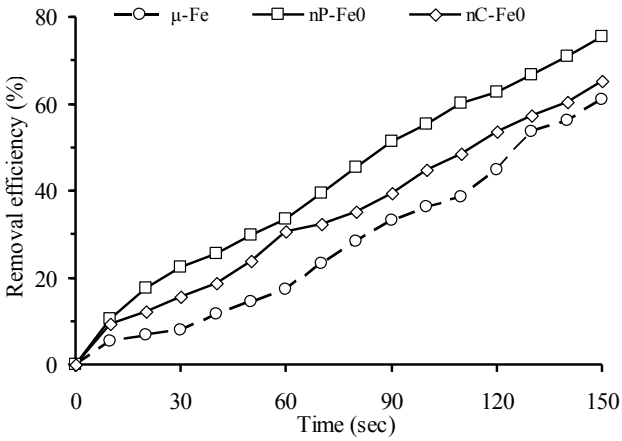

Fig. 2. CB removal efficiency for the various iron particles (irradiated with 250 W MW energy for 150 sec).

3.3 Reaction Mechanisms

Analyses of the product analyses after CB reduction by adding 1.0 g nC-Fe0 at 25 oC for 240 min show that the major product is benzene. Analyzed using GC/MSD, the tail gas collected at the completion of the MW treatment contains benzene as the major end-product. Further FTIR analysis results show strong absorption peaks between 2320 and 2380 cm-1, and obvious weak absorption peaks in 665~670, 3598~3630, and 3703~3730 cm-1, these observations suggest that the unknown species is CO2. The chloride concentration in the original solution is 2.9 ppm; it increases to 6.3 ppm after the MW treatment.

On the other hand, the non-uniform absorption of MW energy by zero-valent iron particles may produce local hot spots with surface temperature reaching about 435 oC that is

much higher than the surrounding temperature. Hence, the high-temperature oxidation can easily occur causing mineralization of benzene to form CO2. The major role of zero-valent iron is to react with CB and to generate electrons leading to the reduction and dechlorination of CB with the formation of Fe2+ or Fe+3-compounds and H2. When the MW penetrates the solution to reach the surface of zero-valent iron particles, it increases the zero-valent iron oxidation rate by creating more active sites on the surface to CB decomposition. Additionally, contacts between the high-temperature iron particle surface and H2 gas will induce iron reduction that proceeds simultaneously with CB dechlorination, and benzene mineralization as schematically shown in Fig. 3.

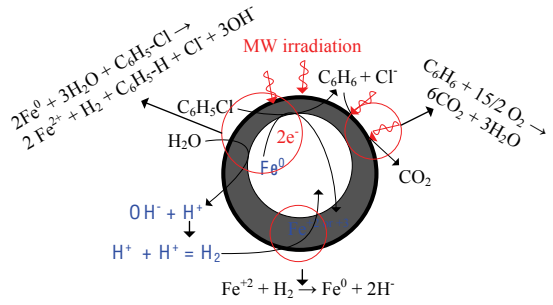

Fig. 3. Schematic diagram shown the MW irradiation reaching the surface of zero-valent iron particles to initiate reductive reactions for decomposing chlorobenzene.

4. Conclusion

Three types of zero-valent iron particle, μ-Fe, nP-Fe0, and nC-Fe0, are used as the microwave absorption media to enhance the removal of chlorobenzene. Laboratory data demonstrate that the MW energy enhances the CB removing 13.6 times (61.2% vs. 4.5% for μ-Fe), 2.8 times (76.5% vs. 27.5% for nP-Fe0) and 3.6 times (65.4% vs. 18.1% for nC-Fe0) more CB, and the CB activation energy decreases to 16.8 kJ/mol (μ-Fe), 3.2 kJ/mol (nP-Fe0) and 3.5 kJ/mol (nC-Fe0). The MW radiation penetrates the CB solution to reach Fe0 surface for increasing iron oxidizes, and surface activity, thus enhancing the CB removal. Additionally, the ZVI is highly oxidative, its surface activity is one of the important parameters to affect the removal of contaminant. Better CB removal is also contributed by the reduction of CB activation energy in the presence of MW irradiation.

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